Transport Modeling of Simple Fluids and Nano-Colloids: Thermal Conduction Mechanisms and Coarse Projection

by

Jacob Eapen

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Abstract

In the first part of this thesis, the modes of microscopic energy fluctuations governing heat flow in nano-colloids are quantitatively assessed by combining linear response theory with molecular dynamics (MD) simulations. The intrinsic thermal conductivity is decomposed into self and cross correlations of the three modes that make up the microscopic heat flux vector, namely, the kinetic, the potential and the virial. By this decomposition analysis, the interplay between the molecular mechanisms that govern the variation of the thermal conductivity with volume fraction and solid-fluid interaction is examined. For a specific system of nanosized platinum clusters which interact strongly with host liquid xenon, a significant thermal conductivity enhancement is obtained as a result of self correlation in the potential energy flux. The effect saturates at higher volume fractions due to the cross-mode correlation between the potential and the virial flux.

A strong solid-fluid coupling also introduces an amorphous-like structural transition and a pronounced cage effect that significantly reduces the self diffusion of the nano-clusters. These attendant structural and diffusive effects, unlike the self correlation of the potential flux, are amenable to experimental observations. The cluster-fluid interface is characterized by large fluctuations in the potential energy which is indicative of an unusual exchange of potential energy among the interfacial fluid atoms. For small nano-clusters, the interfacial layers interact with each other to form a percolating network. The research findings highlight the importance of surface interactions and show that the interfacial thermal resistance emanating from the self correlation of the collision flux is not the limiting mechanism for heat transfer in nano-colloids.

This thesis also addresses several theoretical concerns regarding the microscopic thermal transport in colloids by using non-equilibrium molecular dynamics simulations (NEMD). The time averaged microscopic heat flux which assumes spatial homogeneity is shown to be applicable to nano-colloidal systems. Further, it is demonstrated that the thermal conductivity from a NEMD simulation is statistically equivalent to that of an equilibrium linear response evaluation only under certain dynamic conditions at the cluster-fluid interface. The concept of interfacial dynamical similarity is developed to establish this equivalence.
The proposed thermal conduction model is consistent with several experimental observations such as the anomalous enhancement at small volume fractions with very small nanoparticles (3-10nm), limiting behavior at higher volume fractions, and the lack of correlation of the enhancement to the intrinsic thermal conductivity of the nano-clusters. The model also suggests possible avenues for optimizing the colloids by developing nano-clusters that have functionalized surface layers to maximize the interactions with the fluid atoms.

In the second part of this thesis, smooth field estimators based on statistical inference and smoothing kernels are developed to transfer molecular data to the continuum for hybrid and equation-free multiscale simulations. The field estimators are then employed to implement coarse projection, a multiscale integration scheme, for a shear driven flow in an enclosure. This thesis shows that the spatial continuity and smoothness of the microscopically generated coarse variables, geometrically similar initial conditions and the separation of timescales are essential for the correct coarse field evolution with coarse projection.

Thesis Supervisor: Sidney Yip
Title: Professor of Nuclear Science and Engineering, and Materials Science and Engineering
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1. Introduction and Scope

1.1 Colloids

Fine dispersion of insoluble solid particles in a liquid is known as a colloidal suspension. Colloids are ubiquitous. They are found in nature such as in living cells and are also commonly encountered in the chemical and biological industry. The technologically relevant colloids often have water as the base medium with the particles composed of macro molecules or large agglomeration of molecules. The smallest linear dimension of the solid particles generally ranges from 10 Å and 1 μm.

The modern science of colloids, which dates back to early studies by Faraday in 1856 [1], is multidisciplinary with overlapping domains in physics, chemistry, material science, biology among several others [2, 3]. Traditionally and not surprisingly, colloids are investigated for their diffusive and rheological properties. The diffusive properties are of paramount interest in the biological sciences while a fundamental understanding of the shear behavior is essential in the chemical industry. The study of heat transport in solid dispersions is relatively recent. Ahuja in 1975 [4, 5] showed that polystyrene suspensions in aqueous glycerin and sodium chloride can increase the heat transfer by a factor of two under laminar flow conditions with marginal changes in the friction factor. Even with such impressive data, particle dispersions were not generally considered as a useful heat transfer enhancement technique. The major drawback came from the micron sized particles which pose significant corrosion and erosion hazards in engineering systems.

With the advent of nanotechnology, it has become possible to manufacture colloids with a variety of nano-sized particles such as oxides, carbides and metals. Unlike the suspensions with micron sized particles, nano-colloids can form stable systems with very little settling with appropriate chemical conditioning. This raises the exciting possibility of employing nano-
colloids for enhancing the heat transfer in systems where a fluid is used as a medium to transfer energy.

The focus of this thesis is on the thermal conduction mechanisms in a nano-colloid. The study of thermal conduction has both practical and intrinsic value. On the practical side, enhanced thermal conductivities can augment the heat transfer under laminar flow conditions and are potentially useful for microfluidics applications. On the theoretical front, the conduction mechanisms in colloidal systems are relatively unknown, especially at nano-scales. This thesis will theoretically investigate the possible modes of thermal conduction through a combination of linear response theory and molecular dynamics simulations.

1.2 Thermal Conduction Experiments in Nano-Colloids

The first thermal conductivity experiments with nano-sized particles were reported by Masuda et al in Japan [6] in 1993 with a hot-wire probe. They demonstrated that thermal conductivity of ultra fine suspensions of alumina, silica and other oxides in water can increase as much as 30% for a particle volume fraction of 4.3%. These enhancements are much higher than what are classically predicted with the effective medium theories [7]. In the United States, Choi [8] in 1995 at the Argonne National Laboratory proposed to construct a new class of engineered fluids with superior heat transfer capabilities. Since then, a series of experiments (a majority using hot-wire measurement system) were performed with nano-colloids, and enhanced thermal conductivity enhancements and anomalous trends were reported by several research groups.

The term nanofluid was first coined by Choi for denoting this new class of engineered fluids. In many respects, the terminology is relevant because of the use of nano-sized materials. One inadvertent diversion with the new terminology is that complex colloidal characteristics such as surface charges and other interfacial characteristics that appear to play a key role in the thermal transport processes have not received the appropriate recognition they deserve. Therefore, in this thesis, colloidal suspensions with nano-sized \([O(1-100 \text{ nm})]\) particles are simply referred to as nano-colloids. This study focuses on colloids with nanoparticles that are approximately spherical.
X. Wang et al [9] reported enhanced thermal conductivities for alumina and cupric oxide (CuO) with a variety of base fluids including water and ethylene glycol. They observed that the thermal conductivity enhancement was approximately proportional to the volume fraction of the particles. With alumina particles (28 nm mean diameter) in ethylene glycol, they observed a maximum of 40% increase in the conductivity with a volume fraction of 8%. Eastman et al [10] showed that, without additives, 10 nm copper particles in ethylene glycol could enhance the conductivity only by 2% with a volume fraction of 0.1%. The enhancement however, increased to 10% for the same volume fraction and 40% for a volume fraction of 0.2% when small quantities (<1%) of thioglycolic acid was added. This was the first evidence (though not recognized in the paper) that the thermal conduction mechanism has a strong dependence on the chemical interactions, possibly at the cluster interface. A similar conclusion was drawn from the work of Patel et al [11] which showed that covalent (thiolate) bonded smaller particles had lower thermal conductivities than uncoated bigger particles. The above results indicated that chemical bonding at the surface has a significant influence on the nature of thermal conduction mechanism.

Hong et al [12, 13] measured thermal conductivity of 10 nm iron colloidal systems in ethylene glycol and showed the enhancements to be a non-linear function of volume fraction. Further, the enhancements were substantially higher than those of copper nanoparticles. This was rather surprising given the larger intrinsic thermal conductivity of copper. It was also shown that smaller particles of the same type lead to a larger enhancement. More recently, the Fe₃O₄ colloids were reported to have a higher thermal conductivity than alumina or cupric oxide [14] even though the latter materials had a better thermal conductivity. These results show that the effective thermal conductivity of a colloid, in general, does not follow the classical formalism of Maxwell where the conductivity is simply a function of the volume fraction and the corresponding conductivities of the phases. Instead, they suggest a more complex interaction of the solvent with the nanoparticles.

Das et al [15] measured the conductivities of alumina and cupric oxide in water for different temperatures ranging from 20 °C to 50 °C and for different loading conditions. At variance with the effective medium theory, they observed a linear increase in the conductivity ratio with temperature for both the materials. For the same loading fraction, however, the rate of increase
was higher for cupric oxide than alumina. Similar trends were seen with gold particles (4nm) in toluene [11] even though the enhancement showed a saturating behavior at higher temperatures. Incidentally, an astonishing 11% increase was reported for almost vanishing concentration of 0.008% for gold nano-particles with a thiolate covering. This unusually large enhancement with gold nanoparticles however, has not been reproduced at other research laboratories. For example, Putnam and co-workers using a laser beam deflection technique [16] on alkanethiolate-protected Au nanoparticles (2 nm diameter) in toluene at a maximum volume fraction of 0.35% reported only marginal deviation from the prediction of effective medium theory. A rational explanation to the discrepancies in [16] and [11] is not possible as both experiments have not characterized the chemical characteristics of the colloid such as the surface charges.

There are several other heat transfer properties such as the heat transfer coefficient [17, 18], viscosity and critical heat flux [19-23] which are of interest to the thermal industry. These colloidal properties, however, are not covered in the present study.

1.3 Complex Colloidal Characteristics and Thermal Conductivity

Metallic and oxide particles at the nanoscale are highly reactive. When a colloid is prepared with such nanoparticles in aqueous media, complex physical and chemical adsorption mechanisms are expected at the particle surface. An uncharged surface can acquire charges either by preferential adsorption of an ion from the solution, or the ionization or dissociation of a surface group which results in a proton transfers [2]. The adsorption of $H^+$ and $OH^-$ on insoluble oxides generally falls into the first category while in the metal-solution interfaces accumulation of electrons at the interface is main mechanism of charging.

A charged colloidal particle will be surrounded by ions that are of opposite sign. Even though there is an overall charge neutrality, the interface itself can affect the transport processes. The surrounding ions can move under the influence of thermal diffusion or an electric field and the region of charge imbalance due to the presence of charged particle can be of the order of few molecular dimensions [3]. The distribution of charges on the particles and presence of counterbalancing charges in the solution is known as the electrical double layer. Often, the
double layer, consists of two parts, an inner compact region (called Stern layer) which consists of ions which are bound tightly to the surface and the outer ‘diffuse’ region where ions are free to move. The electric potential at the interface between the Stern and diffusive layers is called the zeta potential. The zeta potential is a function of surface charge of the colloidal particles and the adsorbed layer in the Stern layer, and is an indicator of colloidal stability.

It is clear from the previously cited experiments that the thermal conductivity enhancement is simply not a function of volume fraction or any geometrical shape factor. More specific results are obtained by Xie et al [24] where it is shown that the thermal conductivity in an aqueous media is a function of pH (a measure of the hydrogen ions) of the colloidal system. The conductivity enhancement was observed to decrease when the pH was increased from 2 to 12. The experiments by Lee et al [25] remain to date, the only experiment to highlight the importance of surface charges on the nanoparticle. They have shown that the thermal conductivity is proportional to the product of the charges site density and the ion density. Remarkably, the enhancement was shown to vary from 1% to 12% by simply adjusting the pH at the same volume fraction. The experimental evidences thus far, suggest the overriding importance of surface interactions.

1.4 Theoretical Modeling of Thermal Conductivity

The early attempts to explain the anomalous behavior seen in nano-colloids were made with the effective medium theories of Maxwell [7] for composite materials. This theory is applicable to dilute, isotropic, homogeneous colloids with randomly dispersed spherical particles having uniform particle size. Maxwell’s theory was originally formulated for predicting electrical properties such as electrical conductivity and dielectric constant. Maxwell’s formalism give reasonable conformity with experimental data for micron-sized particles at low particle concentrations [26]. Hamilton and Crosser (H&C) subsequently modified Maxwell’s theory for non-spherical particles [27]. As shown by Keblinski et al, most of the oxide data on thermal conductivity of colloids adhere to the effective medium theories [28]. A possible explanation is that the nanoparticles are relatively large (≥20 nm) and the chemical interactions which occur at the interface may have only a weak influence on the thermal conductivity. In contrast, the
colloids with smaller sized particles ($\leq 10$ nm) show unusually large conductivity enhancements [10], non-linear increase with volume fraction with a limiting behavior [12, 29], and apparent size dependency [13] which are not captured by the effective medium theories.

Keblinski et al [30] and Eastman et al [31] elucidated four possible mechanisms for the anomalous conductivity behavior seen in nano-colloids. These mechanisms were either hydrodynamic in origin or were based on concepts from solid-state physics. The temperature and size dependency suggested a correlation to the Brownian motion of the particles. However, a simple order-of-magnitude calculation and molecular dynamics (MD) simulations [30, 32] show that the Brownian motion hydrodynamic effects are negligible. Liquid layering around the particles was offered as another mechanism in [31] and [30]. The essential idea was that liquid molecules can form a layer around the solid particles thereby enhancing the local ordering. Since phonon or vibrational energy transfer in crystalline solid is very effective, such local ordering in the liquid could potentially lead to enhanced heat transport. An MD simulation [33], however, showed that liquid layering had no perceptible effect on the thermal conductivity.

The third mechanism was related to the nature of heat transport in nano-particles. The authors rightly point out that the generally accepted diffusive transport mechanism may not be valid and heat transport can be influenced by ballistic phonons at nanoscales. If the ballistic phonons initiated in one particle can persist in the liquid and get transmitted to another solid particle, then the heat transport can significantly increase. The (damped) phonon mean free path in the liquid is typically small because the local ordering is limited to few atomic diameters. Since, particles are constantly moving by Brownian motion, there is a possibility that somewhat coherent phonon transfer is possible even with low particle concentrations if the particles sizes are close to a nanometer. In such a scenario, the inter-particle distance becomes comparable to the particle diameter itself. Such coherent transport is reported for acoustic excitations in colloidal systems where the diameter of the particles is comparable to the wavelength of sound. It is interesting to note that the ballistic phonon mechanism relies on both the hydrodynamics and solid-state concepts.
The author believes that the above mechanism may perhaps embody the paradigm of heat transport in nano-colloids. It is shown in Chapter 3 that such concerted or coherent energy transfer is possible under certain cluster-fluid interfacial conditions. Thermal energy however, is not transferred by vibrational (phonon-like) modes but through a cooperative exchange in the potential energy among the interfacial atoms. Such a cooperative mechanism can in principle, explain the size dependency and the anomalous enhancement observed in metallic colloids with a diameter of the order of 1 nm.

Lastly, Keblinski et al [30] and Eastman et al [31] find clustering of nano-particles can enhance the thermal conduction paths. This is an unlikely mechanism for conductivity enhancement at low volume fractions as large regions of host fluid without the clusters can create additional thermal resistance. Motivated by the possibility of percolating structures, Wang et al developed a model based on fractal dimensions [34]. This model shows some promise even though it may not be adequate as a general theoretical tool.

The first microscopic simulation is performed by Bhattacharya et al [35] using Brownian dynamics where the solvent particles are neglected and their effects are represented by a combination of random and frictional forces. The solute particles are then allowed to move according to Newton’s second law of motion. The forces on the solute particles are evaluated from an assumed form of a two-body empirical potential with two empirical constants $A$ and $B$ which are fitted to reproduce the experimental data. Even though the simulation results shows the right trend for the thermal conductivity with oxide particles, there are several drawbacks of this approach:

- The only conserved variable in a Brownian Dynamics is the mass and the use of Brownian dynamics for thermal conductivity simulations is inappropriate. Dissipative Particle Dynamics (DPD) with energy conservation [36] however, is an alternative approach.

- The classical Green-Kubo formalism given in [35] needs correction in a Brownian dynamics simulation. The governing phase-space trajectories pertain to those of the
Fokker-Planck equation which are discontinuous and stochastic [37]. It may be noted that the classical Green-Kubo formalism [38] is derived from the time-symmetric Liouville equation [39].

- It is assumed that the enhancements from the thermal conductivity solely arise from the particle-particle repulsion. This appears to be unreasonable as several experiments suggest the importance of solute-fluid interactions.

Furthermore, the form of the solute-solute potential is assumed and to match the experimental data, the constants are constrained to take unphysical values [28]. The parallel mode of accessing the effective conductivity from that of the solute through the volume fraction is also unphysical as several experiments indicate. The theoretically correct approach is to employ realistic interatomic potentials for solvent and solute, and perform true molecular dynamics simulations. The simulations and analyses performed in this thesis follow this dictum.

The hydrodynamic model proposed by Kumar et al [40] employs the Fourier law of conduction and elementary concepts from the kinetic theory [38]. The model attempts to explain the anomalous heat transfer observed in nano-colloids for different temperatures and nano particle diameters but the arguments are somewhat heuristic. To make contact with the experimental results, a rather high mean free path of $O(1 \text{ cm})$ is required which is clearly unphysical [28].

Two relatively recent hydrodynamic models [41, 42] suggest that the Brownian motion of the particles drag the fluid along with them thereby transferring more heat by convection or bulk motion of the fluid atoms. The macro-scale convection behavior is assumed at nano-scales by invoking the macro-scale heat transfer correlations for flow around a solid sphere. Even though impressive agreements are obtained with the experimental data including the variation with temperature and size, the central concept of micro-convection may be debatable as shown in [32]. All the hydrodynamic models entail the use of a ‘Brownian velocity’ which is not a formal concept in Brownian or Langevin dynamics. As a result, Brownian velocities are defined in an ad-hoc manner [40-42]. Furthermore, non-dimensional parameters such as Reynolds number ($Re$) are defined differently in each model. Prasher et al [42] defines a $Re$ that is based on the
thermal speed which is inversely proportional to the square root of particle diameter. Jang and Choi [41], on the other hand, have a definition based on the classical Einstein diffusion constant which turns out to be independent of particle diameter.

It is instructive to compare the relative magnitudes of the Brownian velocities from different models. For 10 nm alumina nanoparticles in water, the Prasher et al model gives a Brownian velocity of $O(100 \text{ cm/s})$ while Jang and Choi model predicts a value of $O(1 \text{ cm/s})$. In thermal diffusion or a thermal conductivity experiments with reasonable temperature gradients, the colloidal particles move at velocities that are of the $O(1 \text{ cm/s})$. This is the velocity by which any micro-convection mechanism can transfer the heat transfer information through the velocity field. It is evident that Prasher et al model is overestimating the mean drift speeds of colloidal particles. The Brownian velocity by Prasher et al definition, is random and a directed motion of the particles in response to the temperature gradient is an average of these random velocities. Clearly, the average velocity is only a fraction of the Brownian or thermal velocities. By choosing the rather high value for the velocity $O(100 \text{ cm/s})$, an unnaturally high heat transfer coefficient and a thermal conductivity is obtained. The better agreement seen in Jang and Choi model is offset by the use of an arbitrary heat transfer correlation to match the data. As pointed out by Prasher et al [42], a rather ad-hoc thermal boundary layer and a parallel mode of heat conduction is assumed in this model. Thus, there is a fair amount of arbitrariness in the interpretation of the Brownian models.

The physical origin of micro-convection is also ambiguous. Even though the nanoparticle relaxation is much slower than those of the fluid molecules, at the time scales accessible to experiments, both the nanoparticles and fluid molecules are transparent to the non-equilibrium conditions which can exist at shorter time scales. This means that a representative region in space containing both colloidal particles and fluid molecules achieve a local equilibrium state with an identifiable local temperature during the measurement process. MD simulations [32] have verified the assumption of local thermodynamic equilibrium for colloidal systems even under severe non-equilibrium conditions. The motivation for the micro-convection mechanism in [42] appear to come from particle to fluid heat transfer for macroscale fluidized beds. Clearly, the parallel breaks down at the nanoscale from a thermodynamic point of view.
Thermal conduction is a molecular phenomena and it demands a molecular level explanation. It is clear that the theoretical models for colloidal systems thus far, do not capture the essential physics.

1.5 Linear Response Theory

Linear response theory [43, 44] is a powerful and a general framework that is suitable for analyzing all the molecular transport phenomena. In this theory, the transport coefficients can be expressed as time correlation function of appropriate autocorrelation functions. In an equilibrium state, spontaneous fluctuations occur all the time and time correlations are spatio-temporal functions that describe these fluctuations [45]. The connection between the time correlation functions and transport properties comes from the celebrated Onsager’s regression hypothesis which states that the regression or de-correlation of the thermal fluctuations at equilibrium follows the macroscopic law of relaxation of small non-equilibrium disturbances [46, 47]. Thus, the time correlation formalism gives a framework where the transport coefficients can be evaluated under equilibrium conditions. The definition of time correlation does not assume anything on the physical state of the medium. Thus it is the most apposite theoretical framework for studying the thermal transport behavior of a colloid. The time correlation functions are calculated by averaging the appropriate dynamic variables over time using equilibrium molecular dynamics (MD) simulations [48, 49] and invoking the ergodic hypothesis of the equivalence of time and ensemble averaging [38].

1.6 Coarse Projection and Field Estimators

Colloids can exhibit complex rheological properties and display very interesting shear behavior. Depending on the shear rate, shear thinning and thickening can be observed [2, 3]. Thinning refers to a decrease in effective viscosity while thickening leads to the opposite effect. In the traditional modeling, empirical constitutive equations for the properties and relationship between stresses and strain rates are postulated for characterization of such complex behavior. In principle, the most complex behavior can be predicted from the first principles by characterizing the microscopic interactions involving atoms and molecules. Simulators such as molecular dynamics
(MD) and Monte Carlo (MC) are efficient for simulating the microscopic phenomena. The present-day computing resources, however, severely limits their applicability to molecular dimensions and time scales. Coarse projection is devised to simulate macroscopic phenomena exclusively using the microscopic simulators such as molecular dynamics.

Coarse projection belongs to a bigger family of the so called *equation-free* multiscale methodology [50-77]. A striking feature of this methodology is that the governing equations of the continuum are not required to be known in the closed form even though it is assumed that they exist conceptually. The essential idea is to use short and intelligent microscopic bursts of appropriately initialized molecular simulations and then evaluate the evolution of pertinent macroscopic field variables. The continuity of coarse variables both in space and time, and separation of time scales provide a theoretical basis for the correct evolution of coarse variables. Rather than coupling the molecular simulators with the continuum, the equation-free approach bypasses the coarse field descriptions entirely and works exclusively with microscopic simulators using a series of numerical operations.

Coarse grained or bin averages in MD or microscopic simulations often suffer from noisy fluctuations or poor resolution. Most often, the intrinsic fluctuations in the particle simulation appear as non-physical spatial noise in the field representation. This behavior arises primarily due to the *ad-hoc* bin averaging procedure that is commonly employed for extracting the field information. In the bin averaging method, the molecular domain is divided into spatial bins and averages of the MD variables are taken over each bin. These averages are construed as representative of the underlying field. Bin averaging however, leads to compromises in spatial resolution which are inherently unsatisfying. For example, if the bin sizes are too small, the fields will have a rough and jagged topology. Additional interpolation is generally necessary to smoothen out the non-physical distortions. On the other hand, if the bins are too big, local information gets smeared out. It is clear that an accurate and smooth field description is an essential ingredient to multiscale modeling.
1.7 Scope of the Thesis

This thesis has two focus areas. In the first part, the thermal conduction mechanisms in nano-colloids are evaluated by using a combination of linear response theory and molecular dynamics (MD) simulations. In the second, statistical and kernel field estimators are developed for implementation of coarse projection, a multiscale integration methodology.

The primary focus of this thesis is to understand the various thermal conduction mechanisms in a nano-colloid without making any a priori assumptions on the physical processes. The linear response formalism, elucidated in Chapter 2, is first applied to a model system of sub-nanometer platinum (Pt) clusters finely dispersed in liquid xenon (Xe). Molecular dynamics (MD) simulations are employed to determine the appropriate time correlation functions. The theory and the implementation of a MD simulation are given in Appendix A. Since this is the first reported systematic investigation on the thermal transport in nano-colloids, the choice of the materials reflects the need for economic but insightful analyses, and reasonably accurate interatomic potentials. It is certainly within means to study a more complex colloid such as copper and water but is not attempted for two reasons. Water has electrostatic forces and related complexities [78, 79] that can hinder a physical interpretation of microscopic conduction modes. Furthermore, sufficiently accurate potentials do not exist for the complex cross-interaction between the common metallic and oxide nanoparticles, and water. On the contrary, the potential between Xe and Pt are derived from a variety of experimental data including scattering measurements, thermal desorption rates and thermodynamic properties [80]. The experiments [25] indicate that surface interactions appear to be important in the thermal transport and it is important to have a representative interaction in the model system. In this thesis, the cross-interaction between fluid and solid atoms serves as the prototype for the surface and interfacial effects.

The Xe-Xe interactions are well characterized by the classical Lennard Jones (LJ) potential. Reported values of thermal and fluid properties with LJ potential for noble gas elements and mixtures are in good agreement with those from the experiments [81, 82]. The Pt-Pt interactions for bulk systems can be adequately described by a embedded atom potential (EAM) [83]. The solid clusters in this study are limited to few tens of atoms to maximize the interactions with the
fluid atoms. It is not immediately clear whether the many-body effects that characterize the bulk properties in the EAM potential are relevant to clusters that consist of surface atoms. Taking a cue from the experiments, the thermal conductivity of Fe colloids is higher than that with Cu [12] even though the thermal conductivity of Fe is five times lower than that of Cu. Similar behavior is seen with FeO₄ colloid [14] with a lower particle thermal conductivity in relation to other oxides such as titania [29] and alumina, but exhibiting a higher colloidal thermal conductivity. This implies that the intrinsic thermal conductivity of the nanoparticles plays only a minor role in the conduction process, possibly limited to dilute nano-colloids. For this reason, a simple two body LJ potential is assumed for the Pt-Pt interactions. The sensitivity of the conduction mechanism to the solid atom interactions will be explicitly verified.

The thermal conductivity is calculated as a time correlation of heat flux autocorrelation function [38]. The microscopic heat flux vector is decomposed into three fluctuation modes namely, the kinetic flux (K), potential flux (P) and the virial or collisional flux (C). Using the three modes, the thermal conductivity is decomposed into nine components, three self-correlation (KK, PP and CC) and six cross-correlations (CP, CK etc). Moreover, each component is a sum over atom species, Xe-Xe, Xe-Pt, and Pt-Pt. In this manner, the interplay between the molecular mechanisms that govern the thermal conductivity is examined. As the name implies, KK correlation denotes the conductivity contribution from the kinetic motion of the atoms. This component, therefore, can test whether Brownian motion of the particles plays a significant role in the conduction mechanism. The CC correlation is most prominent in solids and liquids. It represents work transfer arising from the molecular interactions and in particular, they represent the phonon or vibrational modes in a solid. For this reason, phonon conductivity is often approximated solely by the CC correlation in solids [84]. As the significance of PP and the other cross-correlations are currently unknown, systematic investigations will be performed to trace their physical origin and the relevance in nano-colloids. Xe-Pt simulations and analyses are given in Chapter 3.

A generic colloid with clusters made of non-linear springs is investigated next to evaluate the importance of fluid-solid cross interaction on the thermal conduction mechanisms. The attractive potential well is taken as a measure of the cross-interaction and is systematically varied to study
its effect on the various components of the thermal conductivity. This investigation serves three purposes. In [31] it is suggested that solid-like layering of liquid particles can be anticipated in close proximity to the fluid atoms. The first objective therefore, is to explicitly analyze the structural formation of fluid atoms around a cluster and quantify its bearing on the thermal conductivity. The second objective is to calculate the self-diffusion coefficients of the nanoclusters for varying levels of cross interaction. This task will further verify the role of Brownian motion of the nanoparticles in the conduction mechanism. It is well-accepted that the solid-fluid interfaces are generally characterized by a high thermal resistance which arises from the mismatch of the vibrational frequencies of the solid and liquid atoms [85]. Since the vibrational frequencies of a liquid are typically lower than those in a solid, the high frequency phonons initiated in the clusters can get scattered at the solid-fluid interface introducing a thermal or the Kapitza resistance [85, 86] that can reduce the thermal conductivities significantly. The interfacial conduction resistance is a legitimate objection to the enhanced conductivities observed in nano-colloids. A recent investigation has shown that [87] two nanoparticles which are separated by a distance smaller than the particle diameter, shows a thermal resistance lower than the contact resistance. As seen from the decomposition analysis, there are possibilities of conduction mechanisms other than that emanating from the $CC$ correlation. The third objective therefore is to be systematically vary the cross-interaction to study the behavior of different self and cross-correlations. The pertinent results and observations are discussed in Chapter 4.

This thesis also addresses the theoretical concerns regarding the thermal conductivity and the heat flux which is not uniquely defined for colloids [88]. For example, if both temperature and concentration gradients are present, then energy can be transported by both conduction and diffusion of the molecules. First, the correspondence between the experimentally observed conductivities and those evaluated from the linear response theory are brought out. The nature of the instantaneous microscopic heat flux is then examined in the context of equilibrium fluctuations and thermodynamics. It is sometimes regarded that the classical microscopic expression for the heat flux is not appropriate for non-homogeneous systems such as colloids [89]. With the help of non-equilibrium molecular dynamics simulations ($NEMD$), the suitability of the heat flux expression is evaluated. Another theoretical concern is regarding the validity of the linear response theory itself for nano-colloids. One viewpoint is that the linear response
theory for thermal conduction is applicable only if the spatial variation of the applied heat flux must be equivalent to that of the temperature [90]. On the other hand, the linear response theory assumes no more than a characteristic colloidal volume smaller than the macroscopic dimensions but large enough to have local thermodynamic equilibrium [44], a necessary condition for defining effective properties. It is therefore, possible to identify a time scale where the macroscopic gradients and thermodynamic variables correspond to that of the non-equilibrium state but with a local equilibrium distribution for the microscopic variables. In this thesis, the theoretical appropriateness of using the linear response theory in colloids will be evaluated. In addition, the cluster-fluid interface will be examined for deviations from equilibrium conditions. Typical NEMD simulations are characterized by astronomical gradients in the temperature \(O(10^{10}\text{ K/m})\). However, they do not cause a departure from the local equilibrium distribution for homogeneous systems [91]. In a colloidal system with interfaces, it is not known \textit{a priori}, whether equilibrium distribution can be maintained locally. This thesis will evaluate the conditions which can significantly affect the interfacial dynamics and transport. The \textit{NEMD} simulations and results are explained in Chapter 5.

In the second part of this thesis, a set of smooth statistical field estimators is developed based on maximum entropy principle constrained by moments derived from particle data. The maximum entropy (ME) estimator identifies the least biased distribution that is consistent with the prescribed set of constraints. The statistical field estimators are compared to those from conventional bin and kernel averages. The estimators are first applied to characterize the flow fields from a \textit{MD} simulation of a shear driven flow in an enclosure and then benchmarked to the fields derived from continuum simulations. Coarse projection, a multiscale integration scheme is then implemented with the microscopically generated fields. The key idea is to use short and intelligent microscopic bursts of appropriately initialized molecular simulations and evaluate the evolution of the pertinent macroscopic field variables. This thesis examines, in the context of a shear driven flow in an enclosure, whether the spatial continuity and smoothness of the microscopically generated coarse variables and the separation of time scales, result in a dynamically correct coarse evolution. Field estimators and coarse projection are elucidated in Chapters 6. Finally, the major findings of this thesis are summarized in Chapter 7.
2. Molecular Transport with Linear Response Theory

2.1 Linear Phenomenological Theory

Phenomenological relationships based on empirical observations are generally used to characterize transport. A simple example is the Fourier's law of thermal conduction which states that the heat flux across a plane is proportional to the gradient in the temperature. The proportionality constant is known as the thermal conductivity which is a property of the medium. At the macroscopic or continuum level, thermal conductivity is simply regarded as an empirical constant which in principle, can be accessed by experiments.

Thermal conduction belongs to the more general family of transport phenomena which arise when a system initially in equilibrium is perturbed by an external force or disturbance. A system is said to be in equilibrium when there intensive state variables such as density and temperature are invariant with time and all the gradients of the variables are absent. So under equilibrium conditions there are no macroscopic flow of mass, momentum and energy. When such a system is disturbed by an external or internal disturbance, the system is considered to be in a non-equilibrium state. Local thermodynamic equilibrium (LTE) is often invoked for systems that are marginally out of equilibrium. LTE states that all the thermodynamic functions exist for each element of the system and the thermodynamic quantities for a non-equilibrium system are the same functions of the local state variables as the corresponding equilibrium quantities [92]. LTE does not follow from the first and second laws of thermodynamics but is an additional assumption. If the gradients in the thermodynamics functions are small or if the time variation of these functions is slow compared to the slowest relaxation of the system, then LTE can be considered to be a good approximation.
A linear phenomenological theory is usually employed to characterize the non-equilibrium transport processes. This theory is described in some detail to highlight the coupled transport in colloids and is adapted from [44, 88, 92]. Historically, transport relationships have been experimentally determined between fluxes which develop in response to gradients in the system. The well-known phenomenological relationships for mass and momentum transfer are given by the Fick’s law of diffusion and the Newton’s law of viscosity. As previously stated, Fourier’s law is used to describe thermal conduction. When two or more gradients are present in the system, then the above constitutive relationships are not valid, in general. For example, if both temperature and concentration gradients are present, then energy can be transported by both conduction and diffusion of the molecules. As a generalization, the linear phenomenological theory postulates that the fluxes are linear homogeneous functions of the corresponding gradients. This linearity is expressed as [88]

\[ \mathbf{J} = \mathbf{L} \hat{\mathbf{X}} = \sum_{k=1}^{n} L_{ik} \hat{X}_k \quad (i=1,2,...,n) \]  

(2.1)

where \( \mathbf{J} \) and \( \hat{\mathbf{X}} \) are the generalized flux and gradient vectors respectively. \( \mathbf{L} \) is a matrix containing the phenomenological coefficients. The cross coefficients \( L_{ik} \) and \( L_{ki} \) are equal which follows from another postulate of the linear phenomenological theory which asserts that the matrix \( \mathbf{L} \) is symmetric. The symmetric relationship, while a postulate in the macroscopic thermodynamics, can be derived from statistical mechanics on the basis of microscopic irreversibility and is known as the Onsager reciprocal relationships. When \( L_{ik} = 0 \), the familiar constitutive relationships are recovered. The fluxes and gradients (or the thermodynamic 'forces') are connected to the second law of thermodynamics through the entropy production (\( \sigma \)) given by

\[ \sigma = \sum_{i=1}^{n} J_i \hat{X}_i \]  

(2.2)

A primary objective of this thesis is to provide an understanding of the thermal transport mechanisms in a colloid. The two gradients that are expected, in the absence of chemical
reactions and external fields, are the temperature and the concentration (equivalently the chemical potential). It is possible by linear transformation to create new fluxes and gradients which satisfy Onsager’s reciprocity conditions. For example, heat flux in a multi-component system cannot be uniquely defined as it is impossible to separate the internal energy flux into purely diffusive and conductive terms. This can be readily seen from the microscopic picture as described in [92]. The total energy of a system of a certain volume is the sum of its kinetic and potential energy. If a molecule leaves the system boundary, then the kinetic energy loss may be attributed to diffusion. If however, a molecule inside the boundary transfers its kinetic energy to a molecule which is outside the boundary, then this loss can be accounted as the heat loss. So for the kinetic energy, there is no ambiguity in partitioning the total energy flux. It is however, not so evident for the potential energy which is the sum of all the potential energies interactions. In other words, kinetic energy of a molecule can be uniquely defined while the potential energy can only be defined for a system of molecules. Often, the potential energy interaction is divided equally between two molecules if they have a pair-wise interaction. There is no rigorous justification, however, for this arbitrary procedure even though it is a useful procedure in the microscopic theoretical development. Thus, changes in the potential energy when a molecule escapes the boundary or when it interacts with one another within the system cannot be uniquely partitioned into diffusive and conductive contributions.

A common definition for the heat flux follows from the second law of thermodynamics. For an $n$ component system it is given by [88]

$$J_q = \mathbf{\dot{J}}_q - \sum_{k=1}^{n} \kappa^k J^k$$  \hspace{1cm} (2.3)

where $\mathbf{\dot{J}}_q$ is the heat flux which is usually measured in an experiment and $J_q$ is the ‘reduced’ heat flux that is responsible for conduction in a multi-component system. This choice leads to

$$J_q = L_{qq} X_q + \sum_{k=1}^{n-1} L_{qk} \nabla X^k$$  \hspace{1cm} (2.4)
\[ J^i = L_{iq} X_q + \sum_{k=1}^{n-1} L_{ik} \nabla X^k \]  

(2.5)

with

\[ X_q = -\frac{\nabla T}{T^2} \]  

(2.6)

\[ X^k = \frac{-\nabla (\mu^k - \mu^n)}{T} \]  

(2.7)

where \( J \) is the mass flux, \( T \) is the temperature, \( \mu \) is the chemical potential and the subscripts \( k \) and \( n \) stand for any two species. For a simple binary colloidal system with components \((a, \beta)\), the phenomenological relationships reduces to

\[ J_a = -L_{qq} \frac{\nabla T}{T^2} - L_{q1} \frac{1}{T} \nabla (\mu^\alpha - \mu^\beta)_T \]  

(2.8)

\[ J^\alpha = -L_{1q} \frac{\nabla T}{T^2} - L_{11} \frac{1}{T} \nabla (\mu^\alpha - \mu^\beta)_T \]  

(2.9)

In experiments, diffusion is associated with a concentration gradient \((x)\) rather than the chemical potential. By invoking Gibbs-Duhem identity [88]

\[ \sum_{k=\alpha}^{\beta} x^k (\nabla \mu^k)_{T,p} = 0 \]  

(2.10)

and noting

\[ (\nabla \mu^\alpha)_{T,p} = \left( \frac{\partial \mu^\alpha}{\partial x^\alpha} \right)_{T,p} \nabla x^\alpha \]  

(2.11)

the following expressions are obtained
\[ \mathbf{J}_q = -L_{qq} \frac{\nabla T}{T^2} - L_{q1} \frac{1}{T x^\beta} \left( \frac{\partial \mu^\alpha}{\partial x^\alpha} \right)_{T,p} \nabla x^\alpha \] (2.12)

\[ \mathbf{J}^\alpha = -L_{\alpha q} \frac{\nabla T}{T^2} - L_{\alpha 1} \frac{1}{T x^\beta} \left( \frac{\partial \mu^\alpha}{\partial x^\alpha} \right)_{T,p} \nabla x^\alpha \] (2.13)

The second law of thermodynamics gives

\[ \sigma = J_1 X_1 + J_2 X_2 = L_{11} X_1^2 + (L_{12} + L_{21}) X_1 X_2 + L_{21} X_2^2 \geq 0 \] (2.14)

The necessary conditions for non-negative entropy production are: (1) \( \mathbf{L} \) should be semi-positive definite. (2) \( \mathbf{L} \) is symmetric (Onsager reciprocity condition). These conditions result in [88]

\[ L_{11} \geq 0, \quad L_{qq} \geq 0 \] (2.15)

\[ L_{qq} L_{11} - \frac{1}{4} (L_{q1} + L_{q1})^2 = L_{qq} L_{11} - (L_{q1})^2 \geq 0 \] (2.16)

The above relationships provide the limits on the phenomenological transport coefficients. The diffusion flux \( \mathbf{J} \) in the phenomenological equations is defined in the center of mass (CM) coordinate frame. It is defined as

\[ \mathbf{J}^\alpha = \rho^\alpha \left( v^\alpha - v_{CM} \right) \] (2.17)

where \( v_{CM} \) is the barycentric or CM velocity. According to a theorem by Prigogine [44, 88], the diffusion flux defined in any frame of reference leaves the entropy production invariant. For practical purposes, diffusion can therefore, be measured in lab coordinates. Also note that in equilibrium molecular dynamics simulations (MD), \( v_{CM} \) is set to zero to maintain zero net momentum.

The phenomenological coefficients (\( \mathbf{L} \)) are related to experimental coefficients as
\[ \kappa = \frac{L_{qq}}{T^2} \]  
\[ D'' = \frac{L_{q1}}{\rho x^a x^\beta T^2} \]  
\[ D_T = \frac{L_{1q}}{\rho x^a x^\beta T^2} \]  
\[ D_{12} = \frac{L_{11}}{\rho x^\beta T} \left( \frac{\partial \mu^a}{\partial x^a} \right)_{T, p} \]  

In the above expressions, \(D_T\), \(D''\) and \(D_{12}\) stand for the thermal diffusion coefficient, the Dufour coefficient and the mutual (binary) diffusion coefficient respectively. The density of the system is given by \(\rho\). Thermal diffusion coefficient (\(D_T\)) accounts for the flow of matter with a temperature gradient while the Dufour coefficient (\(D''\)) is a measure of the inverse effect which is the flow of heat due to the concentration gradient. Onsager's reciprocity theorem ensures that the coefficients \(D_T\) and \(D''\) are equal. The ratio of \(D_T\) to \(D_{12}\) is generally known as the Soret coefficient. \(\kappa\) is the thermal conductivity of the colloidal system and it is clear that it is a native property to the colloid without any contribution from the diffusion. For this reason, \(\kappa\) will be referred to as the intrinsic thermal conductivity of the colloid. As will be discussed subsequently, typical experiments do not measure the intrinsic thermal conductivity. Now, the set of flux relationships can be written as

\[ J_q = -\kappa \nabla T - \rho \left( \frac{\partial \mu^a}{\partial x^a} \right)_{T, p} TD'' \nabla x^a \]  
\[ J'' = -\rho x^a x^\beta D_T \nabla T - \rho D_{12} \nabla x^a \]  

With the law of entropy, the Onsager reciprocity relationship and the positivity of \(\left( \frac{\partial \mu^a}{\partial x^a} \right)_{T, p}\), the following conditions on the transport coefficients can be derived [88]
The phenomenological theory, therefore, shows that the thermal conductivity and the mutual diffusion constant should be non-negative at all times while allowing for sign changes in the thermal diffusion and Dufour coefficients. If the thermal diffusion coefficient is positive, it means that the particles (in a fluid) are diffusing from a higher temperature to a lower temperature and vice-versa. The same analogy holds for the Dufour effect.

As seen before, there are multiple definitions for heat flux which leads to different effective thermal conductivities for the system. In an experiment, measurement can be made at the beginning ($\nabla x^\alpha = 0$) or at the end ($J^\alpha = 0$). The four thermal conductivities for these limiting conditions can be written as [88]

\begin{align*}
J_q &= -\zeta \nabla T, \quad \hat{J}_q = -\hat{\zeta} \nabla T \quad (\nabla x^\alpha = 0) \\
J^\alpha &= -\lambda \nabla T, \quad \hat{J}^\alpha = -\hat{\lambda} \nabla T \quad (J^\alpha = 0)
\end{align*}  

(2.26) (2.27)

The reduced heat flux ($J_q$) is associated with two thermal conductivities ($\zeta, \lambda$) and the heat flux ($\hat{J}_q$) with ($\hat{\zeta}, \hat{\lambda}$). The difference between the heat fluxes are given in Eqn. (2.3) is solely due to the heat carried by the diffusing particles. It can be shown that [88]

\begin{align*}
\zeta &= \kappa, \quad \hat{\zeta} = \kappa + D_\tau (h^\alpha - h^\beta) \rho x^\alpha x^\beta \\
\lambda &= \kappa - \frac{(D_\tau)^2}{D_{12}} \left( \frac{\partial \mu^\alpha}{\partial x^\alpha} \right) \rho \left( x^\alpha \right)^2 x^\beta T, \quad \hat{\lambda} = \hat{\lambda}
\end{align*}  

(2.28) (2.29)
Thus at the end of the measurement when the mass fluxes are zero, the reduced thermal conductivity ($\lambda$) is *always* less than the intrinsic thermal conductivity ($\kappa$). At the beginning of the experiment when there are no concentration gradients, the effective thermal conductivity ($\xi$) can be higher or lower than the intrinsic thermal conductivity depending on the sign of the thermal diffusion coefficient and the difference in the partial enthalpies ($h$). It is interesting to note that the typical condition in an experiment does not measure the intrinsic thermal conductivity ($\kappa$). Usually, these differences in the thermal conductivities are small (few percents) for typical colloids. Now, the correspondence between the experimentally observed conductivities and heat fluxes, and those which can be theoretically determined is not always clear. The following sections will address this concern by following the appropriate developments in statistical mechanics and linear response theory.

### 2.2 Phase Space and Liouville Equation

The linear phenomenological theory described in the previous section lays the foundation for the thermal transport in colloid. It showed the multiplicity of definitions for the heat flux and thermal conductivities which is unlike that in a pure isotropic state where there are unique definitions for all the transport coefficients and the fluxes. The transport coefficients in the linear phenomenological theory are all macroscopic in nature and are expected to be derived through experiments. The transport coefficients, however, are ultimately dependent on the molecular mechanisms and several frameworks exist where all the transport coefficients are derivable from microscopic physics. The kinetic theory of Boltzmann [93] and the extension by Bogolubov [44], Chapman and Enskog, and the time correlation formalism [38, 39, 43, 45, 94] developed by Green, Kubo, Callen, Zwanzig, Mori and others are two such frameworks.

The kinetic theory of Boltzmann and the time correlation formalism start from the fundamental concept of phase space and its evolution which is described by the Liouville equation which is the most fundamental equation in statistical mechanics applicable to both equilibrium and non-equilibrium systems. Liouville equation is central to both the derivation of Boltzmann transport equation and the derivation of transport coefficients in the time correlation formalism. Therefore, the basic concepts are first reviewed (adapted from References [38, 39, 43, 45, 94]). In a system
of $N$ particles, a $6N$-dimensional phase space can be constructed from the $3N$ spatial coordinates and $3N$ momentum coordinates. A point in the phase space completely specifies the microscopic dynamical state of the $N$-particle system and a set of such phase points constitutes an ensemble of systems. When the phase points become infinitely dense, there will be a continuum of phase points. Any region in the phase space can then be described by a distribution function

$$f_N(p_1, p_2, ..., p_N, r_1, r_2, ..., r_N, t) = f_N(p, r, t)$$

(mathematically, a multidimensional probability density function) which gives the fraction of the phase points in an infinitesimal element of the phase space $dT \equiv (dp_1, dp_2, ..., dp_N, dr_1, dr_2, ..., dr_N)$. The evolution equation of the phase points can be formulated from the conservation property of the distribution function which is given by

$$\frac{\partial f_N}{\partial t} = \nabla \cdot (f_N u)$$

(2.30)

where $u$ is given by

$$u = (p_1, p_2, ..., p_N, r_1, r_2, ..., r_N)$$

(2.31)

In a conservative system, the distribution function is a constant along a trajectory in the phase space. Using Hamilton’s equations of motion

$$\dot{p}_i = -\frac{\partial H}{\partial r_i}, \quad \dot{q}_i = \frac{\partial H}{\partial p_i}$$

(2.32)

the evolution equation for $f_N$, known as Liouville equation, is expressed as

$$\frac{\partial f_N}{\partial t} + \{H, f_N\}_{PB} = 0$$

(2.33)

$H$ in the above equation stands for the Hamiltonian which is the sum of the potential and kinetic energies in the absence of external fields. $PB$ refers to Poisson bracket which is given by

$$\{H, f_N\}_{PB} = \sum_{j=1}^{N} \frac{\partial H}{\partial p_j} \frac{\partial f_N}{\partial r_j} - \frac{\partial H}{\partial r_j} \frac{\partial f_N}{\partial p_j}$$

(2.34)
The Liouville equation is also written as

\[
\frac{\partial f_N}{\partial t} = -iLf_N
\]  

(2.35)

where \( L \) is the Liouville operator which in Cartesian coordinates is given by

\[
L = -i \left( \sum_{j=1}^{N} \frac{\mathbf{p}_j}{m_j} \nabla_{\mathbf{r}_j} + \sum_{j=1}^{N} \mathbf{F}_j \nabla_{\mathbf{p}_j} \right)
\]  

(2.36)

where \( \nabla_{\mathbf{r}_j} \) and \( \nabla_{\mathbf{p}_j} \) are the gradients with respect to spatial and momentum coordinates respectively. \( \mathbf{F}_j \) is total force on the \( j \)-th particle. The formal solution to the Liouville equation is given by

\[
f_N(p,r,t) = e^{-iLt} f_N(p,r,0)
\]  

(2.37)

The propagator \( e^{-iLt} \), called the \( f \)-propagator, propagates the distribution function and is given by \([39]\)

\[
e^{-iLt} = \sum_{n=0}^{\infty} \frac{(-t)^n}{n!} (iL)^n
\]  

(2.38)

Any function in the phase space evolves according to the so-called \( p \)-propagator given by \( e^{iL_t} \). The evolution of a dynamical variable \( A \) is given by

\[
A(\Gamma,t) = e^{iL_t} A(\Gamma,0)
\]  

(2.39)

When the equations of motion are derivable from a Hamiltonian, then the phase space is incompressible and the following condition holds: \( L = \mathcal{E} \). In this thesis, it is assumed that the
phase space is incompressible and a Hamiltonian exists which makes the two operators identical. Nevertheless, for the sake of completeness, the differences are noted in the derivations. For the derivation of the transport properties, it is not clear whether the equations of motion can be reduced from a Hamiltonian. The approach followed in this thesis assumes the existence of an effective Hamiltonian. Note that the operator $iL$ generates the distribution $\rho$ (which is the defined as the equilibrium distribution function) while the propagator $e^{-iLt}$ preserves $\rho$. This arises from the basic property of $L$ being self-adjoint or Hermetian ($L = L^\dagger$). The propagator $e^{iEt}$ is unitary which means that it preserves the norm in the Liouville space identified as an inner-product or Hilbert space.

2.3 Time Correlation Functions and Onsager’s Regression Hypothesis

In the classical Boltzmann kinetic theory, the N-particle distribution function is reduced to a single particle distribution function and has a further assumption of allowing only binary collisions between atoms or molecules. Bogolubov extends the classical formulation to moderately dense gases by showing that the single particle distribution is still sufficient but reasonably physical results are derived only when the interatomic potentials are purely repulsive and the collisions are limited to ternary interactions. The colloids which are investigated in this thesis have attractive potentials and thus, the kinetic theory of Boltzmann as a general framework is not appropriate for the study of colloids.

A more appropriate approach for characterizing the transport process in colloids is through a relatively new approach based on time correlation functions. In an equilibrium state, spontaneous fluctuations occur all the time and time correlations are spatio-temporal functions that describe these fluctuations. A formal definition of a correlation function of two variables $A$ and $B$ is given by [39]

$$C_{AB}(t) = \int d\Gamma f_0^0 B^* e^{i\Gamma t} A \equiv \langle A(t)B^* \rangle$$

(2.40)
where $f^0_N$ is the equilibrium distribution function which corresponds to the steady unperturbed equations of motion with no explicit time dependence, and the star corresponds to the complex conjugate. Classical time correlations are not dependent on a particular choice of time and hence, they are functions of only the differences in time (called the stationary property). The correlation function now can be expressed as

$$C_{AB}(t) = \int d\tau f^0_N(\tau)B^*e^{i\mathcal{L}t}A$$

$$= \int d\tau \left( e^{-i\mathcal{L}t}f^0_N \right)B^*e^{i\mathcal{L}t}A$$

$$= \int d\tau f^0_N \left( e^{i\mathcal{L}t}B^* \right)\left( e^{i\mathcal{L}(t+\tau)}A \right)$$

$$= \int d\tau f^0_N A(t+\tau)B^*(\tau)$$

The variables that are employed in this thesis are all real and without loss of generality, $\tau$ can be set to zero. Thus the correlation function can be written as

$$C_{AB}(t) = \int d\tau f^0_N A(t)B(0) \equiv \langle A(t)B(0) \rangle$$

where the pointed brackets denote the ensemble average. When the same variable is considered, the resulting expression becomes the auto-correlation function

$$C_{AA}(t) = \int d\tau f^0_N A(t)A(0) \equiv \langle A(t)A(0) \rangle$$

The correlation functions so far described are based on the ensemble average but can be connected to time averages through the ergodic hypothesis. Originally developed by Boltzmann and Maxwell, the ergodic hypothesis attempts to impart a dynamical basis for the statistical mechanics. Simply put, it postulates an equivalence between the ensemble average and the time average of an observable. It is expressed as
\begin{equation}
C_{AB}(t) = \int d\Gamma f_N^0 A(t) A(0) \equiv \langle A(t)B(0) \rangle \Leftrightarrow \lim_{t \to \infty} \frac{1}{t} \int_0^t d\tau A(\tau)B(0) \tag{2.47}
\end{equation}

This is an important result from a practical point of view because the time correlations functions can be now be averaged with the knowledge of the time history of the variables. In molecular dynamics simulations, the ergodic hypothesis is exploited to compute the time correlation functions. Time correlation functions have a similar status as that of the partition functions in equilibrium statistical mechanics [38]. The partition function is unique for a particular ensemble but separate time correlations functions exist which correspond to different non-equilibrium states. Unlike the partition function, time correlation functions (strictly speaking, their mathematical analogue in frequency space) are directly accessible to experiments such as neutron scattering [45].

The connection between the time correlation functions and transport properties comes from the celebrated Onsager’s regression hypothesis which states: \textit{the relaxation of macroscopic non-equilibrium disturbances is governed by the same laws as the regression of spontaneous microscopic fluctuations in an equilibrium system} [43]. This hypothesis essentially means that there is fundamentally no way of distinguishing between a non-equilibrium system, say a system with thermal gradient, relaxing to its equilibrium state (which corresponds to zero gradients) and the correlations of the spontaneous fluctuations at equilibrium. The heart of the hypothesis is that the equilibrium fluctuations get de-correlated at large times and become independent. The ‘regression’ of the fluctuations stands for the decay of the correlations which in turn is a measure of the ‘inertia’ of a non-equilibrium system relaxing towards equilibrium. An example will be the decay of the fluctuations of the shear stress and the shear viscosity of the fluid. Of course, the non-equilibrium system has to be close to equilibrium conditions for this hypothesis to hold. Onsager’s hypothesis can be derived from a more general linear response theory which includes thermal and other types of process such as electrical perturbations. The non-equilibrium state can be thought as a perturbation from an external force which induces a time-dependent response which is assumed to be linear with the perturbation. An important result from the linear response theory is the fluctuation-dissipation theorem proved in 1951 by Callen and Welton [43] and Onsager’s hypothesis is a consequence of this theorem.
In this thesis, the conduction mechanisms and transport coefficients are evaluated from linear response theory which is explained in greater detail in Section 2.6. The time correlation functions themselves are evaluated from equilibrium, classical, molecular dynamics simulations (MD) [48, 49] which are briefly described in Appendix A.

2.4 Instantaneous Microscopic Fluxes

As seen previously, the transport coefficients are based on fluxes. Therefore, to describe the transport properties from the time correlation approach, instantaneous microscopic fluxes need to be defined. The ensemble average of such microscopic fluxes corresponds to the experimentally observable (macroscopic) fluxes. In this section, the microscopic fluxes will be derived and a physical decomposition of the heat flux vector is presented which turns out to be extremely useful in uncovering the mechanism of thermal conduction. In Section 2.5, the ensemble averages are discussed and the appropriateness for use in inhomogeneous systems such as in colloids will be verified.

The conservation laws are applicable to both the microscopic and the macroscopic realms. So at any instant in time, mass, momentum and energy are conserved. The microscopic mass density ($\rho$), momentum density ($j$) and energy density ($e$) are given by [44]

$$\rho(r,t) = \sum_{k=1}^{N} m_k \delta(r_k - r)$$  \hspace{1cm} (2.48)

$$j(r,t) = \sum_{k=1}^{N} p_k \delta(r_k - r)$$  \hspace{1cm} (2.49)

$$e(r,t) = \left( \sum_{k=1}^{N} \frac{p_k^2}{2m_k} + \frac{1}{2} \sum_{j \neq k}^{N} \Phi(r_{jk}) \right) \delta(r_k - r)$$  \hspace{1cm} (2.50)

where $m$ is the mass, $p$ is the momentum and $\Phi$ is the potential energy. There are $N$ number of atoms each tagged by $k$. The three dimensional delta functions place the atoms at a given macroscopic radius $r$ and they have units of $1/V$ where $V$ is the volume. $V$ is such that it is small in comparison to macroscopic scale but sufficiently larger than the molecular dimensions. It is
also tacitly implied in the energy density formulation that the potential energy interactions are pair-wise (j,k) and it is shared equally among the molecules.

The Liouville equation gives the time derivative of a dynamical variable $A(\Gamma)$ as

$$\dot{A} = \sum_{k=1}^{N} \frac{p_k}{m_k} \nabla_{r_k} A - \sum_{k \neq j}^{N} \nabla_{r_k} \Phi(r_{jk}) \cdot \nabla_{p_k} A$$  \hspace{1cm} (2.51)

Using Eqn. (2.51) and Eqn. (2.48) the time rate of change of density can be derived as [44]

$$\dot{\rho}(r,t) = -\nabla_r \cdot j(r,t)$$  \hspace{1cm} (2.52)

The above equation simply shows mass is conserved at all times. Similarly, the rate of change in momentum density can be written as

$$\dot{j}(r,t) = \sum_{k=1}^{N} \frac{p_k}{m_k} \nabla_{r_k} \delta(r_k - r) - \sum_{j \neq k}^{N} \delta(r_k - r) \nabla_{r_k} \Phi(r_{jk})$$  \hspace{1cm} (2.53)

The second term containing the force can be written as

$$\sum_{j \neq k}^{N} \delta(r_k - r) \nabla_{r_k} \Phi(r_{jk}) = \frac{1}{2} \sum_{j \neq k}^{N} \left[ \delta(r_k - r) \nabla_{r_k} \Phi(r_{jk}) + \delta(r_j - r) \nabla_{r_j} \Phi(r_{jk}) \right]$$  \hspace{1cm} (2.54)

which can be simplified as

$$\sum_{j \neq k}^{N} \delta(r_k - r) \nabla_{r_k} \Phi(r_{jk}) = \frac{1}{2} \sum_{j \neq k}^{N} \left[ \left( \delta(r_k - r) - \delta(r_j - r) \right) \nabla_{r_k} \Phi(r_{jk}) \right]$$  \hspace{1cm} (2.55)

Note the peculiar difference in the delta function for the second term. It can be further simplified by assuming that the delta functions are analytical. This allows a Taylor series expansion as
\[ \delta(r_k - r) \delta(r_l - r) = -r_{jk} \cdot \nabla_r \Theta_{ij} \delta(r_k - r) \] (2.56)

where the operator \( \Theta_{ij} \) is given by [39]

\[ \Theta_{jk} = 1 - \frac{1}{2!} r_{jk} \cdot \nabla_r + \ldots + \frac{1}{n!} \left[ -r_{jk} \cdot \nabla_r \right]^{n-1} \] (2.57)

The delta functions are slowly varying over the range where the potential is applicable and therefore, \( \Theta_{ij} \) needs to be considered only to the first order. Strictly speaking, the delta functions are not functions in a mathematical sense. As mentioned previously, the primary purpose of these functions is to localize the atoms or molecules within a volume small on the macroscopic scale but reasonably large on the molecular scale. Thus it is safe to take the first order approximation and neglect the higher order terms as long as the system size is much larger (say, by one order) than the range of delta functions which is arbitrarily chosen as a few molecular dimensions.

Finally, the rate of change of momentum density can be written as

\[ \dot{j}(r, t) = -\nabla_r j_r(r) \] (2.58)

where \( j_r(r) \) is the microscopic shear stress tensor which is given by

\[ \dot{j}_r(r, t) = \sum_{k=1}^{N} \frac{p_k}{m_k} \delta(r_k - r) - \frac{1}{2} \sum_{j \neq k}^{N} \left[ r_{jk} \otimes \nabla_r \Phi(r_{jk}) \delta(r_k - r) \right] \] (2.59)

Similarly, the energy density rate can be expressed as a microscopic conservation law

\[ \dot{e}(r, t) = -\nabla_r \cdot j_q(r) \] (2.60)

where
\[ \mathbf{j}_q(r,t) = \sum_{k=1}^{N} \frac{p_k^2}{2m_k} \mathbf{P}_k \delta(r_k - \mathbf{r}) - \frac{1}{2} \sum_{j \neq k}^{N} \left[ \mathbf{r}_{jk} \otimes \nabla \Phi(r_{jk}) \right] \mathbf{P}_k \delta(r_k - \mathbf{r}) + \frac{1}{2} \sum_{j \neq k}^{N} \mathbf{F}(r_{jk}) \mathbf{P}_k \delta(r_k - \mathbf{r}) \]  

(2.61)

The above equation is for a single component system. On simplification, the following is obtained.

\[ \mathbf{j}_q(r,t) = \sum_{k=1}^{N} \frac{p_k^2}{2m_k} \mathbf{v}_k \delta(r_k - \mathbf{r}) + \frac{1}{2} \sum_{j \neq k}^{N} \mathbf{v}_k \delta(r_k - \mathbf{r}) + \frac{1}{2} \sum_{j \neq k}^{N} \left[ \mathbf{r}_{jk} \otimes \mathbf{F}(r_{jk}) \right] \mathbf{v}_k \delta(r_k - \mathbf{r}) \]  

(2.62)

In the above expression, \( \mathbf{v} \) is the velocity and \( \mathbf{F} \) is the force. It is now seen that the heat flux vector can be decomposed into three modes, the flux carried by the kinetic energy (K), flux carried by the potential energy (P) and the flux carried by the collisions or work done by the stress tensor (C). The physical significance of these modes will be discussed in greater depth in Chapter 3.

There exists a microscopic analogue for the diffusional heat flux given by Eqn. (2.3). The microscopic heat flux is given by [44].

\[ \mathbf{j}_q(r,t) = \mathbf{j}_q(r,t) - \sum_s \langle h^s \rangle \hat{j}^s(r,t) \]  

(2.63)

where \( s \) is the number of components in the system, and \( \mathbf{j}_q \) and \( \hat{j}_q \) are the reduced (conductive) and diffusional heat flux respectively. The term \( h \) stands for the specific partial enthalpy and the second term on the right denotes the partial enthalpy flux. The flux carried by the mean kinetic energy has been neglected in Eqn. (2.63). Comparing with Eqn. (2.3) it can be seen that there is a one-to-one correspondence between the macroscopic and microscopic heat flux expressions. The full expansion for a two component system will result in [95]

\[ \mathbf{j}_q(r,t) = \left( \frac{1}{2} \sum_{k=a}^{N_k} \sum_{i=a}^{N_i} m_i^a \langle v_i^a \rangle^2 v_i^a + \sum_{k=a}^{N_k} \sum_{i=a}^{N_i} \sum_{j \neq i}^{N_j} \left[ \mathbf{F}(r_{ij}) + r_{ij}^a \otimes \mathbf{F}_{ij}^a \right] v_i^a - \sum_{k=a}^{N_k} \langle h_i^a \rangle \sum_{i=a}^{N_i} v_i^a \right) \delta(r_i - \mathbf{r}) \]  

(2.64)
where $\alpha$ and $\beta$ are the two components. The partial enthalpy is now expressed per molecule instead of mass. The evaluation of partial enthalpies requires simplifying assumptions. The mean enthalpy can be computed as the sum of the mean kinetic and potential energies, and the virial [96, 97]. This means that the partial enthalpy of species $\alpha$ can be evaluated as

$$h^\alpha = \left( \sum_{k=1}^{N_\alpha} \frac{p_k^2}{2m_k} \right) + \left( \frac{1}{2} \sum_{j \neq k}^{N_\alpha} \Phi(r_{jk}) \cdot \mathbf{v}_k \right) + \left( \frac{1}{2} \sum_{j \neq k}^{N_\alpha} \left[ r_{jk} \otimes F(r_{jk}) \right] \cdot \mathbf{v}_k \right)$$ (2.65)

Note that the partial enthalpy in the above form has three components which are congruent to the three modes in the heat flux for a single component system. Thus, the decomposition of the heat flux is identical for both single component and binary systems. In the next chapter, the conduction mechanism of a nano-colloid will be explained with this decomposition analysis.

Strictly speaking, partial enthalpies are thermodynamic functions and are in general, not assessable from molecular qualities [96]. The decomposition of the partial enthalpy into kinetic, potential and virial is true for isotopic or equi-potential mixtures, and in less restrictive ideal mixtures. Vogelsang et al [98] has shown that the partial enthalpies based on the molecular quantities are significantly different from those calculated with more accurate thermodynamic simulations. The sum of the partial enthalpies calculated by the molecular approximation, however, is identical to the sum calculated by the thermodynamic simulation. Calling the last term in Eqn. (2.64) as the enthalpy flux $j_h$, the following expression can be written for a two-component colloid,

$$j_h(r,t) = -\frac{\partial}{\partial t} \sum_{i=1}^{N_\alpha} v_i^\alpha \delta(r_i - r) - h^\alpha \sum_{i=1}^{N_\alpha} v_i^\alpha \delta(r_i - r) - h^\beta \sum_{i=1}^{N_\beta} v_i^\beta \delta(r_i - r)$$ (2.66)

where $\alpha$ and $\beta$ denote the solid and the fluid atoms respectively. Since the net momentum is zero

$$j_h(r,t) = \sum_{i=1}^{N_\alpha} v_i^\alpha \left( -h^\alpha + h^\beta \left( \frac{m_\beta}{m_\alpha} \right) \right) \delta(r_i - r)$$ (2.67)
In a colloid, the potential energy and the virial of the solid atoms can be much higher (in magnitude) than those of the fluid atoms, and the total enthalpy can be dominated by the enthalpy of the solid atoms alone. Then for equal masses, Eqn. (2.67) can be approximated as

\[ j_h(r,t) = -(h^a + h^\beta) \sum_{i=1}^{N_a} v_i^a \delta(r_i - r) \]

or,

\[ j_h(r,t) = -(h^{total}) \sum_{i=1}^{N_a} v_i^a \delta(r_i - r) \]  

(2.69)

Thus, within the stated assumptions, an accurate knowledge of the instantaneous partial enthalpies is not essential to get a good estimate of the enthalpy heat flux if one of the enthalpies dominates the sum. Another simplifying assumption is using a single mean enthalpy for each species. Clearly, the mean enthalpy of the surface atoms is different from those of the interior. However, for nanoclusters which are comprised of mostly surface atoms, the mean enthalpy of all cluster atoms will be similar to each other. For a single component, binary heat flux reduces to

\[ j_h(r,t) = \left( \frac{1}{2} \sum_{i=1}^{N} m_i v_i^2 \delta(r_i - r) + \sum_{i=1}^{N} \sum_{j>i}^{N} \Phi(r_{ij}) \cdot v_i \delta(r_i - r) + \sum_{i=1}^{N} \sum_{j>i}^{N} r_{ij} \otimes F_{ij} \cdot v_i \delta(r_i - r) \right) \]

(2.70)

Eqn. (2.70) has an mean enthalpy flux term which is absent in Eqn. (2.62). In an equilibrium molecular dynamics simulation [49], the mean enthalpy flux is identically zero for a single component system because momentum is conserved at every instant. For a binary system, the enthalpy flux can have a non-zero value at any instant which is reflective of the contribution of diffusion to the heat flux at the micro-scale. Also note that in most non-equilibrium simulations, the time averaged enthalpy flux is generally small and therefore, it is seldom considered.

2.5 Ensemble Averages of Microscopic Fluxes

Ensemble averaging makes the microscopic fluxes equivalent to those which are experimentally accessible. However, there are subtleties involved in their use in the theory and simulations. In
the linear response theory, it will be shown that the microscopic *instantaneous* fluxes derived in the Section 2.4 are theoretically appropriate. However, in certain molecular dynamics simulations such as in non-equilibrium simulations, an expression for the ensemble average may be essential. In this section, the average fluxes are derived based on the Irving-Kirkwood procedure as given in [39].

The macroscopic mass density, momentum density and energy density can be constructed from the corresponding microscopic analogues. The mass density can be calculated as

\[
\langle \rho(\mathbf{r},t) \rangle = \int d\mathbf{r} f_N(\mathbf{r},t) \frac{1}{N} \sum_{k=1}^{N} m_k \delta(\mathbf{r}_k - \mathbf{r})
\]

\[= \int d\mathbf{r} f_N(\mathbf{r},0) \frac{1}{N} \sum_{k=1}^{N} m_k \delta(\mathbf{r}_k(t) - \mathbf{r})
\]

\[= \left\langle \sum_{k=1}^{N} m_k \mathbf{r}_k(t) = \mathbf{r} \right\rangle
\]

Similarly, the ensemble average of momentum density is given by

\[
\langle \mathbf{j}(\mathbf{r},t) \rangle = \int d\mathbf{r} f_N(\mathbf{r},t) \frac{1}{N} \sum_{k=1}^{N} \mathbf{p}_k \delta(\mathbf{r}_k - \mathbf{r})
\]

\[= \left\langle \sum_{k=1}^{N} \mathbf{p}_k(t) \mathbf{r}_k(t) = \mathbf{r} \right\rangle
\]

and the energy density takes the form

\[
\langle e(\mathbf{r},t) \rangle = \left\langle \sum_{k=1}^{N} \frac{p_k^2(t)}{2m_k} + \frac{1}{2} \sum_{j \neq k}^{N} \Phi(\mathbf{r}_j,\mathbf{r}_k,t) \right\rangle
\]

The issue of the operator \(\Theta_\theta\) arises in the ensemble averaging also. As explained in the previous section, the focus of this thesis is in studying bulk properties and bulk systems where the system
size is larger than the typical molecular dimensions. Thus, the higher order terms in $\Theta_{ij}$ is insignificant. This will be explicitly shown with computer simulations in Chapter 5.

The same ensemble averaging can be performed for the stress tensor and heat flux vector. These are reproduced in their final form [39]

\[
T(r,t) = \left\langle j_r(r,t) \right\rangle = \left( \sum_{k=1}^{N} \frac{p_k}{m_k} - \frac{1}{2} \sum_{j,k \neq k}^{N} r_{jk} \otimes F_{jk} \right) (2.76)
\]

\[
J_q(r,t) = \left\langle j_q(r,t) \right\rangle = \left( \sum_{k=1}^{N} \frac{p_k^2}{2m_k} v_k + \frac{1}{2} \sum_{j,k \neq k}^{N} I_{\Phi}(r_{jk}) \cdot v_k + \frac{1}{2} \sum_{j,k \neq k}^{N} \left[ r_{jk} \otimes F(r_{jk}) \right] \cdot v_k \right) (2.77)
\]

For a binary system ($\alpha, \beta$), the corresponding expression is

\[
J_q(r,t) = \left( \left( \frac{1}{2} \sum_{k=1}^{N} \sum_{i=1}^{m_k} \left( v_i^k \right)^2 v_i^k + \sum_{k=1}^{N} \sum_{i=1}^{m_k} \sum_{j=1}^{m_j} \left[ I_{\Phi}(r_{ij}^k) + r_{ij}^k \otimes F(r_{ij}^k) \right] \cdot v_i^k - \sum_{k=1}^{N} \sum_{i=1}^{m_k} \left( h^k \right) v_i^k \right) \right) (2.78)
\]

The ensemble average of the enthalpy flux is often negligible compared to the other fluxes.

### 2.6 Linear Response Theory

There are several equivalent ways [94] stating the connection between the transport properties which inherently arise from non-equilibrium conditions and the equilibrium fluctuations. Onsager's hypothesis is treated as a postulate in the time correlation approach while it is a consequence in the linear response theory. In the linear response theory, an external field perturbs the N-particle system and the system response is monitored. A linear response approach as outlined in [44] where the equilibrium distribution function corresponds to that of a canonical or grand canonical ensemble is adopted in this thesis. This theory, in general, is not readily applicable to microcanonical ensemble but suitable remedies are possible as described in [39].
2.6.1 Classical Ensemble

The starting point is the Liouville equation given by Eqn. (2.30). It is assumed that a Hamiltonian \( (H_0) \) exists and when perturbed by an external Hamiltonian \( (H_{\text{ext}}) \) changes the equilibrium distribution function from \( f^0_N \) by an amount \( \delta f_N \). The molecular relaxation determines how fast \( f^0_N \) changes to the new distribution \( f^0_N + \delta f_N \) corresponding to the Hamiltonian \( H_0 + H_{\text{ext}} \). Note that 0 is used as both a subscript and a superscript to denote equilibrium state. The Liouville operator \( (L) \) can be conveniently split into the unperturbed and the perturbed state as \( L_0 + \delta L \) where

\[
L_0 = -i \left( \sum_{j=1}^{N} \frac{\partial H_0}{\partial p_j} \frac{\partial}{\partial r_j} + \sum_{j=1}^{N} \frac{\partial H_0}{\partial r_j} \frac{\partial}{\partial p_j} \right) \tag{2.79}
\]

and

\[
\delta L = -i \left( \sum_{j=1}^{N} \frac{\partial H_{\text{ext}}}{\partial p_j} \frac{\partial}{\partial r_j} + \sum_{j=1}^{N} \frac{\partial H_{\text{ext}}}{\partial r_j} \frac{\partial}{\partial p_j} \right) \tag{2.80}
\]

It is assumed that the distribution function and the Hamiltonian are invariant with time. The equilibrium distribution function can be then expressed in the form

\[
f^0_N = Ce^{-H_0/k_BT} \tag{2.81}
\]

where \( C \) is a constant. Now, the action of \(-i\delta L\) on \( f^0_N \) results in

\[
-i(\delta L)f^0_N = \frac{f^0_N}{k_BT} \left( -\sum_{j=1}^{N} \frac{\partial H_{\text{ext}}}{\partial r_j} \frac{\partial H_0}{\partial p_j} \right) = -\frac{f^0_N}{k_BT} iL_0 H_{\text{ext}} \tag{2.82}
\]

The external perturbation to the Hamiltonian can be written for a dynamical variable \( A \) as
\[ H_{\text{ext}} = -F(t)A(\Gamma) \quad (2.83) \]

where \( F(t) \) contains the explicit time dependence. Combining the above two expressions the following relationship can be obtained

\[-i(\delta L) f_N^0 = -\frac{f_N^0 F(t)}{k_B T} \dot{A}_0 \quad (2.84)\]

Now the Liouville equation on expansion and neglecting higher order terms gives

\[ \frac{\partial (\delta f_N)}{\partial t} = -i \left[ (\delta L) f_N^0 + L_0 (\delta f_N) \right] \quad (2.85) \]

which on integration gives

\[ \delta f_N(t) = -i \int_{-\infty}^{t} dt' e^{i(t-t')L_0} (\delta L) f_N^0 \quad (2.86) \]

It is assumed that the perturbation starts at \( t = -\infty \). Using Eqn. (2.84) the time evolution of the perturbed distribution function is given by

\[ \delta f_N(t) = \frac{f_N^0}{k_B T} \int_{-\infty}^{t} dt' F(t') e^{i(t-t')L_0} \dot{A}_0 \quad (2.87) \]

Using the property, \( e^{iL_0 A(0)} = A(t) \)

\[ \delta f_N(t) = \frac{f_N^0}{k_B T} \int_{-\infty}^{t} dt' F(t') \dot{A}_0 (t'-t) \quad (2.88) \]

Now by shifting the time variable, the following expression results
\[ \delta f_N(t) = \frac{f_N^0}{k_BT} \int_{-\infty}^{0} d\tau F(t+\tau)\dot{A}_0(\tau) \]  

(2.89)

Thus the evolution of the change in the equilibrium distribution function under a small perturbation can be expressed as an integral of a time correlation function involving the rate of change in the dynamical variable \( A_0 \) and the external forcing term \( F \). Geometrically, the change in the equilibrium distribution function is just the area under the above correlation function.

The change in another observable say, \( B \) in time \( t \) due to the application of the perturbation is given by

\[ \langle \delta B(t) \rangle = \int d\Gamma \delta f_N(t)B \]  

(2.90)

This can be further simplified as

\[ \langle \delta B(t) \rangle = \int_{-\infty}^{0} d\tau F(t+\tau)C_{AB}(\tau) \]  

(2.91)

where

\[ C_{AB}(\tau) = \frac{1}{k_BT} \int d\Gamma \int_{-\infty}^{0} \dot{A}(\tau)B(0) = \frac{1}{k_BT} \int d\Gamma \dot{A}(\tau)B(0) \]  

(2.92)

The auto-correlation is simply expressed as

\[ C_{\dot{A}A}(\tau) = \frac{1}{k_BT} \int d\Gamma \dot{A}(\tau)A(0) \]  

(2.93)

Now, the change in \( B \) can be computed as
\[ \langle \delta B(t) \rangle = \frac{1}{k_B T} \int_{-\infty}^{0} d\tau F(t+\tau) \langle \dot{A}(\tau) B(0) \rangle \] (2.94)

Transport properties are related to applied fluxes. The flux of A is given by \( \dot{A} \) and the corresponding flux auto-correlation is

\[ C_{\dot{A}A}(\tau) = \frac{1}{k_B T} \langle \dot{A}(\tau) \dot{A}(0) \rangle \] (2.95)

The change in the expectation value of A will be

\[ \langle \delta A(t) \rangle = \frac{1}{k_B T} \int_{-\infty}^{0} d\tau F(t+\tau) \langle \dot{A}(\tau) A(0) \rangle \] (2.96)

### 2.6.2 Effective Hamiltonian

The previous section saw the development of time correlation functions with a perturbation from an external Hamiltonian. For calculating the transport coefficients, the same framework can be used, provided an effective Hamiltonian can be described. The framework employed in this thesis follows from the original work of Mori as given in [44]. The key idea is to consider a small volume smaller than the macroscopic dimensions but large enough to have local thermodynamic equilibrium. Thus, it is possible to identify a time scale where the macroscopic gradients and thermodynamic variables correspond to that of the non-equilibrium state but with a local equilibrium distribution for the microscopic variables. In this time interval, the number of molecules can be effectively taken to be constant within the region of interest.

Without any external gradients, the distribution function is given by \( f_N^0 = C e^{-H_0/k_B T} \). For the non-equilibrium system an effective Hamiltonian can be constructed from the energy density and the form of the equilibrium distribution as
\[
\left( \frac{H}{k_BT} \right)_{\text{eff}} = \int \left( \sum_{k=1}^{N} \frac{p_k^2}{2m_k} + \frac{1}{2} \sum_{j<k} \Phi(r_{jk}) \right) \delta(r_k - r) \frac{d}{k_BT(r)} \tag{2.97}
\]

As before, the delta function places the molecules at \( r \) and the effective value is the integral over all volume \( V \). To account for the mass diffusion, an effective chemical potential can be defined as

\[
\left( \frac{m^s \mu^s}{k_BT} \right)_{\text{eff}} = \int \frac{m^s \mu^s(r) \rho^s(r)}{k_BT(r)} dr \tag{2.98}
\]

where \( \mu \) and \( m \) are the chemical potential and mass respectively for each species \( s \). Now, the distribution in this grand canonical ensemble can be written as

\[
f_N^* = C \exp \left( \frac{-H + \sum_s m^s \mu^s - R}{k_BT} \right) \tag{2.99}
\]

where \( R \) is the residue given by

\[
R = -H + \sum_s m^s \mu^s + \int \frac{T}{V} \left\{ e(r) - \sum_s \mu^s(r) \rho^s(r) \right\} dr \tag{2.100}
\]

When the residue \( R \) is zero, the distribution function \( f_N^* \) corresponds to that of a grand-canonical ensemble. When there are changes in the macroscopic variables, there will be a deviation from the equilibrium distribution. After a somewhat lengthy derivation [44], the time rate of change of the residue can be written as

\[
\dot{R} = \int \left\{ j_q(r) \cdot X_q - \sum_s j^s(r) \cdot X^s \right\} dr \tag{2.101}
\]
where

\[
X_q = -\frac{1}{T} \nabla_r T \\
X^s = -\frac{T}{T(r)} \nabla_r \left( \mu^s \right)_T
\]  

(2.102)  

(2.103)

Note that \( s \) stands for the number of species and recall that the entropy production is given by

\[
\sigma = \sum_{i=1}^{n} J_i \dot{X}_i \text{ where } J \text{ and } \dot{X} \text{ stand for the flux and the thermodynamic force respectively.}
\]

Assume there is such an equivalence at the microscopic (larger than molecular dimensions but smaller than macroscopic) realm. The residue rate \( \dot{R} \) plays the role of entropy as it is a measure of the irreversibilities. Therefore, the following expression can be postulated

\[
\dot{R} = \sum_{n} \dot{j} \cdot X^n
\]  

(2.104)

where \( \dot{j} \) and \( X^n \) are the flux and ‘force’ terms respectively in Eqn. (2.101) Now the ensemble average or the expectation value of any flux \( \mathcal{I} \) can be expressed as

\[
\langle \mathcal{I} \rangle = \frac{1}{k_B T} \int_0^{\infty} d\tau \langle \mathcal{I}(0) \dot{R}(\tau) \rangle
\]  

(2.105)

Note that the macroscopic variables do not change in the time period where the correlation between \( A \) and \( R \) becomes negligible. This is a consequence of the large difference between the molecular and the macroscopic or continuum time scales. The above relationship can be expressed as

\[
\langle \mathcal{I}_m \rangle = \sum_{n} \int_0^{\infty} d\tau G_{\mathcal{I}_m \mathcal{I}_n} (\tau) \frac{X_n}{k_B T}
\]  

(2.106)
where \( n \) are the number of components in the Eqn. (2.101). The correlation function itself is given by

\[
G_{\mathcal{Z}_m \mathcal{Z}_n}(r) = \langle \mathcal{Z}_m(r) \mathcal{Z}_n(0) \rangle
\]

(2.107)

### 2.7 Transport Properties with Linear Response Theory

All the transport coefficients now can be derived as a function of correlation functions. Only the derivation for thermal conductivity is shown here. The expressions for other transport coefficients can be found in [48, 49]. The volume averaged heat flux vector for a binary system is given by

\[
\mathcal{J}_q = \int \frac{1}{2} \sum_{k=a}^{\beta} \sum_{i=1}^{N_k} (\nu_i^a)^2 \nu_i^a + \sum_{k=a}^{\beta} \sum_{i=1}^{N_k} \sum_{j>i}^{N_k} \left[ \mathbf{I} \Phi(r_{ij}) + r_{ij}^\beta \otimes \mathbf{F}_{ij}^\beta \right] \nu_i^a \nu_j^a - \sum_{k=a}^{\beta} \left( Q_i^a \sum_{i=1}^{N_k} \nu_i^a \right) \delta(r_i-r_j) dr
\]

(2.108)

The ensemble average of the heat flux vector can be written as

\[
\langle \mathcal{J}_q \rangle = \frac{1}{k_B T^2} \int_0^\infty d\tau G_{\mathcal{Z}_q \mathcal{Z}_q}(\tau) \nabla_r T + T \sum_{s=a}^{\beta} G_{\mathcal{Z}_q \mathcal{Z}_s}(r) \nabla_r \left( \mu_s^a \right)_r
\]

(2.109)

But \( \langle \mathcal{J}_q \rangle = \mathbf{J}_q \)

(2.110)

Compare Eqn. (2.109) to the macroscopic linear phenomenological flux relationship given by

\[
\mathbf{J}_q = -L_{qq} \nabla T + L_{q1} \frac{1}{T} \nabla \left( \mu^a - \mu^\beta \right)_T
\]

(2.111)

Eqn. (2.111) is identical to Eqn. (2.109) only when

\[
\kappa = \frac{L_{qq}}{T^2} = \frac{1}{V k_B T} \int_0^\infty d\tau \langle \mathcal{Z}(t) \mathcal{Z}(0) \rangle
\]

(2.112)
For cubic isotropic materials, the intrinsic thermal conductivity is given by

\[
\kappa = \frac{1}{3Vk_BT} \int_0^{\infty} d\tau \langle \mathcal{J}(t)\mathcal{J}(0) \rangle
\]  

(2.113)

A notable aspect is that the linear response theory or the time correlation approach gives an expression for the intrinsic thermal conductivity. This is in contrast to experimental techniques where it is virtually impossible to measure the intrinsic thermal conductivity (see Section 2.1). A second feature is that the heat flux vector takes the instantaneous values and not the ensemble values. Finally, it is clear from the derivation that the thermal conductivity from the linear response theory is applicable to heterogeneous media such as colloids as long as there is a clear scale separation in the system. As previously mentioned, the linear response theory is based on the idea that microscopic expressions for fluxes and transport properties can be made within a small volume such that it is smaller than the macroscopic dimensions but large enough to have local thermodynamic equilibrium. The local region, which depends on the specific system which is being considered, will have identifiable properties and thermodynamic functions. The only requirement on the local region is that it needs to have enough atoms for a representative structure and an equilibrium distribution for the microscopic variables.
3. Mechanism of Thermal Transport in Nano-colloids

3.1 Introduction

In Chapter 2, it was discussed that the thermal conductivity and other transport coefficients can be expressed as a function of time correlation functions. The connection between the time correlation functions and transport properties comes from the celebrated Onsager’s regression hypothesis which states that the relaxation of macroscopic non-equilibrium disturbances is governed by the same laws as the regression of spontaneous microscopic fluctuations in an equilibrium system [43]. This hypothesis essentially means that there is fundamentally no way of distinguishing between a non-equilibrium system, say a system with thermal gradient, relaxing to its equilibrium state (which corresponds to zero gradients) and the correlations of the spontaneous fluctuations (in the microscopic heat flux) at equilibrium. This approach is also known as the Green-Kubo (GK) formalism in honor of the eminent scientists, M. S. Green and R. Kubo for their seminal work in the 1950s [99]. In the linear response theory as discussed previously, Onsager’s hypothesis becomes a consequence of the well-known fluctuation-dissipation theorem.

There are no fundamental assumptions made on the mechanism of transport in the linear response approach which is unlike the recently proposed hydrodynamic theories (see Chapter 1). Further, the theory is general enough to include all states of matter including mixtures as long there is a clear scale separation between the macroscopic and microscopic behavior, and the system responds linearly to an external perturbation. Thus, the linear response theory provides an ideal setting to probe the transport mechanisms in colloids. This chapter deals with the thermal conduction in a dilute colloid consisting of nano-sized platinum clusters in liquid xenon. The fluctuations which are required in the time correlation functions are accessed from equilibrium molecular dynamics (MD) simulations. In the MD simulations, the system of atoms moves
according to Newton’s equations of motion [48]. The appropriate correlations are then averaged over many time origins and initial conditions [49].

### 3.2 Modes of Microscopic Heat Flux Fluctuations

In this section, the microscopic flux is decomposed into three fluctuation modes to analyze the conduction mechanisms of the model colloid. The microscopic heat flux for a single component system is given by [also (2.62)]

\[
\mathbf{j}_q(r,t) = \left( \frac{1}{2} \sum_{i=1}^{N} m_i v_i^2 \mathbf{v}_i \delta(r_i - r) + \sum_{i=1}^{N} \sum_{j=1}^{N} \mathbf{I}(\mathbf{r}_i) \mathbf{v}_i \mathbf{v}_j \delta(r_i - r) + \sum_{i=1}^{N} \sum_{j=1}^{N} \mathbf{r}_i \otimes \mathbf{F}_i \mathbf{v}_j \delta(r_i - r) \right)
\]

(3.1)

The above expression shows that the total heat flux is a sum of the flux carried by the kinetic energy \( K \), the potential energy \( P \) and the virial \( C \). Physically, the first two terms \( K \) and \( P \) represents the energy transported across an imaginary plane. The third term emanates from the transfer of work done by the virial or the shear stress tensor which results from the molecular interaction or ‘collision’ among the constituent atoms. Thus, the heat flux can be written as

\[
\mathbf{j}_q(r,t) = \mathbf{j}_q^K(r,t) + \mathbf{j}_q^P(r,t) + \mathbf{j}_q^C(r,t)
\]

(3.2)

The above decomposition forms the heart of the analysis on the thermal conduction mechanisms. As shown in this section, this decomposition remains unchanged for a binary system as well. The heat flux for a binary component system which has an extra partial enthalpy flux is given by [also (2.64)]

\[
\mathbf{j}_q(r,t) = \left( \frac{1}{2} \sum_{k=1}^{\beta} \sum_{i=1}^{N_k} m_i (v_i^k)^2 \mathbf{v}_i^k \delta(r_i - r) + \sum_{k=1}^{\beta} \sum_{i=1}^{N_k} \sum_{j=1}^{N_k} \left[ \mathbf{I}(\mathbf{r}_i^k) + \mathbf{r}_i^k \otimes \mathbf{F}_i^k \right] \mathbf{v}_i^k \delta(r_i - r) - \sum_{k=1}^{\beta} \sum_{i=1}^{N_k} v_i^k \delta(r_i - r) \right)
\]

(3.3)

Under equilibrium conditions, the instantaneous enthalpy flux for a single component system is zero at all times. This is a consequence of imposing a net zero momentum for the system. For binary systems, the instantaneous enthalpy flux is not zero, in general. So there is a non-trivial...
contribution from the transport of mean enthalpy to the total microscopic heat flux. In typical non-equilibrium states for colloids, the ensemble averaged enthalpy flux is generally small compared to that from the other three contributions, $K$, $P$ and $C$. The enthalpy flux thus, plays an important role in the instantaneous microscopic heat flux but not for the ensemble average.

The microscopic heat flux thus far, has been interpreted as an analogue of the macroscopic heat flux. In statistical mechanics, the thermodynamic fluxes and the transport coefficients are expressed as the time derivative of the *fluctuations* of the appropriate variables. Note that the fluctuation-dissipation theorem provides a connection between the macroscopic relaxation and the *fluctuations* at equilibrium conditions. It can be shown that Eqn. (3.3) can be written in terms of fluctuating components provided that the mean instantaneous enthalpy is considered to be a sum of the average kinetic energy, potential energy and the virial. First, the single component heat flux is considered. Writing out the expansion explicitly,

\[
\bar{\mathbf{j}}_q = \frac{1}{2} \sum_{i=1}^{N} m_i \mathbf{v}_i^2 \mathbf{v}_i + \sum_{i=1}^{N} \sum_{j \neq i}^{N} \mathbf{I} \Phi(r_{ij}) \mathbf{v}_i \mathbf{v}_j + \sum_{i=1}^{N} \sum_{j \neq i}^{N} \mathbf{r}_{ij} \otimes \mathbf{F}_{ij} \mathbf{v}_i \mathbf{v}_j 
\]

\[
- \left\{ \frac{1}{2} \left( \sum_{i=1}^{N} m_i \mathbf{v}_i^2 \right) \sum_{i=1}^{N} \mathbf{v}_i + \left( \sum_{i=1}^{N} \sum_{j \neq i}^{N} \mathbf{I} \Phi(r_{ij}) \right) \sum_{i=1}^{N} \mathbf{v}_i + \left( \sum_{i=1}^{N} \sum_{j \neq i}^{N} \mathbf{r}_{ij} \otimes \mathbf{F}_{ij} \right) \sum_{i=1}^{N} \mathbf{v}_i \right\} 
\]

(3.4)

Now, consider only the kinetic energy flux,

\[
\bar{\mathbf{j}}_q^K = \frac{1}{2} \sum_{i=1}^{N} m_i \mathbf{v}_i^2 \mathbf{v}_i - \frac{1}{2} \left( \sum_{i=1}^{N} m_i \mathbf{v}_i^2 \right) \sum_{i=1}^{N} \mathbf{v}_i 
\]

(3.5)

which can be rewritten as,

\[
\bar{\mathbf{j}}_q^K = \sum_{i=1}^{N} \left\{ \frac{1}{2} m_i \mathbf{v}_i^2 - \left( \sum_{i=1}^{N} \frac{1}{2} m_i \mathbf{v}_i^2 \right) \right\} \mathbf{v}_i 
\]

(3.6)

or,
The kinetic energy flux \( (K) \) is therefore, expressed solely in terms of fluctuations in the kinetic energy on a per atom basis. If potential and virial (collision) can be identified for single particles, then the total flux can be written as

\[
\tilde{J}_q^{(K)} = \sum_{i=1}^{N} \{\delta E_i^{(K)}\} v_i = \sum_{i=1}^{N} \{\delta E_i^{(K)}\} v_i
\]  

(3.7)

where \( W \) denotes the work performed by the virial. As discussed in Chapter 2, the partitioning of potential energy and virial into contributions from single atoms is not rigorous especially if the system is non-isotopic (equi-potential) or has many body interactions. Nevertheless, it is a common practice to divide the potential energy in a two-body interaction, equally between the two atoms. The same procedure can be in principle, be performed for the virial. Thus, the total heat flux now can be written explicitly in terms of fluctuations of each atom as shown in (3.8).

Now, consider the binary heat flux and as before, the kinetic terms are considered first.

\[
\tilde{J}_q^{(K)} = \frac{1}{2} \sum_{i=1}^{N_a} m_i^{(a)} \left(v_i^{(a)}\right)^2 v_i^{(a)} - \langle E_i^{(Ka)} \rangle \sum_{i=1}^{N_a} v_i^{(a)} + \frac{1}{2} \sum_{i=1}^{N_b} m_i^{(b)} \left(v_i^{(b)}\right)^2 v_i^{(b)} - \langle E_i^{(Kb)} \rangle \sum_{i=1}^{N_b} v_i^{(b)}
\]  

(3.9)

Writing the enthalpy as the sum of kinetic and potential energies and virial, the kinetic energy heat flux can now be written as

\[
\tilde{J}_q^{(K)} = \sum_{i=1}^{N_a} \{\delta E_i^{(Ka)}\} v_i^{(a)} + \sum_{i=1}^{N_b} \{\delta E_i^{(Kb)}\} v_i^{(b)}
\]  

(3.10)

Finally, the total heat flux for the two component system can be expressed as

\[
\tilde{J}_q = \left[ \sum_{i=1}^{N_a} \{\delta E_i^{(Ka)}\} + \sum_{i=1}^{N_b} \{\delta E_i^{(Kb)}\} + \sum_{i=1}^{N_a} \{\delta W_i^{(Ca)}\} \right] v_i^{(a)} + \left[ \sum_{i=1}^{N_a} \{\delta E_i^{(Kb)}\} + \sum_{i=1}^{N_b} \{\delta E_i^{(Kb)}\} + \sum_{i=1}^{N_a} \{\delta W_i^{(Cb)}\} \right] v_i^{(b)}
\]  

(3.11)
Thus, the instantaneous heat flux for a binary system also can be expressed as the fluctuations of three modes, $K$, $P$ and $C$.

### 3.3 Modal Decomposition of Thermal Conductivity

The intrinsic thermal conductivity of a colloid as previously shown in Chapter 2 is given by

$$\kappa = \frac{1}{3V k_B T^2} \int_0^\infty \langle \mathbf{j}_q(t) \mathbf{j}_q(0) \rangle d\tau$$  \hspace{1cm} (3.12)

Since the heat flux has three modes: $\mathbf{j}_q = \mathbf{j}_K^q + \mathbf{j}_P^q + \mathbf{j}_C^q$, the total thermal conductivity will have nine physical modes each representing a correlation function. They can be conveniently grouped together in a matrix as shown below.

$$\hat{\kappa} = \begin{pmatrix}
\kappa_{KK} & \kappa_{PK} & \kappa_{CK} \\
\kappa_{KP} & \kappa_{PP} & \kappa_{CP} \\
\kappa_{KC} & \kappa_{PC} & \kappa_{CC}
\end{pmatrix}$$  \hspace{1cm} (3.13)

Note that the above decomposition is physical and not geometrical. The total thermal conductivity is simply the sum of all the modes. The diagonal contains the self-mode correlations ($KK$, $PP$ and $CC$) and the off-diagonal terms represent the cross-mode correlations ($PK$, $CP$, $KP$, $PK$, $KC$, $CK$). Later on, the physical basis of each component will be explained in depth.

Note the physical meaning of (3.12). The thermal conductivity is proportional to the integral of the heat flux autocorrelation function. Physically, the correlation denotes the projection of the heat flux vector at a current time $t = t$ on to itself at an earlier time $t = t_0$. Thus, if the heat flux vector is correlated at all times, it signifies an infinite thermal conductivity. In typical liquids and gases, the correlation decays exponentially [81] while in solids, a two stage relaxation is generally seen which prolongs the correlation [100, 101]. The lack of a strong correlation in the heat flux vector explains the rather low thermal conductivities in typical liquids and gases.
3.4 Molecular Dynamics with Xe-Pt Colloidal Model

Nano-colloidal experiments so far, have mostly involved dispersions of metallic or oxide particles in typical engineering coolants such as water or ethylene glycol. In view of the complex surface chemical reactions which are not yet identified, a realistic simulation entails the use of expensive quantum-mechanical calculations. In addition, the complexity of the competing processes can also hinder in unveiling the essential molecular mechanism of thermal transport in colloids which to date have not been amenable to theoretical methods. Therefore, in this thesis, a colloidal system consisting of nanosized platinum (Pt) clusters in xenon (Xe) in liquid state is chosen. In Chapter 1, the motivation of selecting the materials and potential is given in more detail.

The only real input to a MD simulation is the interatomic potential. Since there are two components Xe and Pt, there will be three interactions, namely, Xe-Xe, Pt-Pt and Xe-Pt. As discussed in Chapter 1, a two body Lennard-Jones (LJ) 12-6 potential is appropriate for Xe-Xe [102] as Xe is a rare gas element. The transport coefficients obtained for Xe compare favorably with the experimental data (within 2-15%) for a variety of thermodynamic states. Pt has a FCC structure and therefore, a three body potential such as an Embedded Atom Potential (EAM) [83] is appropriate for the Pt-Pt interaction. In this study, each Pt cluster has only about 10-20 atoms and hence, they all can be regarded as surface atoms. In such a situation, a classical three-body potential may not be appropriate. Further and more importantly, it turns out that the interaction among the Pt atoms within a cluster has only a negligible effect on the thermal transport mechanisms. Therefore, a simpler two body potential described by a LJ 12-6 potential [103] is assumed for the Pt-Pt interaction. Since the colloidal systems in this study are dilute, (volume fraction O(1%)), the cluster-cluster interactions are weak. The cross-interaction, as it will be shown later in this chapter, is the most important interaction from a conduction point of view. Xe-Pt interaction, which is fairly isotropic, has been carefully constructed in [80] from a series of experimental data from scattering experiments. In this study, a LJ 12-6 potential is constructed by matching the potential well-depth (e) and the location of the energy minima (2^{1/6} \sigma). The potential parameters are listed in the Table 3.1 and the potentials are plotted in Figure 3.1.
Table 3.1 Lennard-Jones parameters (\( \sigma \), \( \varepsilon \)) for xenon and platinum.

<table>
<thead>
<tr>
<th></th>
<th>Xe-Xe</th>
<th>Xe-Pt</th>
<th>Pt-Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref. [102]</td>
<td>Ref. [80]</td>
<td>Ref. [103]</td>
<td></td>
</tr>
<tr>
<td>( \sigma ) (A)</td>
<td>3.95</td>
<td>2.732</td>
<td>2.54</td>
</tr>
<tr>
<td>( \varepsilon ) (kJ/mol)</td>
<td>1.977</td>
<td>65.77</td>
<td>24.047</td>
</tr>
</tbody>
</table>

For binary mixtures [95] the cross-interaction potential parameters are typically calculated from the well-known Lorentz-Berthelot (LB) mixing rule [95] given by

\[
\sigma_{Xe-Pt}^{LB} = \frac{\sigma_{Xe} + \sigma_{Pt}}{2}
\]

(3.14)

\[
\varepsilon_{Xe-Pt}^{LB} = \sqrt{\varepsilon_{Xe} \varepsilon_{Pt}}
\]

(3.15)

Figure 3.1 Comparison of Lennard-Jones potential for Xe-Xe, Pt-Pt and Xe-Pt interactions.
The experimental data for the $Xe$-$Pt$ cross interaction is quite different from the Lorentz-Berthelot estimate. A notable characteristic is the rather deep $Xe$-$Pt$ potential well which is approximately 12 times stronger than the $Xe$-$Xe$ potential well. This attractive interaction is quite unlike any rare-gas elements [95]. In prior simulations for colloids and interfaces, interactions of solid-like atoms with generic fluid atoms [32, 33] have not considered such extremely large attractive potential. Evidently from the previous figure, the metallic atoms change the characteristics of adjacent fluid atoms. The same is expected for surface atoms that can react strongly to a base solvent. This study, therefore, focuses on the thermal properties which arise from such large cross-interactions which is regarded as a prototype for more complex surface interactions. As will be discussed later on, this unusually large attractive well leads to large fluctuations in the potential energy in the fluid atoms that are in the immediate vicinity of solid clusters. The differences in the location of the energy minima are also important. The $Xe$-$Pt$ energy minimum is nearer to that of the $Pt$-$Pt$ interaction suggesting that $Xe$-$Pt$ characteristics are closer to those of the solid atoms. The rather high attraction between the $Pt$ atoms is sufficient to maintain the integrity of the clusters and therefore, no additional constraints are placed for the $Pt$-$Pt$ interactions within a cluster. A typical snapshot of the configuration is shown in Figure 3.2.

![Figure 3.2 Snapshot of Xe-Pt nano-colloid at the end of a simulation](image)

Figure 3.2 Snapshot of $Xe$-$Pt$ nano-colloid at the end of a simulation
For the MD simulations, geometrically similar Pt clusters, each consisting of 10 atoms, are dispersed randomly in the Xe base fluid. All simulations are performed in a periodic cube of 2048 atoms. The nano-colloid is equilibrated at 200 K and 0 atm using Berendsen barostat and velocity rescaling. To ensure the clusters do not agglomerate, a repulsion potential \( U_\pi(r_c) = A(1 - r_c / r_c)^2 \) is introduced between the clusters, with \( A \) an arbitrary constant (49.43 kJ/mol) and \( r_c \) a cut-off radius (17.78 Å). It is observed that the dominant interaction stems from the attractive Xe-Pt potential and the presence of repulsive potential does not play a significant role in the thermal transport. Likewise, the deep attractive well of the Pt-Pt interaction is only essential to maintain the cluster integrity. Once the equilibration state is attained, typically in 100,000 time steps, the simulation is allowed to proceed without any temperature or pressure control. The heat flux autocorrelation function \((\text{hacf})\) is then averaged over 2000 sets in the NVE ensemble. Each transport coefficient is further averaged over 12 different initial conditions for additional phase-space sampling. The volume fraction is calculated as \( \text{vol}_{\text{Pt}} / 6v \) where \( n \) is the Pt number fraction and \( \rho \) the number density. The relative nearest neighbor distance \( a_{\text{Pt}} \) in the Pt cluster and the packing fraction \( v \) for an FCC lattice is introduced to assign the void inside the cluster to the cluster volume. A nanoparticle number fraction of 80/2048 thus, corresponds to a volume fraction of 0.8% and a number density of approximately \( 1.35 \times 10^{28} / \text{cm}^3 \).

### 3.5 Xe-Pt Thermal Conductivity: Self-Mode Correlations

The thermal conductivity contributions from the self-mode correlations are presented first along with the total thermal conductivity and the prediction from Maxwell's effective medium theory [7]. Figure 3.3 shows the variation of the overall thermal conductivity, \( \kappa \) with the volume fraction, \( \phi \) over the range of 0-0.8%. The first noteworthy result is that the dominant contribution to the thermal conductivity for a pure fluid (\( \phi = 0 \)), is from \( CC(\text{Xe-Xe}) \) self-mode correlation. This accounts for approximately 75% of the total thermal conductivity. The self-mode correlations \( KK(\text{Xe-Xe}) \) and \( PP(\text{Xe-Xe}) \) are negligible, and the cross mode correlations accounts for the remaining fraction. For finite volume fractions, the \( CC \) correlation shows only a small increase over the range of \( \phi \) indicated. This implies that the \( CC(\text{Xe-Pt}) \) and \( CC(\text{Pt-Pt}) \) correlations are relatively small compared to that of \( CC(\text{Xe-Xe}) \). Meanwhile, the total thermal
conductivity, $\kappa$ shows a remarkable increase which is significantly higher than the prediction from Maxwell's effective medium theory. A second notable result in Figure 3. is the significant increase in the $PP$ self-mode correlation. While most of the thermal conductivity comes from $CC$ self-mode correlation, the enhancement almost exclusively comes from the $PP$ correlation. It will be subsequently shown that the $PP$ correlation emanates primarily from the strong $Xe$-$Pt$ interaction and the saturation in $\kappa$ at higher volumes fractions arises from the $PC$ cross-mode correlation.

The physical origin and the implications of the various correlations are now discussed. The $KK$ correlation is practically zero for the base fluid and the colloid which indicates that thermal motion has a negligible effect on the thermal conductivity. This result is at variance with the
recently proposed hydrodynamic theories [40] where it is postulated that the Brownian motion is instrumental in enhancing the thermal conduction. The $KK$ correlation is dominant only for dilute gases with relatively weak interatomic forces. Thus the Brownian motion of the particles (or the fluid atoms) have an insignificant role in the enhancement, a result also obtained by elementary analyses in [32, 104, 105]. Also note the physical interpretation of the $KK$ correlation which represents the energy transfer by the exchange of kinetic energy among the atoms. This interpretation will be useful in identifying the nature of the $PP$ correlation. The $CC$ correlation involves the virial interaction or the work done by the stress tensor. This term contributes most to the thermal conductivity which is typical of liquid (as already demonstrated) and solid states but increases only slightly with volume fraction indicating that the presence of stronger attractive interactions for both $Xe-Pt$ and $Pt-Pt$ has not resulted in an enhanced collisional or phonon-like modes. In solids with low electrical conductivity, thermal conduction mostly occurs from the phonon or lattice vibrations. The heat flux in a quasi-harmonically vibrating lattice exclusively arises from the work transfer across a plane which is represented by the $CC$ correlation. It is for this reason, that in many $MD$ simulations of solids, the heat flux correlation is often approximated by the $CC$ correlation alone [84]. The most remarkable aspect in Figure 3. is the increase of the $PP$ correlation. This is a novel effect in the thermal energy transport which does not exist in a single component system. Making an analogy with the $KK$ correlation, the $PP$ correlation represents the exchange of potential energy among the constituent atoms. This analogy will be explicitly tested subsequently. In dilute gases, the $PP$ correlation is practically zero because of the weak potential energy interactions. Solids atoms have large potential energy interactions. However, the quasi-harmonic vibration of the atoms about their mean positions produces a near-zero potential energy flux and consequently a small $PP$ correlation. To assess the relative importance of self-mode correlations in typical solids and liquids, $MD$ simulations are conducted with Argon in both solid and liquid state, and the results are delineated in Table 3.2. In the solid state, the $KK$ and $PP$ correlations are negligible verifying the previous assertion that kinetic energy and potential flux correlations are short lived. In contrast, the $CC$ correlations form the bulk of the thermal conductivity. In the liquid state, a similar behavior is seen indicating that the direct interactions or damped phonon-like modes among the atoms are instrumental in transferring the thermal energy. Liquid binary systems also follow the same trend. For example, in a 50:50 $Ar-CH4$ mixture, the $PP$ correlation is less than 4% while the $CC$ correlation accounts
for more than 78%. In contrast, for the Xe-Pt nano-colloid, the increase in the total thermal conductivity is largely from the PP correlation.

Table 3.2  Thermal conductivity contributions (W/m-K)
from the self-mode correlations for Argon in solid and liquid state.

<table>
<thead>
<tr>
<th></th>
<th>KK</th>
<th>PP</th>
<th>CC</th>
<th>PC+CP</th>
<th>Total</th>
<th>PP % of Total</th>
<th>CC % of Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>T=30 K (Solid)</td>
<td>0.0003</td>
<td>0.0006</td>
<td>0.7842</td>
<td>0.0192</td>
<td>0.8487</td>
<td>0.08</td>
<td>92.4</td>
</tr>
<tr>
<td>T=40 K (Solid)</td>
<td>0.0004</td>
<td>0.0008</td>
<td>0.4112</td>
<td>0.0163</td>
<td>0.4643</td>
<td>0.18</td>
<td>88.6</td>
</tr>
<tr>
<td>T=50 K (Solid)</td>
<td>0.0005</td>
<td>0.0011</td>
<td>0.3964</td>
<td>0.0145</td>
<td>0.4412</td>
<td>0.24</td>
<td>89.8</td>
</tr>
<tr>
<td>T=60 K (Solid)</td>
<td>0.0006</td>
<td>0.0012</td>
<td>0.2923</td>
<td>0.0164</td>
<td>0.3349</td>
<td>0.37</td>
<td>87.3</td>
</tr>
<tr>
<td>T=101 K (Liquid)</td>
<td>0.0015</td>
<td>0.0034</td>
<td>0.0817</td>
<td>0.0137</td>
<td>0.1005</td>
<td>3.38</td>
<td>81.3</td>
</tr>
</tbody>
</table>

So far, the correlations has been discussed from a system perspective without partitioning the correlations among the three components: Xe-Xe, Xe-Pt and Pt-Pt. It is clear that the Xe-Xe interaction does not play a role in generating the PP correlation. The two possible candidates are Xe-Pt and Pt-Pt interactions.

3.6  Xe-Pt Thermal Conductivity: Component Decomposition

An advantage of the time correlation function approach is that all the dynamical details reflected in the temporal behavior of the heat flux correlation functions are accessible for analyses. Figure 3.(b) shows how PP correlation which is responsible for the conductivity enhancement behave with increasing volume fraction. The onset of oscillations is clearly evident for increasing volume fractions which eventually become more pronounced. The power spectra of the PP correlations are shown in Figure 3.(a). There are three noticeable peaks for finite volume fractions while there are none for the base fluid which is expected of a simple liquid. Interestingly, the three peaks correspond to certain frequencies which can be theoretically
calculated. The frequency of each peak matches well with the estimate using the curvature of the potential well, \( \sqrt{\frac{\partial^3 U}{\partial^3 r_{\text{eq}}}} / 4\pi^3 m \) where \( U \) and \( r_{\text{eq}} \) are the interatomic potential and the equilibration separation distance [101]. The first peak approximately corresponds to the harmonic frequency of vibration about the \( Xe-Xe \) minima which is approximately 1.13 THz. The third peak matches well with the harmonic frequency of \( Pt-Pt \) interaction (approximately, 8.3 THz). Expectedly, the second peak corresponds to the \( Xe-Pt \) interaction. The much stronger \( Xe-Pt \) peak intensity shows that the conductivity enhancement arises from the \( PP(Xe-Pt) \) correlation while the \( PP(Pt-Pt) \) and \( PP(Xe-Xe) \) correlations are relatively insignificant. Thus, the enhancements originate from the cluster-fluid \( PP \) correlation while the magnitude of the conductivity is mainly governed by the host fluid \( CC \) correlation.

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![Figure 3.4](image)

Figure 3.4 (a) Power spectra of potential-potential (PP) heat flux autocorrelation function. (b) PP heat flux autocorrelation function (hacf).
3.7 Potential Energy Fluctuations and Dynamic Interface

The physical mechanism of transport through the potential flux correlations can be better understood through the temporal behavior of the kinetic and potential energy of the atoms close to clusters. To study the spatial nature of the Xe-Pt interactions, five representative Xe atoms are selected from the first coordination shell of a platinum cluster, and follow the temporal behavior in the kinetic \( T \) and potential \( U \) energies of these atoms, keeping in mind that all the five atoms are structurally equivalent in every way. Then the dynamic fluctuation amplitude \( \Lambda \), defined as the standard deviation in the kinetic or potential energies of each atom averaged over all the like atoms, is calculated. For example, \( \Lambda^U \) of the Pt atoms is defined as the standard deviation of the potential energy of each Pt atom averaged over all Pt atoms.

The data shown in Fig. 3.5 is taken from the final 77 ps of a single run (\( \phi = 0.8\% \)) over which the relative change in the total energy is less than 0.001\%. The Xe atoms in close vicinity to the Pt atoms experience large potential energy fluctuations without a concomitant change in the kinetic energy as shown in Figure 3.5(a) and 3.5(b). Several fluid atoms have varying levels of potential energy with some atoms displaying large fluctuations without a noticeable change in their average values (e.g., atom \( A \)). This behavior is similar to that observed in water [106]. A smaller set of fluid atoms show pronounced jumps from one energy level to another (e.g., atom \( B \)) which happens when the fluid atom gets trapped in the potential cage formed by the solid atoms and vice versa. Interestingly, a local cooperativity can be seen in the concerted jumps in \( U(C) \), \( U(D) \) and \( U(E) \) without a noticeable change in the kinetic energy (see \( T \) of atom E) or total energy. This pronounced cooperative exchange thus, provides a mechanism for additional energy transfer.

Figure 3.5c depicts the dynamic fluctuation amplitudes, \( \Lambda^T \) and \( \Lambda^U \), of the fluids atoms placed in different radial shells around the nanoclusters. In the first shell located at 3.16 Å from the cluster, \( \Lambda^U \) is 44\% higher than \( \Lambda^T \). As expected, \( \Lambda^U \) approaches the bulk value away from the nanoclusters. This reinforces the view that the potential energy is cooperatively transferred among the Xe atoms in close proximity \( [O(1 \text{ nm})] \) to the platinum atoms and indicates the presence of a dynamic interface shell around the nanoclusters.
Figure 3.5 (a and b) Kinetic and potential energy fluctuations in a few representative Xe atoms surrounding a Pt cluster. The cooperative exchange of potential energy (U) is evident in atoms C, D and E. (c) Dynamic Fluctuation Amplitude A of the potential and kinetic energy (T) in Xe atoms for different shells around the Pt clusters. (d) Excess A of the Xe atoms and the enhancement in $\kappa$ as a function of volume fraction $\phi$. 
To remove the empiricism of arbitrarily assigning a shell thickness, the excess $A^U$ of the $Xe$ atoms in a nano-colloid simulation relative to $A^U$ of the $Xe$ atoms in the base fluid simulation is calculated. The enhancement in $\kappa$ is seen to be linearly correlated to the excess fluctuations in the $Xe$ atoms as shown in Figure 3.5d, except at higher volume fractions ($\phi \geq 0.5$) which will be discussed in the next section.

3.8 $Xe$-$Pt$ Thermal Conductivity: Cross-Mode Correlation

![Figure 3.6](image)

Figure 3.6 (a) Potential-Collision ($PC$) $hacf$ for different volume fractions. (b) Contribution of $PC+CP$ correlations to the thermal conductivity for different $\phi$. (c) Power spectra of $PC$ $hacf$. 

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Now the effects of the cross-mode correlations are investigated. The four terms involving the kinetic modes \((KP, PK, KC\) and \(CK)\) remain fairly constant for all the volume fractions which is not surprising as the temperature of the simulations is kept constant at 200K. The \(PC\) and \(CP\) correlations, however, shows marked variations as can be seen in Figure 3.. As expected, symmetric cross-mode correlations generally have similar numerical values. The correlation function for \(PC\) starts negative at short times, becomes positive and then decays to zero in an oscillatory fashion. This behavior is quite unlike the self-mode correlations and the four other cross-mode terms. Due to large oscillations, a significant cancellation of area under the curve occurs. Beyond a volume fraction of 0.5 (Figure 3.b), \(\lambda_{PC}+\lambda_{CP}\) decreases sharply and becomes negative. This signifies a resistance to potential energy transfer from the strengthening of vibrational modes in the cluster which is evident in Figure 3.6c where the \(Pt-Pt\) peak shifts towards higher frequencies along with a broadening of the \(Xe-Pt\) interaction modes. The reduction in the conductivity contribution from the \(PC\) correlation thus reflects the change in the slope of the overall thermal conductivity for \(\phi \geq 0.5\).

### 3.9 Discussion

In conclusion, it is shown that the thermal conductivity enhancements in a model \(Xe-Pt\) nano-colloidal system arise from the self correlation of the potential energy flux. Physically, this represents a potential energy exchange among the nanoparticles and the fluid atoms that are in close proximity to the nanoparticles. The \(PP\) correlation emanate from a strong cluster-fluid interaction which creates a dynamic interface around the nanoclusters. At higher particle loading, the enhancement saturates because of negative cross-mode correlation between the potential and the collision flux which interestingly, can occur even for well-dispersed particles. It is worth emphasizing that the present enhancement mechanism occurs only when the cross interactions between the nanoparticles and the fluid atoms are sufficiently strong which is also a necessary condition for low interfacial thermal resistance.

The explanation presented here is consistent with several experimental observations on water and ethylene glycol such as the anomalous enhancement at small volume fractions, saturation at higher values, and the lack of correlation of the enhancement to the intrinsic thermal
conductivity of the nanoparticles [12-14, 29]. The mechanism may also be relevant for a broad class of nano-colloids with nanometer sized colloidal particles. For example, it is anticipated that enhancements with nanoparticles which are lyophobic such as diamond or carbon fullerenes may only be marginal. The theory also suggests possible avenues for optimizing nano-colloids by developing nanoparticles that have functionalized surface layers to maximize the interactions with the fluid atoms.
4. Interfacial Dynamics and Structure

4.1 Introduction

In this Chapter, $MD$ simulations are systematically conducted to study the effect of short-ranged attraction. The main objective is to investigate the changes in the local dynamics and structure, and the diffusional characteristics at various levels of solid-fluid attraction. They are then correlated to the thermal conductivity of the colloid. The structural and diffusional characteristics are easily accessible by experimental techniques such as neutron and light scattering, and can therefore, provide further insights into the mechanism of thermal transport in colloids.

In the model system, solid clusters are uniformly dispersed in a generic Lennard-Jones (LJ) liquid. The solid clusters are created from a $FCC$ lattice and are held together using non-linear springs. The main motivation for this configuration is to use a generic solid-like potential which can assess the sensitivity of the earlier results to the solid-solid interaction. The fluid-fluid ($FF$) and solid-fluid ($SF$) interactions are modeled by standard 12-6 $LJ$ interactions with the parameters given by $(\varepsilon, \sigma)$ and $(\varepsilon_{SF}, \sigma)$ respectively. The coupling between the solid and fluid atoms is measured through the attractive potential well-depth $\varepsilon_{SF}$ relative to that between two fluid atoms ($\varepsilon$).

4.2 Model System with $FENE$ springs

The model in this study consists of five solid clusters of 20 atoms each in a $LJ$ liquid of 1948 atoms. Unlike before, reduced units based on $m$, $\varepsilon$ and $\sigma$ are used throughout in this Chapter and next. All the atoms have the same size ($\sigma$) and mass ($m$). The cluster atoms are held together by a finitely extendable nonlinear elastic ($FENE$) potential which is given by [32, 107]
$U_{FENE} = -A\epsilon \ln \left[ 1 - \left( \frac{r}{B\sigma} \right)^2 \right]$ \hfill (4.1)

where the constants $A$ and $B$ take the values 5.625 and 4.95 respectively. In addition to the above potential, the solid atoms also experience a $LJ$ potential with parameters ($\epsilon, \sigma$). The simulations are carried out at a constant temperature of 1.0 and a volume corresponding to a pressure of 1.296. The density on an average is approximately 0.84. At this state point, the radial distribution function ($r_{df}$) indicates that the base fluid has a structure corresponding to that of a liquid. The volume fraction is calculated as $\pi npa_0^3/6v$ (see Chapter 3). A number fraction of $100/2048$ thus, corresponds to a volume fraction of 3.7%. The system consists of well-dispersed nanoclusters (see Fig. 4.1) that are mostly comprised of surface atoms. Equilibration is typically attained in 100,000 iterations using velocity rescaling and Berendsen barostat. The heat autocorrelation function is then averaged over 2000 sets in the $NVE$ ensemble without the use of any synthetic temperature or pressure control. The thermal conductivity is then averaged over 12 initial conditions and the procedure is repeated for several ratios of $\varepsilon_{SF}/\varepsilon$ ranging from 0.5 to 9.0.

Figure 4.1 Typical $FENE$ cluster configuration. The fluid atoms are not shown.
4.3 Thermal Conductivity

Figure 4.2 depicts the total thermal conductivity ($\kappa$) as a function of $\varepsilon_{SF}/\varepsilon$ ranging from weak coupling ($\varepsilon_{SF}/\varepsilon \approx 1$) to strong coupling ($\varepsilon_{SF}/\varepsilon \gg 1$). Also shown in the figure are the contributions from the self correlation in the kinetic energy flux ($KK$), potential energy flux ($PP$), collision flux ($CC$), and cross correlation of the potential-collision ($PC+CP$) flux. The partial correlations are explained in greater detail in Chapter 3.

Figure 4.2 Effective thermal conductivity ($\kappa$) and the contributions from $KK$, $PP$, $CC$ and $PC+CP$ correlations. The ratio $\varepsilon_{SF}/\varepsilon = 0$ corresponds to the base fluid without the nanoclusters. The solid lines are provided to guide the eye.
The ratio $\varepsilon_{SF}/\varepsilon = 0$ corresponds to the base fluid without the nanoclusters. For $\varepsilon_{SF}/\varepsilon = O(1)$, the enhancement in the total thermal conductivity is relatively small and it largely results from the increase in the contribution from the $CC$ correlation. For example, with a ratio of $\varepsilon_{SF}/\varepsilon = 2$, the increase in the total thermal conductivity is 0.55 while the enhancement from the $CC$, $PP$ and $PC+CP$ contributions are 0.39, 0.05 and 0.06 respectively. The $KK$ correlation is practically zero which signifies a very small contribution from the thermal motion of the atoms to the total $\kappa$. The contribution from the $PP$ interaction steadily rises with increasing $\varepsilon_{SF}/\varepsilon$ and the variation is nearly quadratic. In contrast, the contribution from the $CC$ interaction essentially remains constant for larger values of $\varepsilon_{SF}/\varepsilon$. The lack of significant increase in the $CC$ contribution is somewhat surprising which will be discussed in greater detail when the structure of the fluid around the nanocluster will be discussed. The total $\kappa$ shows an initial dip corresponding to a cross interaction $\varepsilon_{SF}/\varepsilon = 0.5$. The correlations involving collision $(C)$ are expected to decrease when the cross interaction is weaker than that between the fluid atoms. This reduction is manifested as a decrease in the total $\kappa$. For strong cross interactions ($\varepsilon_{SF}/\varepsilon \geq 8$), the total $\kappa$ saturates due to a strong influence from the $PC+CP$ correlation. It is thus, clear that a strong short-ranged attraction which is several times larger than the fluid-fluid interaction is mandatory for a significant increase in the thermal conductivity. This increase, as also demonstrated from the $Xe$-$Pt$ model, arises largely from an unusual contribution from the $PP$ correlation. It is also interesting to note that the enhancement in the thermal conductivity is also not related to the type of interactions between the solid atoms. The clusters in the present study are held together by non-linear springs while those in Chapter 3 are created with a deep $LJ$ potential. Both models show enhancement only when there is a significant cross-interaction between the solid and fluid atoms.

4.4 Interfacial Structure

The structural changes in the fluid atoms are depicted in Figure 4.3. For $\varepsilon_{SF}/\varepsilon \sim 1$, the cross radial distribution function, which is the probability of finding a fluid atom at given radial location given that a solid atom is at the origin, has the characteristics resembling that of a fluid.
Figure 4.3 The cross radial distribution function $g_{SF}(r)$ for several values of $\varepsilon_{SF}/\varepsilon$. Inset (a) shows the fluid-fluid radial distribution function $g_{FF}(r)$ for two bounding values of $\varepsilon_{SF}/\varepsilon$. Inset (b) shows $\alpha$, the ratio of the magnitudes of the first non-zero minima ($g_{\text{min}}$) to the first maxima ($g_{\text{max}}$) in the rdf, and the Wendt and Abraham criterion for liquid-to-amorphous transition which occurs at $\alpha \approx 0.14$.

As $\varepsilon_{SF}/\varepsilon$ increases, the fluid atoms in the vicinity of the clusters get more strongly attracted towards the clusters and move inwards. This is attested by the sharpening of the first peak.
Remarkably, the second peak flattens and then splits into two revealing the definitive signature of amorphous-like transition in the fluid atoms. The fluid-fluid radial distribution function [(inset (a)], on the other hand, is only marginally affected by the higher values of $\varepsilon_{SF}/\varepsilon$. It is thus clear that the fluid atoms pack themselves in a random close pack arrangement only near the vicinity of the solid clusters.

The amorphous-like transition can be measured quantitatively through the Wendt and Abraham criterion [108] which states that the onset of an amorphous state in a \emph{LJ} system is given by $\alpha = \frac{g_{\text{min}}}{g_{\text{max}}} \approx 0.14$, where $g_{\text{min}}$ and $g_{\text{max}}$ are the magnitudes of the first non-zero minima and the first maxima of the radial distribution function respectively. The variation of $\alpha$ [inset(b)] shows that the Wendt and Abraham criterion predicts an amorphous transition when the ratio $\varepsilon_{SF}/\varepsilon$ is approximately 2.5. The radial distribution function shows an incipient shoulder formation at $\varepsilon_{SF}/\varepsilon = 2$ and a double peak formation at $\varepsilon_{SF}/\varepsilon = 3$ which is in good agreement with the Wendt and Abraham criterion.

### 4.5 Interfacial Dynamics

The potential energy fluctuations of the interfacial fluid atoms are now shown to be correlated to the evolution of the aforesaid structural transition. First, the region around a solid atom is divided into different radial shells. The local dynamics of the interfacial region is characterized by the dynamic fluctuation amplitude $\mathcal{A}$ which is defined as the standard deviation of the fluctuations (kinetic and potential energy) of each fluid atom averaged among the like atoms in each shell. Previously in Chapter 3, it was observed that if the potential energy fluctuations exceed those of the kinetic energy, then potential energy exchange takes place among the atoms. Figure 4.4 depicts $\mathcal{A}^U$ taken over a period of 144 in each radial shell for different values of $\varepsilon_{SF}/\varepsilon$. The shells boundaries are placed at radial distances of 1.1, 1.2, 1.4, 1.8 and 4.5 from a solid atom. The kinetic energy in all the shells remains practically the same and deviate very little from the bulk values. This shows that local equilibrium conditions hold good at the interface. For weak cross-interactions, $\varepsilon_{SF}/\varepsilon < 3$, the average potential fluctuations in all the radial shells are less than those of the kinetic energy indicating a lack of cooperativity among the atoms. This is also attested by a weak contribution from the PP correlation to the thermal conductivity (see Figure 4.2). For
$\varepsilon_{SF}/\varepsilon \sim 4$, $A^U$ in shells I-IV becomes more than that of the kinetic energy. At this interaction level, the radial distribution function posses the distinctive signature of an amorphous-like material characterized by the split in the second peak. Thus, the excess fluctuations in the potential energy and a non-trivial contribution from the $PP$ correlation are noticeably correlated to the emergence of an amorphous-like transition at the interface. At the larger radius of 4.5 (Shell V), $A^U$ is smaller than $A^T$ and shows only marginal differences from that of the bulk. Appreciable excess potential energy fluctuations and correspondingly, significant enhancement in the thermal conductivity, can be observed only when the interaction level $\varepsilon_{SF}/\varepsilon$ becomes 4 or more. This observation may explain why the $MD$ simulations in [32, 33] which employed a maximum interaction strength of $\varepsilon_{SF}/\varepsilon=2.25$ failed to show any significant enhancement in the thermal conductivity.

Figure 4.4 Dynamic fluctuation amplitude $A^U$ for fluid atoms in different radial shells surrounding the nanoclusters. The open symbols correspond to $A^T$ of the bulk.
The lack of crystalline order in the fluid atoms is clearly visible from the radial distribution function for all values of $\varepsilon_{SF}/\varepsilon$. This effectively precludes the possibility of having enhanced phonon modes for heat conduction and is remarkably manifested through the near-constant variation of the collision-collision (CC) component of the thermal conductivity. It is known from previous MD studies that even small changes in the crystalline structure such as impurities or vacancies introduce significant reduction in the thermal conductivities [100, 109, 110] due to phonon scattering. Materials in the amorphous state are also known to have a lower thermal conductivity relative to that from the crystalline state [110]. The lack of any significant enhancement in the phonon (CC) modes can be therefore, explained with the lack of long-ranged order in the present simulation.

Finally, the diffusive characteristics of the nano-clusters are demonstrated to be correlated with the structural changes in the fluid. In a colloidal solution, there are two time scales. The shorter time scale is taken to be longer than the duration of a microscopic ‘kick’ that represents the fluid-solid interaction but shorter than the time required for the particle to move its own diameter. An estimate of the short-time diffusion is made from the classical Einstein relationship given by $D_0 = k_BT/6\pi\mu R$ where $T$ is the temperature, $\mu$ is the viscosity of the base fluid and $R$ is the radius of the solid nanocluster. In the present simulation, the nanocluster has a radius $O(1)$ as the solid cluster is exclusively made of surface atoms. The long-time self-diffusion of the solid atoms is calculated from the slope of the mean square displacement as $\lim_{t \to \infty} \frac{\langle [r(t)-r(0)]^2 \rangle}{6t}$. The long-time diffusion coefficient is generally smaller than the short-time coefficient because of solvent mediated hydrodynamic interactions and generally decreases with the volume fraction of the particles.

Figure 4.5 shows that $\beta$, the ratio of long-time diffusion coefficient to the short-time (Einstein) diffusion coefficient, decreases in an exponential manner for increasing values of $\varepsilon_{SF}/\varepsilon$. For the weakest cross-interaction ($\varepsilon_{SF}/\varepsilon = 0.5$), the long-time diffusion coefficient is close to the Einstein coefficient. In contrast, for the strongest cross interaction ($\varepsilon_{SF}/\varepsilon = 9$), the deviation from the Einstein value is more than 80%. This behavior can be understood by examining the velocity autocorrelation $\Psi(t)$ of the solid atoms which is shown in the inset of Figure 4.5. The diffusion coefficient is proportional to the area under $\Psi(t)$ and is identically equal to what is calculated
from the mean square displacement curve [45]. $\Psi(t)$ represents the projection of the velocity of an atom at the current time ($t=t$) along the initial direction of its motion ($t=t_0$). Negative values of $\Psi(t)$, therefore, indicate the entrapment of solid atoms in a cage formed by its immediate neighbors and the subsequent backscattering.

Figure 4.5 The ratio of long-time diffusion coefficient of the solid atoms to the short-time (Einstein) diffusion coefficient ($\beta$) for different values of $\varepsilon_{SF}/\varepsilon$. Inset shows the velocity autocorrelation function $\Psi(t)$ of the solid atoms.
The cage in the present simulation, unlike that observed in pure fluids, is a manifestation of solid atoms being confined to a fluid neighborhood that has an amorphous-like characteristic. Theoretically, the velocity autocorrelation for Einstein diffusion is an exponential decaying function which signifies the absence of hydrodynamic interactions. The relative good agreement between the Einstein and long time diffusion coefficients for $\varepsilon_{SF}/\varepsilon = 0.5$, therefore, comes from the smaller cage effect observed in $\Psi(t)$.

Löwen, Palberg and Simon (LPS) [111] has proposed a dynamic freezing transition criterion which states that a colloid freezes when $\beta$ becomes approximately 0.1. Interestingly, $\beta$ approaches 0.1 in the present simulation for larger values of $\varepsilon_{SF}/\varepsilon$. More work is however, needed to check whether the LPS criterion is applicable to systems where the solvent has local amorphous structure near the colloidal particle. Curiously, the self-diffusion of the nanoclusters does not show any correlation to the enhancement in the thermal conductivity, a behavior which is at variance with the hydrodynamic models [40, 41].

4.6 Discussion

In summary, it is demonstrated using a model nano-colloidal system that a relatively high cross-interaction ($\varepsilon_{SF}/\varepsilon \geq 4$) between the fluid and solid atoms introduces four observable effects namely, a non-trivial contribution from the self correlation in the potential energy flux, a formation of a structural interfacial region, excess potential energy fluctuations at the interface and a pronounced cage effect that decreases the self-diffusion coefficient of the nano-clusters. The concomitant effects are particularly useful from an experimental point of view. While measuring the potential energy fluctuations or the contribution from the PP correlation is a formidable task, measuring the diffusion and the structural realignment at the interfacial region is certainly feasible by scattering techniques or with magnetic resonance imaging. The presence of the structural and the diffusive signatures along with an enhancement in the thermal conductivity can serve as an indirect confirmation to the observations on the unusual mode of potential energy transport in nano-colloids.
Based on the simulations, it is anticipated that the enhanced thermal conductivities observed with nanoparticles in polar solvents such as water may result exclusively from the surface interactions. Indeed, as discussed before, the experiments in [11] show that the thermal conductivity enhancement in a gold nano-colloid is significantly reduced when the nanoparticle surface has a covalent molecular coating. Experiments with oxides in water are more revealing as they show that the enhancement is a strong function of pH which is again a direct consequence of the electrostatic surface interaction [25]. Short-ranged order is also predicted for metal-water interfaces with molecular dynamics simulations. For example, three ordered layers of water are predicted on the Pt (111) surface [112]. In the first layer, water molecules form ice-like structures with the oxygen atoms bound to the Pt atoms while in the second and the third layers, water molecules are hydrogen-bonded to the first and the second layer respectively. This ordering, even with a strong perturbation induced on the surface, persists over a distance of ~1 nm from the Pt surface. It is important to note that this layering arises from the strong short-ranged attraction (25-50 kJ/mol) between the Pt and the water molecules which is comparable to the attraction between the platinum atoms themselves (~66 kJ/mol) [103]. The 1 nm layering is of no consequence to large colloidal particles say, 10 nm and above but certainly affects particles that have a diameter of $O$ (1) nm. Direct experimental evidences are also available on the layering of non-polar, non-conducting liquids which show that the liquid atoms can form 3 to 6 layers at a solid-liquid interface [113]. Based on these evidences, it is reasonable to anticipate a certain amount of local structure in the liquid molecules adjacent to the nanoparticles if there is a significant attraction between the liquid and the solid atoms. This short range order can potentially facilitate the transfer of potential energy among the fluid atoms.
5. Equivalence of Green-Kubo and Non-equilibrium Simulations

5.1 Introduction

The transport coefficients, thus far, are determined through a combination of equilibrium MD simulations and linear response theory or Green-Kubo (GK) formalism. In an alternate route, thermal conductivity can be computed through non-equilibrium (NEMD) simulations [39, 49]. In this Chapter it is first shown that the time averaged microscopic binary heat flux is applicable to dilute nano-colloids that are characterized by both spatial inhomogeneity and non-ideality. Next, the thermal conductivities of identically prepared dilute nano-colloidal dispersions are evaluated with both GK and NEMD simulations. It is shown that NEMD and GK simulations give statistically similar conductivity enhancements only under equivalent dynamic interface conditions. The congruity of the interfacial dynamics is assessed through the dynamic fluctuation amplitude $\Delta$.

5.2 NEMD Simulation

Non-equilibrium (NEMD) simulation for thermal conductivity mimics an experimental procedure whereby a known heat flux ($q^*$) is applied across two sections and the thermal conductivity is determined from the Fourier’s law as

$$\lambda = -\frac{q^*}{dT/dz}$$

(5.1)
where \( \frac{dT}{dz} \) is the temperature gradient. As with the GK method, direct NEMD simulations are widely used for calculating the thermal conductivity and good conformity is generally observed between the methods [90]. Other synthetic NEMD methods (see, for example [96, 114]) provide alternate ways to compute the thermal conductivity and other transport coefficients but are not considered in this thesis. In NEMD methods, an exact knowledge of the microscopic heat flux is not always required. This makes them attractive to study complex systems. Unlike the GK method where difficulties can arise from the slow convergence of the time integral, NEMD methods are generally accepted to be fast. A major limitation stems from the extraordinarily large temperature gradients \([O(10^{10} \text{ K/m})]\) that are prescribed or generated in the system which are several orders higher than those observed in experiments. These gradients make the reference temperature ill-defined and can potentially interfere with the dynamics, a possibility that has not been previously recognized.

A particularly simple and elegant way of direct simulation is through the imposed-flux method [115] where a known heat flux is imposed on the system which generates a linear temperature profile at steady state. This method is compatible with periodic boundary conditions, conserves both energy and momentum, and experiences only limited perturbation effects. Reasonably accurate thermal conductivity estimates have been generated for atomic fluids, and with more complex fluids such as water and n-butane [116]. The simulation box is divided into many slabs perpendicular to one chosen direction, say \( z \), with the edge slabs denoted as ‘cold’ and the center slab as ‘hot’. Periodic velocity exchanges are made between atoms of these slabs such that the hottest atom in the cold slab is substituted with the coldest atom of the hot slab. This unphysical energy transfer generates a heat flux that flows from the middle to the edge slabs. At steady state, a linear temperature profile develops which is symmetric about the hot slab. The heat flux \( (j_q) \) can be computed exactly with the known values of the velocities that are exchanged using the following expression

\[
\dot{J}_q = \frac{1}{2A_x t_{\text{transfers}}} \sum \frac{m}{2} \left( v_h^2 - v_c^2 \right)
\]  

(5.2)
where $A_{xy}$ is the cross-sectional area, $t$ is the simulation time, $m$ is the mass and $v$ is the velocity. Subscripts $h$ and $c$ denote the hot and cold atoms. The factor 2 in (5.2) accounts for the heat flow in two directions about the center slab. In contrast, the time averaged microscopic heat flux $\langle \tilde{j}_h \rangle$ is given by,

$$\langle \tilde{j}_h \rangle = \left( \frac{1}{2} \sum_{k=a}^{b} \sum_{i=1}^{N_k} m_i^k (v_i^k)^2 \right) - \sum_{k=a}^{b} \sum_{i=1}^{N_k} \sum_{j>i}^{N_k} \left[ \mathbf{I} \Phi(r_{ij}^k) + r_{ij}^k \otimes E_{ij}^k \right] \mathbf{v}_i^k - \sum_{k=a}^{b} \left( h^k \right) \sum_{i=1}^{N_k} \mathbf{v}_i^k \right)$$

(5.3)

As discussed before in Chapter 2, the above expression assumes a spatial homogeneity which is not strictly satisfied in a colloidal solution. Through NEMD simulations, the above microscopic expression will be compared to the exact heat flux given by (5.2). Note that both heat fluxes are time averaged quantities.

The NEMD simulations are performed in identical conditions as to those in the GK simulations with FENE springs as describe in Chapter 4. No changes are made in the system size (2048 atoms in a 13.3x13.3x13.3 cubic simulation box (see Figure 4.1), velocity Verlet algorithm, constant energy after equilibration, FENE and LJ potentials, cut-off radius of 4.5 and a time step of 0.002). In most case studies, an exchange frequency of 1 in 60 time steps is found to be optimal to identify a statistically significant slope in the temperature profile. The equilibration is typically done for 100,000 iterations and temperature in each slab is averaged for 150,000 iterations. Further averaging over 8-10 initial conditions are required to generate an acceptable linearity in the temperature profile (measured by the multiple correlation coefficient, $R^2$). By keeping all the simulation parameters identical, it is expected that a fair comparison can be made between the GK and the NEMD simulations.

### 5.3 Time Averaged Heat Flux

First, it is demonstrated that the microscopic binary heat flux expression in (5.3) is suitable for use in colloids that are inherently inhomogeneous and non-ideal. The heat fluxes for a colloid consisting of 5 clusters of 20 atoms each in total of 2048 atoms (volume fraction of 3.7%) are
compared in Figure 5.1. The system temperature is 1.0 and the pressure is approximately 1.3 (both in reduced MD units with the fluid atoms as reference). A strong solid-fluid cross-
interaction strength of $\varepsilon_{sf}/\varepsilon = 7$ is prescribed. Each half of the z-axis in the NEMD simulation cell is divided equally into 12-16 equi-sized slabs. In each slab, the heat flux is averaged over 150,000 iterations after an equilibration period of 100,000 iterations. These slab estimates are then compared to the exact heat flux given by (5.2) developed across the hot and cold slabs in Fig. 5.1.

![Figure 5.1 Comparison of microscopic heat flux computed by (5.3) in different slabs with the exact value computed from (5.2). For the sake of clarity, the exact value is shown as a line. The temperature gradient develops over a distance of 6.6.](image)

The microscopic heat flux shows spatial oscillations which after averaging gives a value of 0.1217. This is only 4.6% less than the exact value 0.1276 calculated from (5.2). The standard deviation of the fluctuation is 0.0032 which is 2.6% of the average value. Similar results are obtained with 10 clusters as shown in Table 5.1. Reasonable agreement is seen between the exact and the microscopic heat flux for the cases considered here despite assuming spatial
homogeneity. The result for model V1 which has one big nanoparticle of 100 atoms is particularly noteworthy because the inhomogeneity clearly hasn’t resulted in a significant deviation in the average microscopic heat flux. This is not entirely surprising as the concept of homogeneity is always relative to the scales that are being considered. In monatomic fluids at molecular scales there are large density fluctuations but by taking its Fourier transform it is readily seen that these are transparent at the continuum scales [45]. The delta functions in (2.56) are slowly varying over the range where the potential is applicable. Thus, the operator $\Theta_y$ in (2.56), which represents the deviation due to inhomogeneity, represents a Taylor expansion of a small parameter $r_y/L$, where $r_y$ is the atomic spacing and $L$ is the largest wavelength of the heat flux vector. The ratio $r_y/L$ in the present simulation is $O(0.1)$ and thus, the operator $\Theta_y$ does not have a significant effect on the computed microscopic heat flux.

Table 5.1. Comparison of microscopic heat flux and exact estimate averaged over 150,000 time iterations and 10 sets of initial conditions. All the models have the same number fraction and use a constant energy algorithm. The final state points show small deviations from the values given below.

| Model | Cluster Arrangement | State $(T,P)$ | $\frac{\delta u}{\delta J_y}$ | Exact $J_y$ | Microscopic $\langle J_y \rangle$ | % Δ $\Delta$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>10 Clusters with 10 Atoms</td>
<td>(1.0, 0.0)</td>
<td>0.1198</td>
<td>0.1149</td>
<td>-4.09</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>10 Clusters with 10 Atoms</td>
<td>(1.0, 1.3)</td>
<td>0.1287</td>
<td>0.1247</td>
<td>-3.11</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>10 Clusters with 10 Atoms</td>
<td>(1.0, 0.0)</td>
<td>0.1114</td>
<td>0.0973</td>
<td>-12.67</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>5 Clusters with 20 Atoms</td>
<td>(1.0, 1.3)</td>
<td>0.1276</td>
<td>0.1231</td>
<td>-3.56</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>5 Clusters with 20 Atoms</td>
<td>(1.0, 1.3)</td>
<td>0.1242</td>
<td>0.1222</td>
<td>-1.61</td>
<td></td>
</tr>
<tr>
<td>VI</td>
<td>1 Cluster with 100 Atoms</td>
<td>(1.0, 1.3)</td>
<td>0.2070</td>
<td>0.1972</td>
<td>-4.7</td>
<td></td>
</tr>
</tbody>
</table>
5.4 Thermal Conductivity

Next, the thermal conductivity of the colloid system are compared and contrasted at different state points, cluster sizes and solid-fluid interaction strengths \((\varepsilon_{SF}/\varepsilon)\) with both \(GK\) and \(NEMD\) simulations. The concept of dynamic similarity at the interface is developed to explain the differences seen in the simulations. A simple criterion for establishing the equivalence of the \(GK\) and \(NEMD\) simulations for colloids is proposed using the dynamic fluctuation amplitude \((A)\).

The previous simulations with \(GK\) in Chapter 4 have revealed that anomalous enhancement in the thermal conductivity at low volume fractions is possible when there is a strong coupling between the fluid and the solid atoms. Two levels of cross-interactions, \(\varepsilon_{SF}/\varepsilon = 2\) (weak) and \(\varepsilon_{SF}/\varepsilon = 7\) (strong) will be now explicitly compared with \(NEMD\) simulations. First the results of the case with \(\varepsilon_{SF}/\varepsilon = 2\) are reported.

5.4.1 Weak Interaction \(\varepsilon_{SF}/\varepsilon = 2\)

Model III colloidal system consists of 10 clusters of 10 atoms each (volume fraction of 3.7) at the state point \((T,P) = (1.0,0.0)\). \(T\) and \(P\) correspond to the temperature and pressure respectively. Note that the averages are computed at constant energy and deviations of 7% or less are observed for the pressure. As for the cases with the heat flux, the temperature profiles are averaged over 150,000 iterations and 10 sets of initial conditions. Note that the other simulation parameters are the same as described in Chapter 4. Figure 5.2 compares the temperature profiles which clearly show a lower slope for the colloid which indicates a larger thermal conductivity. The linearity in the profiles is measured by the multiple correlation coefficient \((R^2)\) which are also shown in Figure 5.2. The heat flux measured by (5.2) gives 0.1052 and 0.1114 for the base fluid and the colloid respectively while the slopes of the corresponding temperature profiles are 0.0263 and 0.0242. The ratio of the heat flux to the temperature gradient gives the thermal conductivity and is calculated to be 4.006 and 4.591 for the base fluid and colloidal system respectively giving an enhancement of 14.6%.
In the \textit{GK} simulation, the integration of the heat flux autocorrelation function gives a thermal conductivity of 4.126 for the base fluid which is only 2.9\% different from that of the \textit{NEMD} simulation. This unusually close match is somewhat fortuitous because the present \textit{NEMD} method, as evidenced in [115], can underestimate the thermal conductivity by 3-16\% for a LJ liquid depending on the algorithm (constant energy versus constant temperature) and energy exchange frequency. For the nano-colloidal system, the \textit{GK} simulation gives a thermal conductivity of 4.89 giving a relative enhancement of 18.6\%. Thus it is seen that the \textit{GK} and \textit{NEMD} simulations give statistically similar results for the nano-colloid with a weak cross interaction.

![Graph]

Figure 5.2. Temperature profiles of the base fluid and nano-colloid (Model III) consisting of 10 clusters of 10 atoms each with $\varepsilon_{SF}/\varepsilon = 2$ at $(T,P) = (1.0, 0.0)$.

The similarity is further verified with a different cluster distribution of 5 clusters with 20 atoms each at the state point $(T,P) = (1.0, 1.38)$. This configuration (Model V) has been already considered in Chapter 4. The configuration of 10 clusters of 10 atoms each is also repeated for this state (Model VII). Figures 5.3 and 5.4 show the temperature profiles for the above cases.
For the base fluid, the heat flux and the temperature gradient are 0.1213 and 0.0201 respectively which gives a thermal conductivity of 6.03. With a constant temperature algorithm instead of constant energy, the thermal conductivity is evaluated to be 6.22. For the same state point considered here but with a much larger system (40×40×40) and a different NEMD algorithm, Ref. [32] reports a value of 6.33. Thus, the present results show limited finite size and algorithmic effects. In contrast, the GK simulation predicts a conductivity of 6.72. As discussed before, the deviation from the NEMD simulations (10.3%) are within the known error bounds of these methods. The focus of this chapter is to make a comparative study between the base fluid and the colloidal system, and hence, the relative changes are deemed more important.

The important simulation results with NEMD and GK for different cluster configurations and state points are summarized in Table 5.2. All the colloidal data are with $\varepsilon_{SF}/\varepsilon = 2$. The most notable result is that for all the models, the relative enhancements agree remarkably well within the statistical uncertainty. Thus, for weakly interacting nano-colloids, both GK and NEMD simulations give statistically equivalent enhancements in the thermal conductivity.

![Figure 5.3 Temperature profiles of the base fluid and the nano-colloid (Model V) consisting of 5 clusters of 20 atoms each with $\varepsilon_{SF}/\varepsilon = 2$ at $(T,P) = (1.0, 1.38)$.](image)

Figure 5.3 Temperature profiles of the base fluid and the nano-colloid (Model V) consisting of 5 clusters of 20 atoms each with $\varepsilon_{SF}/\varepsilon = 2$ at $(T,P) = (1.0, 1.38)$. 
Figure 5.4 Temperature profiles of the base fluid and the nano-colloid (Model VII) consisting of 10 clusters of 10 atoms each with $\varepsilon_{SF}/\varepsilon = 2$ at $(T,P) = (1.0, 1.3)$.

Table 5.2 Thermal conductivities from NEMD and GK simulations for the weak interaction, $\varepsilon_{SF}/\varepsilon = 2$. All the models have the same number fraction and use a constant energy algorithm.

<table>
<thead>
<tr>
<th>Configuration and State</th>
<th>NEMD</th>
<th>GK</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Model</strong></td>
<td><strong>Cluster Configuration</strong></td>
<td><strong>State $(T,P)$</strong></td>
</tr>
<tr>
<td>III</td>
<td>10 Clusters with 10 Atoms</td>
<td>(1.0,0.0)</td>
</tr>
<tr>
<td>V</td>
<td>5 Clusters with 20 Atoms</td>
<td>(1.0,1.3)</td>
</tr>
<tr>
<td>VII</td>
<td>10 Clusters with 10 Atoms</td>
<td>(1.0,1.3)</td>
</tr>
</tbody>
</table>
5.4.2 Strong Interaction $\varepsilon_{SF}/\varepsilon = 7$

Next the results for the stronger interaction (Model I), $\varepsilon_{SF}/\varepsilon = 7$ at $(T,P) = (1.0, 0.0)$ are presented. The temperature profile depicted in Figure 5.5 shows a substantially lower slope than that of the base fluid indicating a larger conductivity enhancement. The heat flux and the temperature slopes are 0.1198 and 0.0228 respectively which gives a thermal conductivity of 5.26. The mechanism of the unusually large enhancement (31.5%), however, is not readily evident from the NEMD simulation but is accessible from the GK simulations.

The thermal conductivity obtained with GK (6.09) is 47.5% more than that of the base fluid (4.13). Thus, the GK method predicts a 16% larger enhancement than NEMD. This is a characteristic of all the simulations with the stronger cross interaction, $\varepsilon_{SF}/\varepsilon = 7$. For the 20 cluster configuration at a pressure of 1.3 (Model IV), the GK thermal conductivity (10.21) is substantially larger than the prediction by NEMD (6.54). In terms of enhancements, the former corresponds to 51.9% while the latter constitutes only a small fraction (8.6%). Table 5.3 summarizes the relative variations between the two methods with $\varepsilon_{SF}/\varepsilon = 7$.

Figure 5.5 Temperature profiles of the base fluid and the nano-colloid (Model I) consisting of 10 clusters with 10 atoms each with $\varepsilon_{SF}/\varepsilon = 7$ at $(T,P) = (1.0, 0.0)$. 
Table 5.3. Thermal conductivities from \textit{NEMD} and \textit{GK} simulations for the strong interaction, $\epsilon_{SF}/\epsilon = 7$

| Model | Cluster Configuration | State\((T,P)\) | $\epsilon_{SF}/\epsilon$ | Base Fluid | Colloid | $\% \Delta$ | Base Fluid | Colloid | $\% \Delta$
<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>10 Clusters with 10 Atoms</td>
<td>(1.0, 0.0)</td>
<td>7</td>
<td>4.00</td>
<td>5.26</td>
<td>+31.5</td>
<td>4.13</td>
<td>6.29</td>
<td>+52.3</td>
</tr>
<tr>
<td>IV</td>
<td>5 Clusters with 20 Atoms</td>
<td>(1.0, 1.3)</td>
<td>7</td>
<td>6.03</td>
<td>6.55</td>
<td>+8.6</td>
<td>6.72</td>
<td>10.21</td>
<td>+51.9</td>
</tr>
<tr>
<td>II</td>
<td>10 Clusters with 10 Atoms</td>
<td>(1.0, 1.3)</td>
<td>7</td>
<td>6.03</td>
<td>6.85</td>
<td>+13.6</td>
<td>6.72</td>
<td>8.27</td>
<td>+23.1</td>
</tr>
</tbody>
</table>

5.4.3 Interfacial Dynamics and Percolating Network

To rationalize the reason behind the relatively large discrepancies, a careful study of the dynamics at the interface is required. As shown in the Chapter 4, a dynamic interface region characterized by an amorphous-like structure develops at the cluster-fluid interface where the fluctuations in the potential energy of the (fluid) atoms become larger than those of the kinetic energy. Physically, this signifies a cooperative exchange of potential energy among the interface fluid atoms.

As also seen in Chapter 4, the cooperative dynamics at the interface and the self-correlation in the potential flux are nicely correlated. The measure of cooperativity is assessed though the dynamic fluctuation parameter $A$. When the ratio $AR \equiv A^U/A^T$ ($U$ and $T$ stand for potential and kinetic energy respectively) becomes greater than 1, it signifies the cooperative potential energy exchange among the interfacial fluid atoms and \textit{vice-versa}. In this chapter, $A$ is used to characterize the dynamic similarity of the \textit{GK} and \textit{NEMD} simulations.
Figure 5.6 Spatial variation of the dynamic fluctuation parameter $\Lambda$ for *NEMD* and *GK* methods with $\epsilon_{SF}/\epsilon = 2$. (a) Model V, 5 Clusters with 20 atoms, $T=1$, $P=1.3$. (b) Model III, 10 Clusters with 10 atoms, $T=1$, $P=0.0$.

Figure 5.6 delineates the radial variation of $\Lambda$ for potential and kinetic energies with the weak interaction, $\epsilon_{SF}/\epsilon = 2$. It is striking to note that in both simulation methods and in both models, the potential energy fluctuations are well within those of the kinetic energy. As discussed before, this indicates a lack of cooperative exchange of potential energy. Indeed, the *GK* simulation does attest to this and shows a negligible contribution from the self correlation in the potential energy. On the other hand for the stronger interaction, $\epsilon_{SF}/\epsilon = 7$, the fluctuation behavior is significantly different. (see Figure 5.7). *NEMD* $\Lambda^p$ shows a near exponential decay while the variation in *GK*
$A^p$ spreads over a larger radial distance. For the NEMD simulations, the radial distance, over which $AR$ is greater than 1, is approximately the same for both models (1.3). In GK, the 20 atom clusters portray a larger spread (2.6) while the 10 atom clusters show a spread of 2.3 approximately. Clearly, the dynamic interfacial layer ($\theta$), which is defined as the spatial region over which $AR \geq 1$, is much smaller ($\sim 1.3$) in the NEMD simulations which drastically reduce the possibility of any cooperative exchange in the potential energy. On the contrary, the GK simulations have a thickness of 2-3. The rather high $A^p$ with NEMD at the first radial location is somewhat puzzling. Since the important feature to note is the excess fluctuations in the potential energy relative to those of the kinetic energy, the absolute magnitude of $A^p$ is of a lesser concern. In the previous chapter, a similar lack of correlation between the conductivity enhancement and the magnitude of the $A^p$ was observed.

For the 20 atom clusters, both in GK and NEMD simulations, the cluster-to-cluster distance varies between 1 and 3 ($\sigma$). This information is accessed from the cluster locations at the end of the simulation runs. In the 10 atom clusters, the maximum separation is smaller. In the NEMD simulation, the dynamic interface layer with the strong cross-interaction ($\varepsilon_{SF}/\varepsilon = 7$) corresponds approximately to the minimum of the separation distance ($1\sigma$) while in the GK simulation, the interface layer is significantly thicker ($2-3\sigma$). Thus, in the GK simulation, the interfacial layer can overlap with each other and form a percolating network among the fluid atoms. This network is physically responsible for the higher thermal conductivity enhancement seen in the GK simulation. Once excess potential energy fluctuations near a cluster are initiated, possibly by a larger temperature, they can be coherently transferred from one interface layer to another effectively increasing the thermal conductivity. For weak cross interactions, $\varepsilon_{SF}/\varepsilon = O(1)$, the interface layers and percolation paths do not develop which precludes the possibility of exchanging potential energy among the atoms. Note that percolating mechanism is manifested only when cluster sizes are small. It is conceivable that a similar mechanism is possible with more complex nano-colloids characterized by electrostatic potential and double layers with particle sizes less than 10 nm. Further experiments or simulations are needed to make a definitive conclusion.
Figure 5.7  Spatial variation of the dynamic fluctuation parameter $A$ for $NEMD$ and $GK$ methods with $\varepsilon_{SF}/\varepsilon = 7$. (a) Model IV, 5 Clusters with 20 atoms, $T=1, P=1.3$. (b) Model I, 10 Clusters with 10 atoms, $T=1, P=0.0$.

It is important to note that $A^K$ with $GK$ shows a near constant radial variation which indicates that the interface and the bulk regions are in equilibrium conditions. The interfacial regions in $NEMD$ show lower fluctuations in the kinetic energy ($A^K$) which approach the equilibrium values far away from the clusters. This is attributed to the high temperature gradients in the system. If the $LJ$ fluid corresponds to Argon, then the temperature gradient is of the order of $10^{10}$ K/m which is
several orders larger than what is realized in an experiment. In contrast, the $GK$ simulation is always in equilibrium and has closer correspondence to an experiment where only very small deviations from equilibrium conditions are expected. For a homogeneous system such as in a pure fluid, the kinetic energy fluctuations in $NEMD$, even in the presence of the large temperature gradients, do not show any significant spatial variation and the velocity distribution remains near Maxwellian [91]. The presence of interfaces however, significantly affects the dynamics of the $NEMD$ simulations.

5.4.4 Mode Decomposition

The decomposition analysis as described in Chapter 3 is employed to gain better insight into the different modes that are resolved with $NEMD$. In Table 5.4, the thermal conductivity contributions from the dominant modes are elucidated for the weaker interaction strength of $\varepsilon_{SF}/\varepsilon = 2$ and compared to those from the base fluid. The contributions from the stronger interaction, $\varepsilon_{SF}/\varepsilon = 7$, are listed in Table 5.5.

When the cross interaction is weak ($\varepsilon_{SF}/\varepsilon = 2$), the contribution from self-correlation of the potential energy flux ($PP$) to the total thermal conductivity is less than 3% which is correlated to the lack of excess potential energy fluctuations in the interfacial layer. The relative change in the $CC$ correlation constitutes most the enhancement. 10 atoms cluster at the higher pressure (Model III) also gives similar results. Given the close similarity of the $GK$ enhancements to those of the $NEMD$, it is reasonable conclude that $NEMD$ simulations are able to resolve the $CC$ correlations satisfactorily in a weakly cross-interacting nano-colloid. For the stronger interaction of $\varepsilon_{SF}/\varepsilon = 7$ (Table 5.5), the agreement is not as strong which makes it harder to arrive at a definitive conclusion. Nevertheless, the order of magnitude suggests that most of the enhancements in the $NEMD$ come from the $CC$ correlations. Note that the sum of the partial correlations are generally seen to 5% (or less) more than the total correlation. The difference arises from the errors incurred in the calculation of area under the autocorrelation functions. In particular, the non-monotonic and oscillatory behavior of $PC$ and $CP$ cross correlation introduces a larger error than the other correlations.
Table 5.4. Thermal conductivity contributions from CC, PP and PC+CP correlations, and comparison to the enhancement in NEMD. The cross interaction strength for all the colloidal systems is $\varepsilon_{sp}/\varepsilon = 2$. The % $\Delta$ change is calculated with reference to the total thermal conductivity.

<table>
<thead>
<tr>
<th></th>
<th>Base Fluid</th>
<th>Model V 5 Clusters of 20</th>
<th>$\Delta$ (%)</th>
<th>NEMD $\Delta \lambda$ (%)</th>
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<tbody>
<tr>
<td><strong>CC</strong></td>
<td>5.15</td>
<td>5.54</td>
<td>5.8</td>
<td></td>
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<tr>
<td><strong>PP</strong></td>
<td>0.19</td>
<td>0.24</td>
<td>0.7</td>
<td>6.8</td>
</tr>
<tr>
<td><strong>PC+CP</strong></td>
<td>1.04</td>
<td>1.10</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>6.72</td>
<td>7.27</td>
<td>8.0</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Base Fluid</th>
<th>Model III 10 Clusters Of 10</th>
<th>$\Delta$ (%)</th>
<th>NEMD $\Delta \lambda$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CC</strong></td>
<td>2.83</td>
<td>3.48</td>
<td>15.7</td>
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<tr>
<td><strong>PP</strong></td>
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<td>0.32</td>
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<tr>
<td><strong>PC+CP</strong></td>
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<td>0.76</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>4.13</td>
<td>4.89</td>
<td>18.4</td>
<td></td>
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</tbody>
</table>
Table 5.5 Thermal conductivity contributions from CC, PP and PC+CP correlations, and comparison to the enhancement in NEMD. The cross interaction strength for all the colloidal systems is $\epsilon_{SF}/\epsilon = 7$. The % $\Delta$ change is calculated with reference to the total thermal conductivity.

<table>
<thead>
<tr>
<th></th>
<th>Base Fluid</th>
<th>Model IV 5 Clusters of 20</th>
<th>$\Delta$ (%)</th>
<th>$\Delta\lambda$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CC</strong></td>
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<td>6.06</td>
<td>13.5</td>
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<tr>
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<td>0.19</td>
<td>1.88</td>
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<tr>
<td><strong>PC+CP</strong></td>
<td>1.04</td>
<td>1.94</td>
<td>13.4</td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>6.72</td>
<td>10.21</td>
<td>51.9</td>
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</table>

<table>
<thead>
<tr>
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<th>Base Fluid</th>
<th>Model I 10 Clusters Of 10</th>
<th>$\Delta$ (%)</th>
<th>$\Delta\lambda$ (%)</th>
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<tr>
<td><strong>CC</strong></td>
<td>2.83</td>
<td>4.97</td>
<td>51.8</td>
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<tr>
<td><strong>PP</strong></td>
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<td>71.9</td>
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<td><strong>PC+CP</strong></td>
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<td>-2.2</td>
<td>-69.7</td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>4.13</td>
<td>6.29</td>
<td>52.3</td>
<td></td>
</tr>
</tbody>
</table>

A closer inspection of Table 5.5 reveals an interesting difference. It was earlier shown in Chapter 3 that the negative contribution from cross correlation for $PC+CP$ which arise at a relatively high volume fraction. In Model IV with the 20 atom clusters, the $PC+CP$ cross interaction is positive and contributes as much as the $PP$ contribution to the total thermal conductivity. On the contrary, Model I which has 10 atom clusters at a smaller pressure, shows a negative contribution which almost balances out the positive contribution from the $PP$ correlation. The bulk of the enhancement thus, solely comes from the $CC$ correlation. This is not to say that the stronger cross interaction has no discernible effect on dynamics as illustrated by the presence of an interfacial dynamic layer shown in Figure 5.7b. As discussed in Chapter 4, the negative $PC+CP$ correlation indicates a resistance to the cooperative transfer of potential energy from the strengthening of vibrations modes in the cluster. The lack of a better congruence between $GK$ and $NEMD$ results is attributed to the unfavorable $NEMD$ interfacial dynamics with strong cross interactions.

5.4.5 Interfacial Structure

Earlier in Chapter 4, it was shown that a strong cross interaction leads to an amorphous-like structural arrangement of fluid atoms in close proximity to the cluster. The structural changes in both $NEMD$ and $GK$ are analyzed as before by computing the cross radial distribution function $g_{PF}(r)$. Figures 5.8 and 5.9 compare the $g_{PF}(r)$ with $GK$ and $NEMD$ simulations for two cross interaction strengths, $\epsilon_{SF}/\epsilon = 2$ and $\epsilon_{SF}/\epsilon = 7$. For the weaker cross interaction, $g_{PF}(r)$ has signature resembling that of a dense fluid and expectedly, both $NEMD$ and $GK$ near identical variation. Given the differences in the interfacial dynamics, the near identical variation for the stronger interaction is rather surprising. Both methods display a splitting of the second peak which as discussed before, is a characteristic of random close pack or amorphous-like interfacial structure. One possible explanation for this similarity is that the local structure is defined by the interatomic potentials. Since the cross interaction strength is the same for both $NEMD$ and $GK$, the structure also remains the same. The difference in the local dynamics arises from the large temperature gradients imposed in $NEMD$ simulations. The interfacial layer which is important for energy transport therefore, is strictly dynamic in origin.
Figure 5.8 Cross radial distribution function with 20 atoms clusters, 
\( \varepsilon_{SF}/\varepsilon = 2, T=1, P=1.3 \) (Model V).

Figure 5.9 Cross radial distribution function with 20 atoms clusters, 
\( \varepsilon_{SF}/\varepsilon = 7, T=1, P=1.3 \) (Model IV).
5.5 Summary and Discussion

Thermal transport in colloids is a relatively new focus for a mature field. On the theoretical front, there are several areas that require clarification. It is sometimes regarded that Green-Kubo formalism is not applicable to inhomogeneous systems [90] such as colloids. Similarly, the suitability of the homogeneous heat flux vector to colloids that have spatial inhomogeneity also raises question [89]. In addition, there are subtleties involved with the non-uniqueness of heat flux vector and thermal conductivity in colloids [88], and the correspondence between the theoretical and the experimentally observable variables.

This work tries to address each of these issues through theory and molecular dynamics (MD) simulations. Using direct non-equilibrium simulations (NEMD), it is first shown that that the time averaged, homogeneous heat flux vector is appropriate for nano-colloids of varying sizes. It is then demonstrated that both Green-Kubo (GK) and NEMD simulations give statistically similar results for nano-colloids that have a weak solid-fluid interaction. Substantial deviation, however, is observed for a strong solid-fluid interaction. This incongruity is explained by showing the differences in the dynamics at the cluster-fluid interface. Developed in Chapter 3, the dynamic fluctuation amplitude ($A$), which is a measure of the local fluctuations, is employed to characterize the dynamic equivalence in GK and NEMD simulations. When the potential energy fluctuations ($A_U$) become more than those of the kinetic energy ($A_T$), potential energy can be cooperatively exchanged among the atoms. In the GK simulations, excess potential energy fluctuations in the fluid atoms are spread over an interfacial thickness of 2-3 ($\sigma$). In NEMD, the corresponding thickness is approximately 1.3 ($\sigma$). Thus, in the GK simulations, the thicker dynamic interfacial layer facilitates interactions with each other to form percolating networks that can transfer the excess potential energy. In the NEMD simulation, the extreme temperature gradient ($10^{10}$K/m) adversely affects the dynamics at the interface when the cross interaction is sufficiently strong.

An enhancement in the thermal conductivity for colloids is not unusual. In the effective medium theories [7], the thermal conductivity enhancements are of the order of the volume fraction. In this study, both GK and NEMD, under certain conditions, show disproportionately large
enhancement with a volume fraction that is almost an order smaller. The mechanisms behind the increase are not evident from the NEMD simulations but are readily accessible through GK. This is the most significant strength of GK or linear response formalism.

A key theoretical objection against the anomalous thermal conductivity enhancement in nanocolloids stems from the solid-fluid interfacial resistance arising from the mismatch of the vibrational frequencies at the interface. The present work with GK shows that interfacial resistance from the CC correlations is not the limiting mechanism in nano-colloids. As discussed before, in a recent theory [87], thermal resistances which are orders of magnitude lower are predicted between two nanoparticles when the inter-particle distance becomes smaller than the particle diameter along with a significantly higher resistance upon contact. These counterintuitive results show the limitation of the traditional analytical methods based on phonons which are inappropriate at nanoscales and solid-fluid interfaces. The present work is similar in spirit and raises the possibility of cooperative modes for colloids at nanoscales.
6. Statistical Field Estimators and Coarse Projection

6.1 Introduction

An accurate field description is an essential ingredient to multiscale modeling which in most cases involves coupling of molecular or microscopic simulators with the continuum field equations [117-121]. A spatial buffer is typically prescribed for transferring data from the continuum to the molecular region and vice versa. The continuum supplies the mean field variables to the molecular simulator and in return, the interfacial or boundary conditions for the continuum are calculated from the molecular simulator. Equation-free multiscale methodology [50-54, 57-73, 75-77], works in a different fashion. Rather than coupling microscopic or molecular simulators with the continuum, the equation-free approach bypasses the continuum models such as Navier-Stokes equation entirely. It works exclusively with microscopic simulators and employs a series of numerical operations that are akin to the buffer transfers in coupled continuum-particle simulations. This methodology is appropriate for phenomena where macroscopic equations are unavailable in the closed form such as in colloidal flows. The basic idea is to use short and intelligent bursts of appropriately initialized microscopic simulations and evaluate the evolution of pertinent macroscopic field variables solely through the microscopic simulators. It is evident that a smooth and accurate field description is essential in this type of multiscale computation. In the equation-free methodology, the particle to field transformation is known as restriction [50] while in coupled MD-continuum simulations it is called P→C transfer [119].

Coarse grained averages in MD simulations often suffer from noisy fluctuations or poor resolution [122]. Most often, the intrinsic fluctuations in the particle simulation appear as non-physical spatial noise in the field representation. This behavior arises primarily due to the ad-hoc bin averaging procedure that is commonly employed for extracting the field information. In the
bin averaging method, the molecular domain is divided into spatial bins and averages of the MD variables are taken over each bin. These averages are construed as representative of the underlying field. Bin averaging however, leads to compromises in spatial resolution which are inherently unsatisfying. For example, if the bin sizes are too small, the fields will have a rough and jagged topology. Additional interpolation is generally necessary to smoothen out the non-physical distortions. On the other hand, if the bins are too big, local information gets smeared out.

Field representation is also significant challenge in smoothed particle hydrodynamics (SPH), and other simulation techniques that employ Lagrangian description of motion [123]. A critical aspect of the SPH technique involves an unbiased estimation of the particle density field. In the standard form of SPH, density estimation is based upon a convolution of discrete particle distribution with an arbitrarily defined kernel function. The field variable at any location is estimated by averaging the discrete data points over an arbitrarily chosen kernel. Smoothness is ensured by the continuity and differentiability of the kernel function. In SPH, the smooth field variables allow the calculation of higher order derivatives without requiring structured computational meshes. While the kernel method is expected to be superior to bin averaging, it is not optimal in that the size (support) and shape (functional form) of the kernel remain arbitrary to some extent.

In this part of the thesis, a systematic approach for constructing smooth and accurate fields from particle data using statistical inference techniques is presented. A parametric method based on maximum likelihood inference is previously formulated to generate velocity and temperature fields [121] in situations where the particles in the system may be assumed to follow a local Maxwellian distribution. This method, however, cannot be applied to macroscopic variables such as the density and stress fields for which the form of the underlying distributions is not known a priori. Here a non-parametric method in which the distribution is determined according to the principle of maximum entropy, with constraints in the form of moments that can be determined from the particle data is proposed. The maximum-entropy method identifies the distribution which is “maximally noncommittal with regard to missing information and that which agrees with what is known, but expresses maximum uncertainty with respect to all other matters” [124, 125]. To investigate the accuracy and smoothness of this estimator several
comparisons of the density fields obtained in this way is carried out with those estimated by kernel and bin averaging. Unlike the kernel method which is empirical in nature, ME estimator is based on a firm mathematical principle even though subjective concerns remain for an efficient practical implementation.

In comparing the maximum-entropy (ME) formulation with the kernel method, a known function with non-linear oscillations is reconstructed first. The former gives a smooth estimate which captures the sharp gradients while the latter, though also smooth, fails to resolve the larger gradients especially near the boundaries. Both methods are then applied to a molecular dynamics (MD) simulation of shear driven flow in an enclosure, a more complex problem than the commonly studied Coutte and Poiseuille flows. It is found that the ME density estimate is a significant improvement over the bin average. Density deficiency near the boundaries, a common drawback of the kernel estimates, is also conspicuously absent in the ME field.

The velocity fields given by the maximum-likelihood (ML) [121] and the kernel estimators are then examined next. Edge artifacts is however, seen only in the latter. Such artifacts, if not identified, can lead to erroneous interpretation of velocity slip at the boundaries. For generating closed streamlines, the generalized vorticity-streamfunction equation is solved instead of directly integrating the velocity field. This approach introduces additional smoothness and performs better than the direct integration scheme. Lastly, continuum simulations using incompressible and compressible Navier-Stokes equations are carried out for benchmarking. For low Reynolds numbers, the ML fields are remarkably similar to those from the continuum simulations, indicating the Newtonian character of the MD flow field.

The theoretical basis and numerical implementation of the statistical field estimators are described in Section 6.2 with particular emphasis on ME method. The method of kernel-based averages is also discussed for comparative studies. The model problem of shear or lid-driven flow in an enclosure is discussed in Section 6.3 along with the details of MD and continuum simulations. The field estimates are presented in Section 6.4 and concluding remarks on the field estimators are made in Section 6.5. In Section 6.6, coarse projection, which is a equation-free
multiscale integration scheme, is implemented with the field estimators. It is shown that a
smooth and accurate field representation is necessary for performing the coarse projection.

6.2 Statistical Field Estimation

6.2.1 Maximum Entropy Method

In statistical inference estimation, the field of interest is regarded as a probability distribution
function. For the particle density and stress fields, the distribution is not known beforehand. This
necessitates the use of a non-parametric method. In this thesis, the maximum entropy method
with constraints in the form of moments is employed. The univariate variational methodology of
M-Djafari [126] is adopted and extended to a multivariate formalism. The basic problem in ME
is to obtain a distribution which satisfies the imposed constraints while maximizing the
uncertainty regarding the missing information, which in turn is measured by the information
entropy. The desired distribution is written as

\[ \hat{\rho}(x) = \arg \max_{\rho} H[\rho] \quad (6.1) \]

Where \( H[\rho] \) is the information entropy functional and \( \rho(x) \) is the field of interest. For quantifying
the entropy the definition of Shannon [127] is employed which is given by

\[ H[\rho] = - \int \rho(x) \ln \rho(x) dx \quad (6.2) \]

The measure of information entropy is not unique; for example, other definitions such as Renyi’s
entropy [128] may be equally appropriate. The choice of (6.2) recognizes the role of
thermodynamic entropy in statistical mechanics.

The maximization in (6.1) is to be carried out subject to certain given constraints, which in the
present problem represent the information from the particle data produced by molecular
simulations. The constraints are in the form of expectation values or ‘generalized’ moments of the distribution,

\[
\int \varphi_m(x) \rho(x) dx = \mu_m \tag{6.3}
\]

where \( \varphi \) is a set of functions such as polynomials or complex exponentials, \( \mu \) represent the moments and \( m \) is a \( D \) dimensional vector with \( D \leq 3 \). Thus using polynomial functions \( \{x^m\} \) as the moment-generating functions (with \( D=1 \)) gives the familiar geometric moments associated with the distribution which is given by

\[
\int x^m \rho(x) dx = \mu_m \tag{6.4}
\]

Since the distribution is the quantity for which the estimator will provide, it may appear that the moments (6.3) are also unknown. However, if the particle positions \( X_n \) are known from a molecular simulation, one can write formally write the particle density field at any point as

\[
\rho(x) = \frac{1}{N} \sum_{n=1}^{N} \delta(x - X_n) \tag{6.5}
\]

where \( N \) is the total number of particles in the system. Inserting (6.5) into (6.3),

\[
\mu_m = \frac{1}{N} \sum_{n=1}^{N} \varphi_m(X_n) \tag{6.6}
\]

So the generalized moments of the density distribution can be expressed in terms of particle data. Similarly, the momentum distribution is

\[
p(x) = \rho(x)v(x) = \frac{1}{N} \sum_{n=1}^{N} m_n v(X_n) \delta(x - X_n) \tag{6.7}
\]
where \( v(x) \) is the velocity field, \( m \) is the mass of each particle and \( V(X) \) are the particle velocities. The corresponding moments of the momentum field then become

\[
\mu_m = \frac{1}{N} \sum_{n=1}^{N} m_n \varphi_m(X_n) \varphi_m(X_n)
\]  
(6.8)

For other distributions such as temperature and stresses similar results can be evaluated [39].

Returning to (6.2), since the entropy functional is known to be concave [128], a unique maximum therefore exists for (6.1). Maximizing the entropy is equivalent to maximizing the Lagrangian

\[
\mathcal{L} = H[\rho] + \sum_{m} \left[ \lambda_m \varphi_m(x) \rho(x) dx \right]
\]  
(6.9)

where \( \{\lambda_m\} \) denote the Lagrange multipliers. The above expression can be rewritten as

\[
\mathcal{L} = - \left[ \rho(x) \ln \rho(x) + \sum_{m} \lambda_m \varphi_m(x) \rho(x) \right] dx
\]  
(6.10)

The desired density distribution is obtained by a functional differentiation with respect to \( \rho(x) \) and equating to zero

\[
\frac{\delta \mathcal{L}}{\delta \rho(x)} = 0
\]  
(6.11)

from which one finds

\[
\rho(x) = \exp \left( - \sum_{m} \lambda_m \varphi_m(x) \right)
\]  
(6.12)
This is an exact expression for the distribution with the Lagrange multipliers \( \{ \lambda_m \} \) as yet undetermined. The latter are given by the set of non-linear equations formed by substituting (6.12) in (6.3)

\[
\int \varphi_m(x) \exp\left(-\sum \lambda_m \varphi_m(x)\right) dx = \mu_m
\] (6.13)

There are no closed form solutions for the Lagrange multipliers and hence, they are solved numerically by the Newton-Raphson method. First the left side of (6.13) is expanded, denoted as \( G_m(\lambda_m) \), in a Taylor series about trial values of the eigenvalue vector \( \lambda_m \), and neglect higher order derivatives to obtain a set of linear equations,

\[
G_m(\lambda_m) = G_m(\lambda^0_m) + (\lambda_m - \lambda^0_m) \nabla G_m(\lambda_m)
\] (6.14)

which are then solved iteratively for \( \lambda_m \) until the relative change in the entropy \( (H) \) becomes less than a pre-assigned tolerance value. This method is second order accurate.

The moment-generating functions \( \varphi_m(x) \) can be viewed as the basis sets for \( \ln \rho(x) \). Two basis sets, polynomials and complex exponentials, \( \{ x^m \} \) and \( \{ \exp(\mathrm{i}m \cdot x) \} \) are used in this thesis. Since the latter form an orthogonal basis set, they can be expected to have good numerical stability. For higher dimensional systems \( (D>1) \), one can construct products of univariate functions; for example, in two dimensions,

\[
\varphi_m(x) = \varphi_m(x) \varphi_m(y)
\] (6.15)

The density field estimator is tested using two kinds of data, the first is data sampled from a known distribution, while the second is produced in an MD simulation of shear-driven flow in a cavity, to be described in Section 6.4. In the first instance, a data set of 15,000 points is generated from the following distribution [129] by using the acceptance-rejection method [130]

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\[ \rho(x) = C \left[ 1.5 + \sin(3\pi x) + \sin \left( \frac{15}{2} \pi x \right) \right] \]  

(6.16)

where \( C \) is a normalization constant. Then the moments from the data points using (6.6) are calculated, and distribution is reconstructed.

Figure 6.1 shows two results of the estimation obtained using polynomial and complex exponential (Fourier) moments. One sees a good agreement between the ME estimate with Fourier moments and the original function, with only slight discrepancies around the turning points and near the boundaries. On the other hand, estimation using polynomial moments constraints is unable to resolve several of the sharp gradients. When more polynomial moments are used, the agreement is not improved (see Figure 6.2) and even more significantly, the algorithm fail to converge for higher moments. This is attributed to the fact that in the Newton procedure of solving (6.13), the polynomial moments lead to a Hilbert matrix known for having high condition numbers (defined as the ratio of largest to lowest eigenvalues). This ill-posedness stems from the non-orthogonality of the sequence \( \{x^n\} \). Because the different powers of \( x \) do not differ greatly from each other at higher moments, the lowest eigenvalues move towards the origin while the larger eigenvalues spread elsewhere [129]. This makes the condition number to increase exponentially with the number of moments, thereby limiting the use of higher moments in practice. Fourier moments do not have such difficulties; their orthogonality leads to well-posed Hermitian Toeplitz matrix with low condition numbers. In Figure 6.3 that estimation using higher Fourier moments are seen to be stable though it is susceptible to small high-frequency oscillations. In all the cases studied, the Fourier moments exhibit a high degree of numerical stability relative to the polynomial moments. It is also pointed out that a reasonably accurate reconstruction is possible even with a substantially fewer number of particles (of the order of 1,000).
Figure 6.1 ME density estimate with polynomial and Fourier moments.

Figure 6.2 Effect of higher polynomial moments.

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Since the kernel method is an alternative approach for density estimation, a direct comparison with the ME estimate is shown in Figure 6.4. The kernel method which is explained in greater detail in Appendix B uses an optimal window width. The kernel results which are obtained with 15,000 particles do not perform well near the boundaries. In particular, the boundary values are underestimated, which is attributed to the integral being truncated in the vicinity of the boundary. This density deficiency is a well-known problem associated with the kernel estimates [123].

The conclusions drawn in the one dimensional case studies are generally applicable to higher dimensions as well. With polynomial moments, the ME algorithm is much harder to converge in two dimensions while Fourier moments do not present this difficulty. Now a ME reconstruction in two dimensions is discussed. Figure 6.5 shows the true distribution which is given by

$$
\rho(x, y) = \frac{(\sin^2 x + \sin^2 3x)(\sin^2 y + \sin^2 3y)}{\pi^2} 
$$

(6.17)
The normalization constant $\pi^2$ ensures that the integral of the density function is unity. In comparison to the one-dimensional test pdf given by (6.16), the two-dimensional pdf has smaller gradients. Figure 6.6 shows the ME estimate with 500 particles and four moments in each direction. A good agreement is seen with the true distribution and also note that edge effects are minimal in the ME estimate. More realistic fields are estimated from MD simulations and are discussed in the results section. If the gradients are small, then a reasonably accurate reconstruction can be made with relatively few particles (of the order of 1,000) and moments ranging from 4 to 6.
Figure 6.5 True pdf in two-dimensions.

Figure 6.6 ME reconstruction in two-dimensions.
6.2.2 Maximum Likelihood (ML) Velocity and Temperature Field Estimator

The basic assumption in this parametric approach [121] is that the particles in the simulation follow a local Maxwellian distribution,

\[ dP = \frac{1}{[2\pi T(x)]^{D/2}} \exp \left( -\frac{|v - \bar{v}(x)|^2}{2T(x)} \right) dxdv \]  
(6.18)

where \( \bar{v} \) is the streaming velocity and \( D \) is the dimensionality of the system. The spatial basis for the field variables \( v \) and \( T \) is written down as

\[ v(x) = \sum_m a_m \phi_m(x) \]  
(6.19)

\[ T(x) = \sum_n b_n \theta_n(x) \]  
(6.20)

where \( \phi \) and \( \theta \) are typically low-order basis functions. The likelihood, \( P \), for the particles to have certain positions and velocities is given by:

\[ P(a_m, b_n) = \prod_{i=1}^{N} dP(x_i, v_i) \]  
(6.21)

The most probable field distribution for velocity and temperature in the parameter space \( \{a_m, b_n\} \) is computed by maximizing the logarithm of this likelihood function [121].

6.3 Model Problem

The effectiveness of the statistical field estimators is shown by considering the behavior of a two-dimensional shear or lid-driven flow in an enclosure as determined by molecular dynamics
simulation and by the continuum Navier-Stokes equations. The idea is to benchmark the distributions obtained from the field estimators against the continuum results.

In the present problem shown schematically in Figure 6.7, the top boundary moves at a constant horizontal velocity $V_{lid}$. For the continuum description, the velocity components at all other wall boundaries are set to zero (no-slip condition). For the MD simulation, the boundaries consist of a few layers of solid atoms; the top array, acting as a lid, is allowed to slide at a constant velocity.

![Figure 6.7 Shear flow in an enclosure.](image)

Driven flow in an enclosure exhibits a variety of complex hydrodynamic behavior such as eddies, secondary flows, instabilities and bifurcations [131]. The incompressible continuum description does not have a closed form solution though for creeping flows, a series solution to a bi-harmonic stream-function equation is possible. An infinite sequence of secondary vortices of diminishing size exists at the lower corners even for arbitrarily small Reynolds ($Re$) numbers [131]. At higher $Re$, the secondary vortices grow in size and strength; detailed prediction of flow patterns is possible only through numerical simulations.

Because of its rich features, driven flow in a cavity is a standard benchmark problem for testing continuum numerical schemes. It is also a problem where the boundaries are well-defined without ambiguity [131]. Unlike in Coutte and Poiseuille flows where relatively intricate inflow
and outflow boundary conditions are required for MD, flow in a driven enclosure poses no such difficulties. This type of flow therefore, is well suited for comparing MD and continuum results.

6.3.1 MD Simulation

MD simulations are performed with a two-body short-smooth potential (Appendix C). The shear viscosity is calculated using the Green-Kubo linear response theory as the time integral of the stress autocorrelation function which is obtained from MD simulations performed on a square domain with periodic boundary conditions. The expression for shear (dynamic) viscosity is [49]

\[ \mu = \frac{1}{V k_B T} \left[ \int_0^\infty \langle \sigma_{xy}(t) \sigma_{xy}(0) \rangle \ dt \right] \]

(6.22)

where \( \sigma_{xy} \) represents the shear stress tensor, \( T \) is the temperature and \( V \) is the volume (area) of the simulation cell. The angular brackets denote a time average over a sufficiently large number of independent samples. For a two-body potential, the shear stress tensor, just like in continuum Newtonian flow, is symmetric.

Equilibrium simulations for determining the viscosity are conducted with approximately 3000 atoms in a square domain measuring 70 by 70 (reduced) units, with runs typically of 9 million time steps with a step size of 0.001. The integral in (6.22) is evaluated using fast Fourier transform as explained in [48]. For the same density and temperature, the calculated viscosity is seen to be insensitive to the system size.

To perform the non-equilibrium simulations with shear flow, fluid atoms are confined in a square enclosure bounded by a few layers of solid atoms on each side which constitutes the physical boundary of the simulation cell. A liquid or gaseous state is created by randomly removing a fraction of the fluid atoms from the computational domain and allowing the system to equilibrate. The MD simulation cell viewed with AtomEye [132] is shown in Figure 6.8.
Shearing of the system is simulated by dragging the top layer at a constant velocity. Due to the external work done on the system the internal energy of the fluid atoms increases with time. A first order thermostat is used to keep the system at constant bulk temperature. All the simulations are performed under the conditions where the local flow velocities are smaller than the thermal velocities, so the system temperature is dominated by the latter. The use of a thermostat is appropriate because the hydrodynamic behavior, which is of primary interest in this thesis, is not sensitive to the method of heat removal even for reasonably large shear rates. Additionally, the long wavelength modes are largely seen to be independent of the details of the interatomic potential used in the simulation.

To integrate the equations of motion Gear’s fifth order predictor-corrector scheme is used [48]. O(N) efficiency is achieved by using a cell-list method, the details of which are given in [121]. The interactions at the boundary are treated through direct fluid-wall interactions. Simulations are carried out for two cells, measuring 200×200 and 100×100 (reduced) units respectively. At \((\rho, T) = (0.48,1)\), the larger system consists of 19,257 fluid atoms and four layers of solid atoms with a total of 23,105 atoms. For the same thermodynamic state, the smaller system comprises of 4814 fluid atoms and 1952 wall atoms. Due to the slow convergence of the long wavelength

Figure 6.8 The simulation cell.
fluctuations, simulation runs are typically executed for 20 to 30 million time steps. Further details are given when the results are discussed in Section 6.4. Also note that Koplik and Banavar [122] have reported a similar MD study focused on the slip behavior near the moving solid boundary.

6.3.2 Continuum Simulation

The fields generated by the estimators are expected to reflect the slow and long wavelength modes of the atomic motion in the MD simulation [45]. A direct way to check the fidelity of the estimation is to compare the fields obtained with the results given by the Navier-Stokes (NS) equations [133]

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \tag{6.23}
\]

\[
\frac{\partial (\rho \mathbf{v})}{\partial t} + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = \nabla \cdot \mathbf{T} + \rho \mathbf{f} \tag{6.24}
\]

\[
\frac{\partial (\rho e)}{\partial t} + \nabla \cdot (\rho e \mathbf{v}) = \nabla \cdot (\mathbf{T} \cdot \mathbf{v} - \mathbf{q}) + \rho \mathbf{f} \cdot \mathbf{v} \tag{6.25}
\]

where \( \mathbf{T} \) is the stress tensor, \( \mathbf{f} \) is the external force and \( \mathbf{q} \) is the heat flux vector. The above equations are closed by invoking Newtonian relations concerning stress and strain rate, Fourier law of heat conduction, Stokes hypothesis connecting the viscosity coefficients and the appropriate equations of state.

Since the NS equations for the driven cavity do not have a closed solution numerical simulations are necessary. A number of solvers have been developed in the past to simulate the flow features of the driven cavity, almost all based on the assumption of incompressible flow. A numerical algorithm involving vorticity and stream function as described by Pozrikidis [134] is employed to simulate the incompressible flow fields. Further details are given in Appendix D.

Molecular dynamics simulations, in general, correspond to neither incompressible flow nor Newtonian behavior, especially at shear speeds comparable to the thermal velocity. To evaluate
the effects of compressibility on the flow field, the flow of a compressible fluid is simulated using Fluent® [135] which discretizes Equations (6.23) through (6.25) into finite volumes and solves the resultant equations with an algebraic multigrid solver. Also note that there are no published results on compressible flow in a driven confined cavity.

To link the MD and continuum simulations one considers two measures, the Reynolds number \((Re)\), the ratio of inertial to viscous force,

\[
Re = \frac{\rho V_{lid} L}{\mu}
\]  

(6.26)

where \(\rho\) is the mass density \(\mu\) is the dynamic viscosity and \(L\) is the linear dimension of the square cavity, and the Mach number based on lid velocity,

\[
M = \frac{V_{lid}}{c}
\]  

(6.27)

where \(c\) is the sound speed sound measured with the properties along the lid. For incompressible continuum simulations, only the Reynolds number appears in the problem. For the MD simulations, incompressibility is verified by evaluating the spatial variations of the density and Mach number fields.

The continuum field equations also tacitly assume that the ratio of mean free path of the molecules to the characteristic length (Knudsen number) is small \((<<1)\) and the shear velocities are much smaller than the thermal velocities of the atoms so that local thermal equilibrium is always maintained at all times. In the MD simulations, the fluid density and system size are such that the Knudsen number is less than 0.01, which constitutes a reasonable condition for the continuum approximation. The shear rates however, are of the order of 0.1, much higher than what is realizable in the macroscopic conditions. So in addition to Reynolds and Mach numbers, the ratio of lid velocity to the mean thermal velocity \((V_{lid}/V_{th})\) needs to be considered in interpreting the comparisons.
6.4 Results

6.4.1 Density Field Estimation

The density fields obtained from the particle data of two MD simulations at the same thermodynamic state are compared first. For the larger simulation cell with a lid velocity of 0.1 (reduced units), the Reynolds number is 30, the Mach number is 0.077 and the ratio of lid velocity to thermal speed ($V_{lid}/V_{th}$) is 0.07. For the smaller system with a higher lid speed of 0.68, the corresponding numbers are 100, 0.523, and 0.48 respectively. In the first case, the evolution of the mean field will be largely independent of the molecular motions, whereas in the second case there can be appreciable dynamical coupling.

Figure 6.9 shows the scatter plot of the atoms for the larger system (19,257 fluid atoms). The particles are more or less evenly spread across the domain although upon closer scrutiny one can discern a slight under-population in the upper right region and a slight over-population in the center and lower region. A near uniform density is anticipated because the thermal speed (1.4) is more than an order higher than the lid velocity (0.1) and the Mach number is small.

Figure 6.10 depicts the density field distribution estimated using the maximum entropy method with 4 Fourier moments while the average based on 169 bins is shown in Figure 6.11. The field representation with ME captures the essential characteristics of the underlying distribution. While the bulk of the domain is clearly close to uniform (within 15%), the non-uniform regions are also quite evident. The essential characteristics are consistent with the scatter plot in revealing a lower density at the upper right corner and a higher density near the central and lower regions. The number of moments controls the smoothing effect in the present method; using more moments tends to resolve the sharper gradients better.
There is no way to determine the optimal number of moments \textit{a priori}. Since all non parametric estimations involve at least one or two parameters, the best estimate is often a matter of intuition based on what one knows about the distribution being estimated [136]. In this thesis, the scatter plots, being a reflection of the molecular data with no analysis, serve as a guide in assessing the fidelity of the estimator. The bin average, as expected, shows a very jagged topology with large and uneven gradients that can lead to numerical artifacts in multiscale simulations. Note that a single snapshot is used to compare the fields. It is fair to say that a reasonable bin average needs an average over several hundred such snapshots to smooth out the sharper gradients. A dramatic improvement in the smoothness was not observed for such a time averaged bin field. This aspect is brought in more detail in the discussion for the next density field where the gradients are more discernible.
Next, the kernel estimate is shown in Figure 6.12. A markedly lower density region is seen along the borders and near the leading edge (top right corner) which is not seen in the scatter plot. This deficiency occurs because the kernel for the particles gets truncated at the system boundary which results in a one-sided contribution to the total density estimate. On the other hand, the ME distribution does not suffer from this edge artifact. The edge deficiency is known to affect the accuracy of SPH simulations which has led to the introduction of virtual particles at the boundaries for remediation.
Figure 6.11 Bin average, single snapshot, 200×200 domain, lid velocity = 0.1.

Now the smaller system with a higher lid speed of 0.68 is considered corresponding to a Reynolds number of 100 and a Mach number of 0.53. The ratio of lid velocity to the thermal velocity is 0.48. The density fields estimated by ME (with 5 moments) and kernel averaging are shown in Figures 6.13 and 6.14 respectively. The corresponding scatter plot is given in Figure 6.15.

The lid velocity, now a significant fraction of the thermal velocity, produces a region of high stress near the leading edge (upper right corner). The flow in the cavity is characterized predominantly by a single large vortex moving in the clockwise direction (discussed later). Due to the greater asymmetry of the stress field in the vicinity of the leading corner, the particles migrate towards the regions of lower stress, thereby causing a higher density at the lower left region. This aggregation represents shear localization that is induced by the confining walls.
Figure 6.12 Gaussian kernel density field, single snapshot, 200×200 domain, lid velocity = 0.1.

From a series of simulations at different densities and temperatures it is seen that this effect of density pileup is roughly proportional to $V_{\text{lid}}/V_{\text{th}}$ and not correlated with the Reynolds number. This also indicates a breakdown of dynamic similarity (where the non-dimensional solutions are identical) when the ratio, $V_{\text{lid}}/V_{\text{th}}$ is $O(1)$. Even with this discernible density gradient, as it discussed later, the velocity distributions appear to be remarkably similar to those from the continuum simulations.
Figure 6.13  ME density field, single snapshot, 5 moments, 100×100 domain, lid velocity = 0.68.

Figure 6.14  Gaussian kernel density field, single snapshot, 100×100 domain, lid velocity = 0.68.
Both ME and kernel methods give the highest density in the lower left region and lowest density in the upper right corner. Notice that as in the large system results, the kernel-estimated field, falls off near the boundaries, while the ME field does not have this difficulty. In the interior, the two estimated fields appear to be quite similar.

Figure 6.16 shows a bin average of the same simulation data with 289 bins based on a single snapshot. In Figure 6.17, the bin density field averaged over 1,000 snapshots over a period of 20,000 time steps. The density field over this period does not change appreciably and the time averaged ME and kernel fields are similar to those depicted in Figures 6.13 and 6.14. While a noticeable improvement in the time averaged bin field is seen, the jaggedness in the topology still persists and the sharp gradients do not altogether disappear simply by extending the duration of time averaging. Theoretically, a smooth bin average is only possible when there are a large number of particles in addition to a sufficiently large number of time-averages. From a multi-scale simulation point of view, this gives a significant advantage to the ME method because for a similar degree of smoothness, bin averaging requires a larger number of particles in addition to a larger number of time averages. Alternatively, interpolation can be used to smooth out the...
jaggedness in the bin field but will require additional and non-trivial effort. ME method is naturally extendable to higher dimensions and as shown in this study, it generates smooth and reasonably accurate fields with limited number of particles and time averages. The time averages for ME method are dictated only by the period that is necessary to arrive at the correct physics. Generally, this period amounts to a few thousand iterations in a molecular dynamics simulations where the higher moments of the distribution 'heals' and becomes functionals of the lower moments that correspond to the macroscopic field variables [62]. No additional averages are required for smoothing purposes in the ME method. The effect of time averages on the density profile at \( x = 0.5 \) with the three methods is shown in Figure 6.18. The bin and kernel fields are averaged over 1000 sets over a period of 20,000 times. The ME estimate which is averaged over just 100 sets in the same time period is smooth and shows the same trend as that is seen in the kernel and the bin averages.

![Figure 6.16 Bin average, single snapshot, 100×100 domain, lid velocity = 0.68.](image)
Figure 6.17 Bin field averaged over 1000 snapshots, 100×100 domain, lid velocity = 0.68.

Figure 6.18 Density profile at x=0.5.
It is worthwhile to note that local features are not always well defined by the ME estimator. The generated distribution displays a somewhat exaggerated undulation, though of small magnitude, which is not evident in the scatter plot. These oscillations are due to the dominance of the lower moments of the distribution. Theoretically, if the first two polynomial moments are employed, then the resulting ME distribution is an exponential function [128]. If three moments are prescribed, then the ME distribution will be a Gaussian. To first order, this is true for Fourier moments too. When a small set of moments are employed, such as four or five (as in the present simulations), the resulting distribution retains some of the Gaussian characteristics. As the number of moments increases, the Gaussian smoothing becomes less prominent. It is also important to note that these undulations are small in magnitude and smooth, as evident in Figure 6.18. Since ME is able to capture the key features of the distribution quite well, the minor waviness will not be a hindrance in multiscale simulations where both accuracy and smoothness are prerequisites.

The present formulation of ME method uses a set of integrated moment constraints and does not employ any local particle information per se. The kernel estimate, on the other hand, accounts for local particle information and is able to resolve the local features better. Later on, a possible improvement to the present formulation to capture the local information is discussed. The numerical cost of the current ME method is $O(N^2)$ but with a FFT implementation, the cost can be brought down to $O(N \log N)$. The convergence of Newton-Raphson scheme is fairly rapid, typically takes less than 50 iterations for the relative error in entropy to decrease by six orders.

### 6.4.2 Velocity and Streamline Fields

The effectiveness of ML field estimators is now demonstrated by comparing the streamlines and the velocity fields with the continuum results. The conventional approach for calculating the streamlines from the velocity and density fields involves a direct integration of the mass flux [49]

$$\Omega(x,y) = \int \rho(x,y)(v_x \, dl_x + v_y \, dl_y)$$  \hspace{3cm} (6.28)
The integral is typically performed by assigning an arbitrary value to the stream function at a grid point and then performing the line integral to evaluate the value at a different grid point. An alternate approach is used here to increase the smoothness by first transforming the mass flux into a generalized vorticity field and then solving the vorticity-streamfunction Poisson equation. This method gives very smooth streamlines and is a definite improvement over (6.28). The details of the formulation are given in Appendix E. The continuum results are obtained directly from the incompressible streamfunction as described in Appendix D.

The generalized streamlines obtained from the MD results are now compared with those from the continuum calculations, in Figures 6.19 and 6.20 respectively. The difference between two adjacent stream-functions, by definition, is a measure of the mass flow rate between them. No fluid can cross the streamlines because the velocity vector is tangent to the surface. In a confined enclosure, all streamlines therefore should close onto themselves to maintain mass conservation. The MD streamlines show this behavior very clearly, which may be taken as a test of the efficacy of the vorticity-stream-function formulation. Direct integration which is cumbersome may lead to artifacts as observed in [122]. Overall, the streamlines generated by the MD data, in spite of having a discernible density gradient, match well with those obtained from the continuum description. This is reasonable when the local flow velocities are smaller than the thermal velocities and the simulation conditions clearly indicate that of the hydrodynamic limit. In both results, the eye of the vortex is shifted towards the right, in the direction of the lid velocity, at about the same horizontal position. From the extent of the streamlines it is seen the flow region covers most of the computational domain in the MD simulation, while in the continuum calculation, very weak anticlockwise eddies appear near the lower corners. In the MD simulation the strength (numerical value of the streamfunction) of the secondary vortices is much larger because of explicit fluid-wall interactions.
Figure 6.19  Generalized streamlines with MD simulation, lid velocity = 0.68, Re=100.

Figure 6.20  Streamlines from incompressible Navier-Stokes equation, Re=100.
Figure 6.21 depicts the horizontal velocity field given by the ML estimator. The fields generated with the continuum simulation and the kernel estimators are given in Figures 6.22 and 6.23 respectively. The ML field is remarkably similar to the continuum. Adjacent to the lid, the former shows a flow velocity nearly the same as that of the lid, except near the corners where it tapers off to zero. This indicates that the commonly invoked no-slip boundary condition is valid for the central regions but not near the corners, an observation which also has been noted by Koplik [122]. At higher lid speeds, substantial slip is seen between the moving boundary and the nearby fluid (results not presented). With the kernel average, while the general flow features are reasonable, the velocity gradients near the lid are more diffuse. In addition, a velocity slip behavior is seen near the upper corners which is not observed in the ML estimate.
Figure 6.22  Horizontal velocity with NS simulation, lid velocity = 0.68, Re=100.

Figure 23  Horizontal velocity with kernel estimator, lid velocity = 0.68, Re=100.
In Figure 6.24 the horizontal component of the velocity along the vertical mid-plane obtained from the MD data and continuum calculations are compared. In Figure 6.25 the vertical velocity at the horizontal mid-plane are plotted. Note that the ML velocity profiles are derived through the estimator without any additional smoothening. The ML estimations are in overall agreement with the continuum description. The kernel estimates compare favorably with the ML estimate in the interiors. As before, the kernel estimation suffers from numerical artifacts at the boundaries, the effect which is clearly seen in Figure 6.25 in the non-zero values at the right and left boundaries. Velocity slip at the boundaries in this case is clearly numerical in origin; it should not be taken as an indication of slip phenomena at the molecular scales. ML estimate does not suffer from such edge artifacts. This is regarded as a key strength of the statistical field estimators.

Figure 6.24 Comparison of horizontal velocity at the vertical mid-plane, Re=100.
Figure 6.25  Comparison of vertical velocity at the horizontal mid-plane, Re=100.

Figure 6.26  Comparison of time averaged ME and bin field estimates,

lid velocity = 0.68, Re=100.
Figure 6.26 shows the vertical velocity profile at the horizontal mid-section for ML and bin estimate after 150,000 $MD$ time steps. Evidently, ML takes a fewer number of iterations to produce a reasonably accurate solution that is also smooth.

A lid speed of 0.68 is a significant fraction of the acoustic speed, taken as $\sqrt{\frac{J}{T}}$ by assuming the fluid behaves like a monatomic ideal gas. At a temperature of 1.0, the acoustic speed is approximately 1.3. Therefore, the highest Mach number in the system is roughly 0.53. Generally, if the Mach number is greater than 0.2, the flow is considered to be compressible. To evaluate whether the compressibility has any appreciable effect on the continuum field variables, the flow of a compressible fluid in an enclosure is investigated using the CFD software Fluent® [135]. Simulations are performed with a fine 150 by 150 grid with all the boundary walls kept at a constant temperature of 300K. The reference pressure is set at the moving lid and the properties of air are assumed for the medium. Using an implicit coupled algorithm, the mass, momentum and energy equations (Equations 6.24 through 6.26) are solved simultaneously and accelerated with algebraic multigrids.

The results, shown in Figure 6.27, indicate that the bulk of the flow remains incompressible, with the compressible regime limited to a thin region along the lid. The velocity fields are only marginally affected by the effect of compressibility (results not shown). The local Mach number profiles with $MD$ as seen in Figure 6.28 are somewhat similar to those from the continuum with the high Mach number regions confined near the lid. The relative closeness of the $MD$ Mach number and the velocity contours with the continuum results indicates that dynamic similarity is partially satisfied at the molecular scales for the shear rates considered in this thesis.
Figure 6.27  Local mach numbers with NS simulation (Fluent), Re=100.

Figure 6.28  Local mach numbers with MD simulation, lid velocity = 0.68, Re=100.
6.5 Discussion on Field Estimators

Bin averaging is the work horse for most MD simulations where the continuum fields are to be constructed from discrete particle data. Poor resolution and statistical noise make the bin method an unsatisfactory choice for performing complex multiscale simulations where smoothness, in addition to accuracy, is a necessity over a relatively short period of time. To avoid the limitations of bin averaging, a set of statistical field estimators is presented which generate smooth and accurate fields. For spatial density distributions, a non-parametric estimator based on the maximum-entropy (ME) principle is proposed. The ME estimator identifies the least biased distribution that is consistent with the prescribed set of constraints which are in form of moments of the distribution. It is shown that the moments can be calculated from the particle data without further assumptions. The results from an MD simulation of a shear driven flow in an enclosure, show that the ME estimation is superior to the bin average. The ME estimate is also compared with the kernel method. Near the boundaries, the kernel method systematically underestimates the density while ME method does not exhibit this artifact.

The streamline and velocity fields generated from maximum likelihood technique (ML) which again are appreciably smoother than the bin average. The velocity averages with the kernel average are also contrasted with those from ML. While the interior flow field is satisfactorily resolved, the edge artifacts near the boundaries pose a difficulty for the kernel average. Velocity slip at the boundaries in kernel method is clearly numerical in origin and it should not be construed as an indication of slip phenomena at the molecular scales. The fact that both ML and ME estimations do not have such difficulties, is shown as a significant strength of statistical field estimators. A method of calculating streamlines by solving the generalized vorticity-streamfunction Poisson equation. This approach not only gives closed streamlines but also adds an extra derivative which imparts additional smoothness.

An interesting form of shear localization is uncovered which is induced by the confining boundaries of the system. From a series of simulations at different densities and temperatures, it is seen that this effect of density pileup is roughly proportional to $V_{1d}/V_{th}$ and not correlated with the Reynolds number. Even with a discernible density gradient in the flow field, the velocity
distributions appear to be remarkably similar to those from the continuum simulations. Dynamic similarity, however, breaks down when the ratio of $V_{\text{lid}}$ to $V_{\text{th}}$ is $O(1)$.

The proposed ME density estimator employs a set of integrated moment constraints. This may be classified as a 'global' approach in contrast to the kernel method which makes direct use of local information. For field representation where there are few data points, it is advantageous to include local particle information directly in the ME estimator. One way to do this is to break down the domain into regions such that each region contains one particle. Then the ME principle can be applied to each region and a piecewise-continuous estimate can be made [128]. Additional smoothness can be imparted by employing higher order moments in the local spacing. This approach is feasible for one-dimension but in two and three dimensions proper spacing is not easily derivable because of lack of order statistics in higher dimensions. Voronoi and Delaunay tessellations [137] provide a reasonable procedure for characterizing the local spacing around a particle. Then the density distribution can be constructed by applying the principle of maximum entropy to each tessellation. This way ME method can access the local information while at the same time provide adequate smoothness.

### 6.6 Coarse Projection

Figure 6.29 Coarse Projective Integration.
Coarse projective integration is a multiscale integration method and it falls into a bigger family of multiscale simulation techniques called the equation-free multiscale methods [50-54, 57-73, 75-77]. Coarse projective integration is a scheme developed to perform computations in microscopic space domains (small space) but for time scales that are relevant to the continuum (long time) [50]. An initial condition, a velocity field for example, is first prescribed in the coarse space that typically has molecular dimensions. The coarse field is lifted to a consistent distribution in the microscopic space. As an example, the particle velocities can be drawn from a Maxwellian distribution with the statistics confirming to the local continuum velocities and temperature. For better statistics, the lifting can be performed to an ensemble of microscopic realizations. The microscopic simulator is then allowed to mature the distribution long enough for the higher moments (of the distribution) to damp-out or heal. This may take several hundred microscopic time-steps. When the microscopic dynamics is evolving, the assumption is that there exists a finite dimensional inertial manifold, which is parameterized by the selected macroscopic statistics, which attracts all the solutions at a exponential rate [62]. This is equivalent to stating that the higher moments of the distribution quickly become functionals of the lower moments which correspond to the macroscopic field variables. Several maturing steps are performed and then the solutions are restricted to the coarse space. Successive coarse profiles are then used to compute the time derivatives of the unknown macroscopic evolution equation. Using the time derivatives the coarse variables can be projected over a long time step, much larger than the time-step typically used in the microscopic simulator. The projection, which can be performed through a simple Forward Euler, is assumed to take place on the slow inertial manifold. After projection, the lift-evolve-restrict sequence is continued till macroscopic convergence is obtained. This sequence is illustrated in the Fig. 6.29.

The separation of scales [62] is at the heart of the coarse projective integration. The basic premise of this methodology is that the microscopic initial states can be constructed with a few lower order moments of the microscopic distribution function. These moments are typically the density and momentum of the macroscopic field. In the case of colloidal fluids, Navier-Stokes equation can be constructed from the first two moments (the density and momentum) of the distribution of molecules in the phase space. Higher moments exist at molecular time scales but
they quickly become functionals of the lower order moments in such a way that the macroscopic
dynamics on the slow manifold are virtually transparent to the higher order moments.

6.6.1 Projective Integration for Partial Differential Equations (PDEs)

The coarse projective integration is motivated from a class for projective integration schemes for
stiff partial differential equations (PDEs) [55, 56]. These are explicit numerical methods which
are applicable to problems where there is a large gap between the time constants of the fast
components and those of the slow components. The fast time constants correspond to
eigenvalues with large (real) negative values while the slow time constants correspond to smaller
negative values. The fast components decay rapidly while the long-time solution is determined
by the slow components. Diffusion dominated problems belong to this classification.

In stiff equations, a single-step numerical integrator is constrained to follow the variation of the
shorter timescales to maintain numerical stability. However, it is possible to take advantage of
the spectral gap between the eigenvalues and construct a two-level integration scheme. An inner
integrator which uses a standard explicit integration scheme is employed for a small number of
steps to damp-out the fast eigen modes. Then an outer polynomial projection step is performed
with a time step that is commensurate with the slow time constants. Since the inner integrator
damps the fast modes the two-level scheme avoids a direct representation of the dominant
subspace. Thus, the outer integrator is numerically stable even with a time step which is several
times larger than dictated by a linear stability analysis [138]. It can be shown that the stability
limits for the outer integrator is governed by the slow components [55].

The projective integration is demonstrated for two prototype one-dimensional linear equations.
The first one is a hyperbolic (wave) equation given by

$$\frac{\partial u}{\partial t} + a \frac{\partial u}{\partial x} = 0$$

(6.29)

while the second one is a parabolic (diffusive) equation which is given by
The eigenvalues of the hyperbolic equation are purely imaginary and equal spaced while those of the parabolic equation are real, negative and unequally spaced. The decaying fast modes in the parabolic equation signify a dissipative behavior while the imaginary eigenvalues in the hyperbolic equation indicate a non-decaying or traversing solution. Therefore, the projective integration is expected to work only for the parabolic equation. This will be tested numerically in the examples below.

Figure 6.30 shows projective integration for the parabolic equation at two different time levels. A central difference scheme is employed with a Fourier Number of 0.4. The integration scheme is forward Euler. For the projective integration, $m$ time steps of inner iterations are followed by projection over a time period corresponding to $M$ time steps. In the specific example of $m=5$ and $M=20$, the solutions match quite closely for both time levels. For the hyperbolic equation (see Fig. 6.31), even with $m=25$ and $M=3$, the solution is significantly different from the true solution. This shows that projective integration works only for problems that are fairly dissipative.

Figure 6.30 Projective integration for parabolic equation. 5 inner steps ($m$) and 20 outer steps ($M$) are used. A central differencing scheme is used for spatial discretization.
Figure 6.31  Projective integration for hyperbolic equation. 25 inner steps \((m)\) and 3 outer steps \((M)\) are used. The wave front moves to the right and wraps around due to the periodic boundary condition. A first order upwind differencing scheme is used [138].

Figure 6.32  Relative error between iterations for projective integration (Integration time, \(T=4.2\)) and constant-step integration \((T=1.5)\) for two-dimensional Navier-Stokes equation at \(Re=100\). 5 inner steps \((m)\) and 10 outer steps \((M)\) are used.
Now projective integration is performed for the two-dimensional Navier-Stokes equation using vorticity transport and stream function approach. Projection is only employed only for the vorticity transport equation which has both hyperbolic and elliptic (dissipative) components. For low \( Re \), it is expected that diffusive behavior dominates. Figure 6.32 shows the temporal behavior of the relative error between iteration in vorticity measured through \( L_2 \) Norm [138]. Every time a projection is made, the relative error shoots up but quickly falls back and maintains a level close to that from constant-step integration. However, projective integration reached a larger time (T=4.2) compared to constant-step integration (T=1.5) with comparable or even slightly better convergence rate. On an iteration basis, this gives a speed-up of approximately 3. A higher speed-up is possible however, at the cost of accuracy.

### 6.6.2 Restriction and Lifting Operators

In the coarse projective scheme, the restriction operator \( (\hat{R}) \) transfers the molecular data to field description while the lifting operator \( (\hat{L}) \) transfers the field data to molecular data. Since the gradients are evaluated from the field data, it is evident that a smooth field representation is required. In this thesis, the fields from the kernel and statistical estimators are employed for the restriction operator. For the lifting operator, a simple injection is employed wherein the nodal continuum field information is ascribed to corresponding region of atoms (reverse binning). This procedure is not critical because the fast molecular momentum relaxation during the maturing stage quickly smears any errors that are introduced in the injection process.

It is important to check whether \( \hat{R}\hat{L} \rightarrow \hat{l} \) [59]. The restriction and lifting operators are tested with the shear driven flow in an enclosure as previously described. Figure 6.33 shows the horizontal velocity profile at the vertical mid-plane with a restriction \( \hat{R}_1 \) followed by a lifting \( \hat{L}_1 \) and a restriction \( \hat{R}_2 \). The first restriction \( \hat{R}_1 \) determines the MD coarse flow field at a particular time step, denoted by \( u_t \). The lifting \( \hat{L}_1 \) is performed immediately following the first restriction. The resultant microscopic data is denoted by \( U \). The MD simulation is allowed to run for a short period (40 time steps) before the second restriction \( \hat{R}_2 \) is performed giving a coarse
field $u_2$. Ideally the action of $\hat{\mathcal{L}}_1(u_1)\hat{\mathcal{R}}_2(U)$ (which gives $u_2$) should deviate only marginally from $u_1$. Figures 6.33 and 6.34 show that the differences between the fields $u_2$ and $u_1$ are indiscernible.

Fig. 6.33 Restriction and lifting operators, horizontal velocity at vertical mid-section.

Fig. 6.34 Restriction and lifting operators, vertical velocity at horizontal mid-section.
6.6.3 **Coarse Projection**

The coarse projection as described in Section 6.6.1 is implemented with the restrictor and lifting operators. The coarse fields are determined by the kernel method and the lifting is implemented by injection. First a long maturing period of 200,000 iterations is initiated over which the initial transients are damped out and a steady state behavior which is geometrically similar to that of the final state is developed. A coarse Euler integration is then performed at a frequency of 10000 iterations with a maturing period of 5000 iterations. Figure 6.35 shows the vertical velocity at the horizontal mid-section for various scenarios.

![Vertical Velocity vs Width of the Cavity](image)

**Fig. 6.35** Comparison of coarse projection with smooth fields and bin averages.
The circles show the steady state continuum solution from the incompressible NS equations. The broken line shows that the MD field at 500,000 iterations are close to the continuum solution. This will be taken as the true solution for projective integration. Even though the MD flow profile has not fully converged at 200,000 iterations, it is geometrically similar to that of the steady profile. This geometrical similarity turns out to be important for the projective integration. The solid line shows the flow profile with projective integration with kernel field estimators for the velocity components only. The dotted line corresponds to projective integration on velocity with bin averaging. The kernel averaging, as shown in Section 6.4.2 gives smooth and reasonably accurate solutions at the interior while bin averaging gives a jagged topology. The flow profile at the end of kernel projection (shown in Figure 6.35) is generated with the statistical field estimator with maximum likelihood technique (ML). The kernel averaging is faster than ML with the present algorithms and hence, preferred for coarse projective integration. Both ML and kernel techniques have comparable smoothness even though the former is seen to be more accurate near the boundaries.

It is clear from Fig. 6.35 that the coarse projection with the smooth kernel estimator in 250,000 iterations is able to converge reasonably well to the MD solution at 500,000 iterations. This gives a speed-up of 2 on an iteration basis. The projection with the bin averaging is very noisy and does not appear to converge to the steady state solution. The smoothness in the flow profiles, therefore, is a necessity for performing projective integration on the coarse variables. It is possible to average the bin variables for a longer time before conducting the projection. However, a longer averaging time makes the projection inefficient and may even take a longer time than the actual MD simulation. It is concluded that for any reasonable projection integration, smooth and accurate field estimation is a mandatory requirement.

For a successful implementation of the coarse projection, the baseline flow profiles have to be geometrically similar to those of the final steady state. In the present simulation, the atoms are given an initial random velocity. Approximately, 200,000 iterations are needed to generate a flow profile which has the geometrical characteristics of the steady state solution. If projective integration is performed to a flow profile which does not have the geometric similarity, the
solution quickly diverges (results not shown). It is therefore, essential that the base line flow profiles should be geometrically similar to that of the steady state solution.

The lifting operator does not play a critical role in the projective integration as long as the atoms receive the information on the average velocity to a reasonable accuracy. For this purpose, direct injection or reverse binning is found to be adequate. For the problem considered in this thesis, the fast momentum relaxation smears the errors introduced by the lifting operator in the maturing stage. If the momentum relaxation is not fast, then more serious errors can occur from the simple injection technique. In this case, however, the coarse projection itself may be in question because it firmly rests on the separation of time scales and low-dimensional long-term dynamics.
Thermal transport in colloids is a relatively new focus area for a mature field. The primary objective of this thesis is to examine the fundamental mechanism of thermal conduction in dilute nano-colloids. The linear response formalism, elucidated in Chapter 2, is first applied to a model system of sub-nanometer platinum (Pt) clusters finely dispersed in liquid xenon (Xe). Since this is the first reported systematic investigation on the thermal transport in nano-colloids, the choice of the materials reflects the need for economic but insightful analyses. The thermal conductivity is calculated as a time correlation of the heat flux autocorrelation function. The microscopic heat flux vector is decomposed into three fluctuation modes namely, the kinetic flux (K), potential flux (P) and the virial or collisional flux (C). Using the three modes, the thermal conductivity is decomposed into nine components, three self-correlations (KK, PP and CC) and six cross-correlations (CP, CK etc). Each component is also a sum over atom species, Xe-Xe, Xe-Pt, and Pt-Pt. In this manner, the interplay between the molecular mechanisms that govern the thermal conductivity is examined.

An unusually high thermal conductivity is observed in the model Xe-Pt nano-colloid system. The significant enhancement arises from the self correlation in the potential energy flux (PP) which represents an exchange of potential energy among the nano-clusters and the fluid atoms that are in close proximity to the clusters. The strong cluster-fluid interaction which creates a dynamic interface around the nanoclusters facilitates this exchange of potential energy. The KK correlation is practically zero which indicates that thermal motion of the cluster (and fluid) atoms has a negligible effect on the thermal conductivity. This result is at variance with the recently proposed hydrodynamic theories where it is postulated that the Brownian motion is instrumental in enhancing the thermal conduction. The CC correlation involves the virial interaction or work done by the stress tensor. This term contributes most to the thermal conductivity which is typical of liquid and solid states but increases only slightly with volume fraction indicating that the presence of stronger attractive interactions for both Xe-Pt and Pt-Pt have not resulted in an enhanced collisional or phonon-like modes. At higher particle loading, the enhancement
saturates because of negative contributions due to cross correlations between $P$ and $C$ modes. Physically, the $PC$ correlation signifies the resistance to the transfer of potential energy due to the strengthening of vibrational modes in the cluster atoms. It is interesting to note that the saturation in the enhancement can occur even with well-dispersed particles.

A generic colloid with clusters made of non-linear springs is investigated next to evaluate the importance of fluid-solid cross interactions. The attractive potential well ($\varepsilon_{SF}/c$) is taken as a measure of the cross-interaction and is systematically varied to study its effect on the various components of the thermal conductivity. It is demonstrated that a relatively high cross-interaction ($\varepsilon_{SF}/c \geq 4$) between the fluid and solid atoms introduces four observable effects namely, a non-trivial contribution from the self correlation in the potential flux, a structural realignment at the interface, excess potential energy fluctuations at the interface and a pronounced cage effect that decreases the self-diffusion coefficient of the nanoclusters. The concomitant effects are particularly useful from an experimental point of view. While measuring the potential energy fluctuations or the contribution from the $PP$ correlation is a formidable task, measuring the diffusion and the structural realignment at the interfacial region is certainly feasible by scattering techniques or with magnetic resonance imaging. The presence of the structural and the diffusive signatures along with an enhancement in the thermal conductivity can serve as an indirect confirmation to the observations on the unusual mode of potential energy transport in nano-colloids.

Based on the simulations, it is anticipated that the enhanced thermal conductivities observed with nanoparticles in polar solvents such as water may result exclusively from the surface interactions. The mechanism may also be pertinent for a broad class of nano-colloids with nanometer sized colloidal particles. It is anticipated that enhancements with nanoparticles which are lyophobic such as diamond or carbon fullerenes may only be marginal. The model also suggests possible avenues for optimizing nano-colloids by developing nanoparticles that have functionalized surface layers to maximize the interactions with the fluid atoms.

This thesis also addresses the theoretical concerns regarding the thermal conductivity and the heat flux which are not uniquely defined for colloids. First, the correspondence between the
experimentally observed conductivities and those evaluated from the linear response theory are brought out. The nature of the instantaneous microscopic heat flux is then examined in the context of equilibrium fluctuations and thermodynamics. It is sometimes regarded that the classical microscopic expression for the heat flux is not appropriate for non-homogeneous systems such as colloids. Another theoretical concern is regarding the validity of the linear response theory itself for nano-colloids. This work addresses these issues through molecular dynamics (MD) simulations. Using direct non-equilibrium simulations (NEMD), it is first shown that the time averaged, homogeneous heat flux vector is appropriate for nano-colloids of varying sizes. It is then demonstrated that both the linear response approach or equivalently, the Green-Kubo formalism (GK) and NEMD simulations give statistically similar results for nano-colloids that have a weak solid-fluid interaction. Substantial deviation, however, is observed for a strong solid-fluid interaction. This incongruity is explained by showing the differences in the dynamics at the cluster-fluid interface. Developed in Chapter 3, the dynamic fluctuation amplitude (A), which is a measure of local fluctuations, is employed to characterize the dynamic equivalence in GK and NEMD simulations. When the potential energy fluctuations (AU) become more than those of the kinetic energy (AT), potential energy can be cooperatively exchanged among the atoms. In the GK simulations, excess potential energy fluctuations in the fluid atoms are spread over an interfacial thickness of 2-3σ. In NEMD, the corresponding thickness is approximately 1.3σ. Thus, in the GK simulations, the thicker dynamic interfacial layer facilitates interactions with each other to form percolating networks that can transfer the excess potential energy. In the NEMD simulation, the extreme temperature gradient (10^{10} K/m) adversely affects the dynamics at the interface when the cross interaction is sufficiently strong.

A key theoretical objection against the anomalous thermal conductivity enhancement in nano-colloids stems from the solid-fluid interfacial resistance arising from the mismatch of the vibrational frequencies at the interface. The present work with GK shows that interfacial resistance from the CC correlations is not the limiting mechanism in nano-colloids. In a recent theory [87], thermal resistances which are orders of magnitude lower are predicted between two nanoparticles when the inter-particle distance becomes smaller than the particle diameter along with a significantly higher resistance upon contact. These counterintuitive results show the limitation of the traditional analytical methods based on phonons which are inappropriate at
nanoscales and solid-fluid interfaces [87]. The present work is similar in spirit and raises the possibility of cooperative or coherent modes for thermal transport in colloids at the nanoscales.

In the second part of this thesis, a set of smooth and accurate field estimators are developed for multiscale simulations. Bin averaging is the work horse for most \textit{MD} simulations where the continuum fields are to be constructed from discrete particle data. Poor resolution and statistical noise make the bin method an unsatisfactory choice for performing complex multiscale simulations where smoothness, in addition to accuracy, is a necessity over a relatively short period of time. To avoid the limitations of bin averaging, a non-parametric estimator based on the maximum-entropy (\textit{ME}) principle is developed. The \textit{ME} estimator identifies the least biased distribution that is consistent with the prescribed set of constraints which are in form of moments of the distribution. It is shown that the moments can be calculated directly from the particle data without further assumptions. The results from a \textit{MD} simulation of a shear driven flow in an enclosure, show that the \textit{ME} estimation is superior to the bin average. The \textit{ME} estimate is also compared with the kernel method. While both methods resolve the details of the interior, the kernel method systematically underestimates the density at the boundaries.

Coarse projection, a multiscale integration scheme is then implemented with the microscopically generated fields. The key idea is to use short and intelligent microscopic bursts of appropriately initialized molecular simulations and evaluate the evolution of the pertinent macroscopic field variables [50]. This thesis shows, in the context of the shear driven flow in an enclosure, that spatial continuity and smoothness of the microscopically generated coarse variables, geometrically similar initial conditions and the separation of time scales are essential for the correct coarse field evolution with coarse projection.
References


A. Molecular Dynamics and Benchmark Exercises

The molecular dynamics program for investigating the thermal conduction mechanism is based on the approach followed by Rapaport [49]. Velocity Verlet scheme is employed for the time integration of Newton’s second law of motion. This method can be derived from splitting the Liouville operator ([139], also see Chapter 2) as \( L = L_1 + L_2 \) where

\[
iL_1 = \sum_{j=1}^{N} F_j \frac{\partial}{\partial p_j}
\]

(A.1)

\[
iL_2 = \sum_{j=1}^{N} v_j \frac{\partial}{\partial r_j}
\]

(A.2)

By applying \( e^{itL} \) to the phase space vector \( \Gamma \), the Velocity-Verlet equations are derived. They are

\[
v_i(t + \frac{\delta t}{2}) = v_i(t + \delta t) + \frac{F_i(t)}{m_i} \delta t
\]

(A.3)

\[
r_i(t + \delta t) = r_i(t) + v_i\left(t + \frac{\delta t}{2}\right) \delta t
\]

(A.4)

\[
v_i(t + \delta t) = v_i\left(t + \frac{\delta t}{2}\right) + \frac{F_i(t + \delta t)}{m_i} \delta t
\]

(A.5)

Velocity-Verlet scheme is symplectic which means that it conserves the phase space volume. It is seen that Velocity-Verlet scheme has excellent long time energy conservation properties.
O(N) efficiency is achieved by a cell and neighbor list [49]. All the simulations for the nano-
colloid, both equilibrium and non-equilibrium, are performed with a total of 2048 atoms with
periodic boundary conditions and a cut-off radius of 4.5. Finite size effects are seen to be
negligible with this system size. During equilibration, typically for 100,000 iterations,
temperature and pressure are maintained with a Berendsen external bath [140] or simple velocity
rescaling. The production runs for transport properties are made in the $NVE$ ensemble [48]
without the use of any synthetic temperature or pressure controller. It is also seen that transport
properties are generally unaffected by the choice of pressure/temperature controlling techniques.
Furthermore, only minor differences are observed when artificial dynamics (with the external
bath) are employed during the production runs.

The transport properties are evaluated with the over-lapping data technique outlined in [49].
Twelve different initial conditions are generally used to sample the phase space effectively. For
the cases with equilibrium simulations, sampling of additional phase space is a necessity as the
thermal conductivity shows significant variations depending on the cluster formation. Several
initial conditions are also required for the non-equilibrium simulations for deriving a linear
temperature profile.

![Figure A.1 Ar-Methane Mixture Thermal Conductivity: MD-Experiment Comparison at
$(T,P) = (120\text{K}, 1\text{ atm})$.](image)

Figure A.2 Ar-Methane Mixture Viscosity: MD-Experiment Comparison at 
\((T,P) = (120K, 1 \text{ atm}).\)

Figure A.3 Ar-Kr Mixture Thermal Conductivity: MD-Experiment Comparison at 
\((T,P) = (120K, 1 \text{ atm}).\)
The present molecular dynamics program is written in C++ (nanoWorld) and is benchmarked with several results from the literature [82, 141]. Figure A.1 shows the thermal conductivity of Ar-Methane mixture at atmospheric pressure and at 120 K. Figure A.2 depicts the viscosity for the same mixture and the same conditions. Figures A.3 and A.4 delineates the thermal conductivity and viscosity of Ar-Kr mixtures.

Figures A.1 to A.4 show that the present results are in good agreement with the published data. It is also of interest to note that the enthalpy flux has only a trivial effect on the thermal conductivity as highlighted in [97]. Finally, the radial distribution functions of a random mixture of xenon and platinum atoms (some small clusters) are compared in Figures A.5-A.7 with those generated with DLPOLY [142], a multipurpose MD program. Very good agreement can be noticed from the figures.
Figure A.5  Xe-Xe Radial Distribution Function.

Figure A.6  Xe-Pt Radial Distribution Function.
Figure A.7  Pt-Pt Radial Distribution Function.
B. Kernel Field Estimators

Kernel averaging is a widely used technique in non-parametric density estimation [136]. In this method, the distribution \( \rho(x) \) is the average of kernel or smoothing functions centered on the given particle positions \( X \). The particle density distribution \( \rho(x) \) of \( N \) particles as given by (6.5) is

\[
\rho(x) = \frac{1}{N} \sum_{n=1}^{N} \delta(x - X_n)
\]  

(B.1)

In the kernel method a smooth function is substituted for the delta function to obtain

\[
\rho(x) = \frac{1}{N} \sum_{n=1}^{N} K(x - X_n, h_n)
\]  

(B.2)

where \( K(\cdot) \) is the smoothing kernel function and \( h \) is the smoothing scale (window width) which determines the support of \( K(\cdot) \). Note that the smoothing scale can be different for each particle. \( K(\cdot) \) is usually taken to be a symmetric function even though this is not a strict requirement.

To represent a *bona fide* density distribution, the kernel should have the following properties [123],

\[
\int_{\Omega} K(x - X, h) dX = 1
\]  

(B.3)

\[
K(x - X, h) \geq 0
\]  

(B.4)

\[
\lim_{h \to 0} K(x - X, h) = \delta(x - X)
\]  

(B.5)
Smoothness is a desired characteristic of the kernel function. In this thesis, a Gaussian kernel with zero co-variance is chosen which is given by,

$$K(x) = \frac{1}{(2\pi)^{D/2}} \exp\left(-\frac{1}{2}x^Tx\right)$$  \hspace{1cm} (B.6)$$

where $D$ is the physical dimension of the system. The density distribution with a single smoothing length is evaluated as:

$$\rho(x) = \frac{1}{Nh^D} \sum_{n=1}^{N} K\left(\frac{x - X_n}{h}\right)$$  \hspace{1cm} (B.7)$$

Other kernel functions such as Epanetchnikov and Biweight [136] are available but offer no significant computational advantage. Further, very small support localizes the field which is undesirable in the regions of low density. The optimal smoothing scale is calculated by minimizing the asymptotic integrated square bias and integrated variance [143]. For most cases studied in this thesis, this window width has been found to be optimal in the sense that it resolved the sharp gradients without causing large undulations.

The kernel estimation method can be extended to evaluate the momentum and temperature fields. Substituting a smooth function for the delta function in (6.7),

$$p(x) = \frac{1}{N} \sum_{n=1}^{N} V(X)_n K\left(\frac{x - X_n}{h}\right)$$  \hspace{1cm} (B.8)$$

Since velocity field is given by

$$v(x) = p(x)/\rho(x)$$  \hspace{1cm} (B.9)$$

The kernel estimate for the velocity takes the form
\[
\mathbf{v}(x) = \frac{\sum_{n=1}^{N} \mathbf{V}(X_n) K(x - X_n, h_n)}{\sum_{n=1}^{N} K(x - X_n, h_n)}
\] 

(B.10)

The local temperature field can be calculated as

\[
T(x) = \frac{\frac{1}{2} \sum_{n=1}^{N} |\mathbf{V}(X_n) - \mathbf{v}(x)|^2 K(x - X_n, h_n)}{\frac{D}{2} \sum_{n=1}^{N} K(x - X_n, h_n)}
\] 

(B.11)
C. Short-Smooth Potential

The atoms interact through a short-smooth (SS) potential which is given by (Figure C.1):

\[
V(r) = \begin{cases} 
  \alpha(1-r)^4 - \beta(1-r)^2, & r < 1 \\
  0, & r \geq 1
\end{cases}
\]  

(C.1)

where \(\alpha\) and \(\beta\) are two constants. It is compared with the standard Lennard-Jones 12-6 potential in Figure C.1.

![Figure C.1 Short-Smooth (SS) Inter-Atomic Potential.](image)

The primary units of length and energy are the cut-off distance \(r_c\) at which the potential is valued zero and potential well depth \(\epsilon\) respectively, and are both scaled to unity. Consequently, a single parameter \(r_0\), the equilibrium inter-particle distance, controls the shape of the potential. The distance \(r_0\) is normalized with respect to \(r_c\) such that it is always less than unity. In this study, \(r_0\) is arbitrarily fixed at 0.85. The two parameters that modulate the potential \(\alpha\) and \(\beta\) are given by:
\[ \alpha = (1 - r_0)^{-d}, \quad \beta = 2(1 - r_0)^{-2} \]  

(C.2)

Evidently, the range of short-smooth potential is much smaller than the \( LJ \) 12-6 potential and this translates into significant savings in computational time. Note that the potential energy well (\( \varepsilon \)) is the same as that of the \( LJ \) potential. However the reference length (\( \sigma \)) for the short-smooth potential is nominally longer than that of the \( LJ \) potential with the same physical well position.

The phase-diagram with the short-smooth potential is unavailable and is expected to be different from that of a \( LJ \) system. The liquid-gas equilibrium phase shrinks when the attractive part of the potential becomes short ranged [144]. In some sense, short-smooth potential (SS) is a caricature of a conformal, or a truncated and shifted \( LJ \) 12-6 potential. Pair potentials are conformal when their plots can be constructed by adjusting the values of \( \sigma \) and \( \varepsilon \). For two-dimensional \( LJ \) 12-6, the critical temperature and density in reduced units are 0.52 and 0.36 respectively [145]. The critical temperature reduces to 0.46 when the \( LJ \) 12-6 potential is truncated at 2.5\( \sigma \) and shifted. The critical density, however, changes only by a small fraction to 0.35. Similar results are obtained for \( LJ \) potentials such as 32-6 that have significantly shorter attractive range [144]. It is clear that the phase diagram with SS potential will be different from that of a 2D \( LJ \) 12-6 potential. Based on the similarity with the truncated and shifted potentials, it can be argued that the critical temperature of SS potential will be lower than that with \( LJ \) 12-6 potential which is 0.52 in two-dimensions.

Radial distribution function (\( rdf \)) gives a reasonable confirmation of the thermodynamic state. Figure C.2 shows the \( rdf \) with short-smooth potential for different densities at a temperature of 1.0. Note that at \( (\rho, T) = (0.48, I) \), the state of the system is close to that of a gas while it is more solid-like at a density \( (\rho, T) = (1.44, I) \). The effect of temperature on \( rdf \) is depicted in Figure C.3. All of the simulations with SS potential performed in this thesis are with \( (0.48, I) \).
Figure C.2  Radial Distribution Function at $T = 1$.

Figure C.3  Radial Distribution Function at $\rho = 0.96$. 
D. Vorticity-Stream Function Approach

The incompressible equations for Newtonian fluid flow in the absence of body forces are given by [133]

\[ \nabla \cdot \mathbf{v} = 0 \]  \hspace{1cm} (D.1)

\[ \rho \left( \frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} \right) = -\nabla p + \mu \nabla^2 \mathbf{v} \]  \hspace{1cm} (D.2)

Computational difficulties often associated with the above set of non-linear equations are alleviated by employing the following mathematical transformation [134]:

\[ \omega = \nabla \times \mathbf{v} \]  \hspace{1cm} (D.3)

\[ u = \frac{\partial \psi}{\partial y}, \quad v = -\frac{\partial \psi}{\partial x} \]  \hspace{1cm} (D.4)

\( \omega = \omega \mathbf{k} \) where \( \mathbf{k} \) is the unit vector along axis perpendicular to the computational domain. \( \psi \) is the stream function, and \( u \) and \( v \) denote the two components of the velocity vector. Note that this transformation automatically satisfies the mass continuity equation. The transport of vorticity can be written in terms of a single scalar equation [134]. It is given by:

\[ \frac{\partial \omega}{\partial t} + u \frac{\partial \omega}{\partial x} + v \frac{\partial \omega}{\partial y} = \left( \frac{1}{Re_L} \right) \nabla^2 \omega \]  \hspace{1cm} (D.5)
As can be noted, vorticity is convected by the velocity components (gradients of the stream function) and also gets dissipated. The vorticity is connected to the streamfunction through the following equation:

\[ \nabla^2 \psi = -\omega \]  

(D.6)

A significant advantage of vorticity-stream function approach is in the elimination of the pressure term. This facilitates a solver on regular non-staggered grids. In addition, there is only one transport equation as against two in the primitive variables approach. The stream function equation also falls in the Poisson class which has very efficient numerical solution techniques such as Krylov and multi-grid methods.

The streamfunction and vorticity transport equations are solved with a finite-difference algorithm on a non-staggered grid [134]. At the solid walls, the velocity components are zero by no-slip assumption. Hence, the stream function is arbitrarily set to zero at the stationary walls. Since the boundary conditions for vorticity do not exist in a natural way, the stream function is expanded with the Taylor’s series and a second order approximation for the vorticity is applied on the walls [146].

The direct numerical algorithm given by Pozrikidis [134] is adopted which starts with a guessed vorticity field. New streamfunction values are evaluated by solving the Poisson equation for streamfunction, Equation (D.6). The velocity components are calculated on all the interior nodes and the boundary vorticity values are evaluated. Next the vorticity field is predicted using the steady-state version of Equation (D.5). The \( L_2 \) norm of the vorticity is compared between successive iterations. Convergence is established when the relative error becomes less than an arbitrarily assigned value of \( 10^{-6} \).
E. Generalized Vorticity and Stream Function

For steady flow, the mass conservation is:

\[ \nabla \cdot (\rho \mathbf{v}) = \frac{\partial (\rho u)}{\partial x} + \frac{\partial (\rho v)}{\partial y} = 0 \]  \hspace{1cm} (E.1)

Define a generalized stream function \( \Omega \) such that:

\[ \frac{\partial \Omega}{\partial y} = \rho u \quad \text{and} \quad \frac{\partial \Omega}{\partial x} = -\rho v \]  \hspace{1cm} (E.2)

The function \( \Omega \) is similar to the stream function \( \psi \) for incompressible flow. Now, define a generalized vorticity \( \zeta \) as:

\[ \zeta \equiv \nabla \times (\rho \mathbf{v}) \]  \hspace{1cm} (E.3)

The scalar component (for 2D) is given by:

\[ \zeta = \frac{\partial (\rho v)}{\partial x} - \frac{\partial (\rho u)}{\partial y} \]  \hspace{1cm} (E.4)

Combining Equations (E.2) and (E.4),

\[ \nabla^2 \Omega = -\zeta \]  \hspace{1cm} (E.5)

\( \Omega \) has the same physical interpretation as that of \( \psi \). The difference (in the values) of two streamlines is proportional to the mass flow rate between them.