Reply to “Comment on ‘Determination of the bulk melting temperature of nickel using Monte Carlo simulations: Inaccuracy of extrapolation from cluster melting temperatures’”

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The thermodynamic integration (TI) method for determining the melting temperature has to be performed with great care to ensure accuracy. Since the slopes of the Gibbs free energy curves as a function of temperature (or pressure) are usually rather close, small shifts in the free energy curves can lead to a large change in the calculated melting temperature. In this Reply to a Comment by Harvey and Gheribi [Phys. Rev. B 84, 096102 (2011)] on our paper [Phys. Rev. B 81, 064112 (2010)], we show that the error in the calculated melting temperature of nickel induced by some technical imperfections in our application of the TI method, as noticed and described in the Comment, is small compared to the error bar given in our paper. We also clarify supposed doubts about the accuracy of the TI method based on Johnson’s free energy expression and parametrization [Johnson et al., Mol. Phys. 78, 591 (1993)] of the Lennard-Jones fluid.

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Before replying to Harvey and Gheribi’s criticism of some technical points of our application of the thermodynamic integration (TI) method to determine the melting temperature of nickel according to the pure nickel (Ni) part of the interatomic carbon-nickel (CNi) tight binding potential by Amara et al., we will first respond to their comment that our selection of the used interatomic Ni potential would be inadequate and that “the interatomic potential used by Los and Pellenq can only describe qualitatively the fusion of Ni which is incompatible with the main objective of their work.”

Nowadays there exist many (semi-)empirical, reactive potentials for as many different system types, which in general are initially only tested within a certain limited application domain. It is not possible to test a potential for any situation in one single work, because the phase space is simply too large. Usually a certain potential reveals its qualities and weak points in subsequent works by the same or other authors. This is a quite common and normal way of how things evolve.

The Ni part of the mentioned CNi potential has been parametrized by fitting it to the properties of the solid fcc phase and to the interactions of Ni with C in a simple way, using canonical values for the hopping parameters. However, for the application to nanotube growth, which was the main driving force to building this potential, the liquid phase is also important, because the tube is grown at high temperatures (∼1000 K) from liquid Ni droplets containing the carbon component. It is thus of crucial importance to know the melting temperature of clusters, \( T_m, cl \), according to this potential, which was the initial motivation of our work. In this context, the determination of the bulk melting temperature, \( T_m \), as a reference value is a logical step. In our paper, we considered both clusters and bulk.

The rather high bulk melting temperature found by extrapolation from the cluster melting temperatures for increasingly large clusters prompted us to determine \( T_m \) using the more rigorous TI method. The fact that the TI method gives a significantly lower (by 325 K) value forms the basis of the first important conclusion of our paper, namely, that the first (extrapolation) method can be very inaccurate in a misleading way, as we explain in our paper. A second important result of our paper is that the Ni part of the issued CNi potential yields a \( T_m \) of about 2010 K, a fact which was not known before and which we believe is very useful information for those who consider the possibility of applying the issued NiC potential for the simulation of carbon nanotube growth. The discrepancy of about 15% of our calculated \( T_m \) with the experimental value (1726 K) was not surprising to us in view of the 40% too high value of the \( C_{44} \) elastic constant as compared to the experimental value. And, as Harvey and Gheribi show in their Fig. 1, also the experimental liquid density around \( T_m \) is not reproduced with high accuracy by the Ni potential used. Getting a close agreement with the experimental \( T_m \) was not an objective of our work.

We now proceed to discuss Harvey and Gheribi’s three points of criticism regarding our technical performance of the TI method. They remark that our simulations at 2100 K are done in the two-phase region of the equilibrium phase diagram according to the cut and shifted Lennard-Jones (cs-LJ) potential, referring to their Fig. 2 to show this. Phase separation should indeed be avoided in the TI method for known reasons. However, we believe that in the present case no numerical difficulties are to be expected, since the issued state point (lower open circle of their Fig. 2) rather lies on the border between the one- and the two-phase region than in the two-phase region. Typically, when phase separation occurs this is signaled by large fluctuations and a jump in the internal energy. In our simulations such effects were not observed, as is also demonstrated by the smoothness of the integrand for the liquid phase close to \( \lambda = 0 \), shown in Fig. 5(a) of our paper. Although we admit that it is safer to stay a bit farther away from the two-phase domain, the present situation could not motivate us to repeat the rather laborious calculations with a larger value of the \( \sigma \) parameter of the cs-LJ potential.

The second point of criticism is that the size of the smallest of the two systems for which we applied the TI method, i.e., the one with 256 atoms, would be too small, since the cutoff radius of \( 4\sigma = 8.4 \) Å of the cs-LJ potential is larger than half the box size \( L/2 \approx 7.39 \) Å. It is indeed true that the minimal image size...
The minimal image convention cannot be applied in this case, since a given atom $i$ can have more than one interaction with different periodic images of an atom $j$. However, in our calculations we do not use the minimal image convention, but all interactions are taken into account. Given this fact, Harvey and Gheribi comment that our box would bias a certain long-range order (LRO) which is not present in the liquid. Although, strictly speaking, this is true one can expect that the “error” induced by this should be quite small in the present case, as it concerns only a limited number of interactions lying in the outer tail of the cs-LJ potential, where the interactions have become very weak.

To verify this, we have done some additional simulations at 2300 K. Figure 1 gives the radial distribution functions (RDFs) for the cs-LJ systems with $N = 256$ and 500 atoms, the latter not being “too small”. Both RDFs are equal, there is no drop beyond 7.39 Å, and no trace of any structure, signaling the latter not being “too small”. Both RDFs are equal, there is no drop beyond 7.39 Å, and no trace of any structure, signaling the latter not being “too small”. Both RDFs are equal, there is no drop beyond 7.39 Å, and no trace of any structure, signaling the latter not being “too small”.

In Table I, we compare the equilibrium densities according to the Ni potential for the two system sizes. Note that the $\lambda$ integration is performed at the equilibrium density according to the cs-LJ potential for the two system sizes. Possible numerical problems due to a too small box would be signaled by a “large” difference in the internal energies according to the cs-LJ potential at these densities for the two system sizes. All respective values are quite close, excluding a significant error in $T_m$ due to a too small box for the system with 256 atoms.

The last point of criticism concerns the finite size correction (FSC) of the Stirling approximation of $\ln(N!)$, a term which appears in the free energy of the liquid phase to correct for the indistinguishability of the particles. We have indeed not included this FSC, equal to $\ln(2\pi N)/(2N)$, because we thought it would be negligible. But, indeed, a correction of 0.015 eV/atom for the system with 256 atoms, as reported by Harvey and Gheribi in their Comment as we received it after acceptance, would change $T_m$ by as much as 50 K. However, they seem to have assigned units of eV/atom to the dimensionless quantity, as can be concluded by looking at Table II, where we report the FSC in dimensionless units and in eV/atom for the two used system sizes. Our absolute FSC of 0.00286 eV/atom for the system with 256 atoms at $T = 2300$ K is much smaller than their value. (In the proof corrections of the Comment, Harvey and Gheribi corrected their value, replacing “0.015 eV/atom” by “0.015 $k_B T$ eV/atom”.)

We have nevertheless recalculated the free energy curves for the liquid phase including the FSC to the Stirling approximation. The result is shown in Fig. 2. For the system with 256 atoms it changes $T_m$ from 2032 to 2042 K, whereas for the system with 500 atoms $T_m$ changes from 1996 to 2000 K. In both cases, the modification is amply within the error bars of 40 and 45 K, respectively. Within the context of our paper, a

![FIG. 1. (Color online) RDFs for the cs-IL fluid determined from MC simulations for a simulation box with 256 atoms (full red curve) and one with 500 atoms (dashed blue curve), both at a density equal to $\rho = 0.079215$ atoms/Å$^3$. The vertical dotted line represents half the simulation box size $L/2$ for the smallest system. Because we do not use the minimal image convention, no drop of the RDF occurs beyond $L/2$ for that system.](image1)

![FIG. 2. (Color online) Free energy curves as a function of temperature for the liquid and solid phases, as in Fig. 5(b) of our paper, but here the curves for the liquid including the FCS correction to the Stirling approximation are added (long-dashed red line for the system with 500 atoms and dashed-dotted red line for the system with 256 atoms).](image2)

<table>
<thead>
<tr>
<th>$N$</th>
<th>$\rho$ (atoms/Å$^3$)</th>
<th>$U$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>246</td>
<td>0.079215</td>
<td>$-1.0423 \pm 0.00046$</td>
</tr>
<tr>
<td>500</td>
<td>0.079148</td>
<td>$-1.0417 \pm 0.00024$</td>
</tr>
<tr>
<td>500</td>
<td>0.079215</td>
<td>$-1.0426 \pm 0.00024$</td>
</tr>
</tbody>
</table>

![TABLE II. Values of the finite size correction to the Stirling approximation in dimensionless units and in eV/atom at 2300 K for the system with 256 atoms and at 2100 K for the system with 500 atoms.](table2)
change of a few kelvins in the average calculated $T_m$ is quite small and does not change any of our conclusions.

Finally, we want to address Harvey and Gheribi’s comment that they refute our supposed doubts about Johnson’s free energy expression and parametrization\(^5\) for the (cs-)LJ fluid. First of all, we do not have these doubts. Second, Harvey and Gheribi seem to think that we would have such doubts because of the discrepancy between our calculated $T_m$ and the experimental $T_m$. However, from the context of the issued part of the text of our paper (last two paragraphs in Sec. VI), it is clear that such doubts would not come from the just mentioned discrepancy but from the large “discrepancy” between the $T_m$ from the TI method and the $T_m$ that follows from extrapolating the melting temperatures of a series of finite clusters according to the same interaction potential! But in fact, the latter “discrepancy” is not a true discrepancy, as we gave an explanation for it in Sec. V, but it is nevertheless unexpected and remarkable.

Although we think that Harvey and Gheribi have overestimated the error due to some technical imperfections in our performance of the TI method, we understand their concern about the precision of the TI method. We use this opportunity to stress that we do not have serious doubts about the accuracy of the TI method based on Johnson’s free energy description of the (cs-)LF fluid phase within the accuracy given in Johnson’s paper.\(^5\) The results in our paper do not really justify such doubts.

To conclude, we thank Harvey and Gheribi for pointing us to the FSC to the Stirling approximation, and we hope that their Comment and our Reply will both contribute to a constructive evaluation of the TI method.

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