

II. Equilibrium Thermodynamics

Lecture 7: Statistical Thermodynamics

Notes by ChangHoon Lim (and MZB)

Open circuit voltage of galvanic cell is

$$V_0 = \frac{\Delta G_{net.reaction}}{-ne}$$

To understand compositional effects on ΔG , we need to consider some simple statistical model.

1. Lattice gas

We consider a “lattice gas” of N indistinguishable finite-sized particles ($N_s - N$ indistinguishable holes) confined to a lattice of N_s available fixed lattice sites.

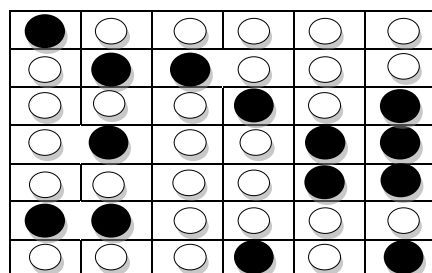


Figure 1. Lattice sites with particles (black) and holes (white)

The entropy of the system, defined by the great physicist Ludwig Eduard Boltzmann (1844-1906) is

$$S = k_B \ln \Omega$$

where k_B is Boltzmann’s constant and Ω is the number of distinguishable (degenerate) states of the system. This assumes an “ideal solution” or “ideal mixture” of particles and holes.

$$\Omega = \binom{N_s}{N} = \frac{N_s!}{N!(N_s - N)!}$$

In the thermodynamic limit, we let N and $N_s - N$ go to infinity with the filling fraction $x = \frac{N}{N_s}$

held constant and use Stirling’s formula: $N! \sim \left(\frac{N}{e}\right)^N \sqrt{2\pi N}$

A notation: $f(x) \sim g(x)$ as $x \rightarrow x_0$, which we read “ $f(x)$ is asymptotic to $g(x)$ as $x \rightarrow x_0$ ”

$$\text{means } \lim_{x \rightarrow x_0} \frac{f(x)}{g(x)} = 1$$

The derivation of Stirling’s formula is shown at appendix.

In the thermodynamic limit,

$$\frac{S}{k_B} = \ln \Omega = \ln \frac{N_s!}{N!(N_s - N)!} \sim N_s \ln N_s - N_s - (N \ln N - N) - (N_s - N) \ln(N_s - N) + (N_s - N)$$

Define the entropy density per site as $s = \frac{S}{N_s}$ with the filling fraction $x = \frac{N}{N_s}$

$$\frac{s}{k_B} \sim \ln N_s - x \ln N - (1 - x) \ln(N_s - N) - \underbrace{(1 - x) \ln N_s + (1 - x) \ln N_s}$$

$$\frac{s}{k_B} \sim -x \ln x - (1 - x) \ln(1 - x)$$

Therefore, in the thermodynamic limit, $s = -k_B[x \ln x + (1 - x) \ln(1 - x)]$

More generally, for an “ideal solution” of M components/species ($i=1, 2, \dots, M$) and holes

$$s = -k_B \sum_{i=0}^M x_i \ln x_i$$

where $x_0 = 1 - \sum_{i=1}^M x_i$

2. Electrochemical potential

Suppose the N particles have charge ze and feel a mean electropotential ϕ

Then, the total Gibbs free energy is

$$G = H - TS + zeN\phi$$

At constant T , P and ϕ ,

$$\Delta G = \Delta H - T\Delta S + \Delta(zeN)\phi$$

The electrochemical potential per particle, defined as the change in Gibbs free energy per particle, is

$$\mu = \left(\frac{\Delta G}{\Delta N} \right)_{T, P, \phi} = \left(\frac{\partial g}{\partial x} \right)_{T, P, \phi}$$

where $g = G/N_s$ is Gibbs free energy per site. Using g , s , and $h = H/N_s$

$$g = h - Ts + \rho\phi = h - Ts + ze\phi$$

where $\rho = \frac{zeN}{N_s} = zex$. Thus, $\mu = \left(\frac{\partial g}{\partial x} \right)_{T,P,\phi} = h'(x) - Ts'(x) + ze\phi$

For lattice gas, $s = -k_B[x \ln x + (1-x) \ln(1-x)]$

Hence, $s'(x) = -k_B[\ln x + 1 - \ln(1-x) - 1] = -k_B \ln \left(\frac{x}{1-x} \right)$

The electrochemical potential for lattice gas is

$$\mu(x) = h'(x) + k_B T \ln \left(\frac{x}{1-x} \right) + ze\phi$$

More generally, for an “ideal solution” of M components/species ($i=1, 2, \dots, M$) and holes

$$\mu_i(x) = \frac{\partial h}{\partial x_i} + k_B T \ln \left(\frac{x_i}{x_0} \right) + z_i e\phi$$

where $x_0 = 1 - \sum_{i=1}^M x_i$

3. Dilute Solutions

In dilute limit, for ideal mixing, $x_i \rightarrow 0$, $x_0 \rightarrow 1$

$$\mu_i(x) = \frac{\partial h}{\partial x_i} + k_B T \ln x_i + z_i e\phi = \frac{\partial h}{\partial x_i} + \mu_i^{dilute}$$

More generally, $\mu_i = \mu_i^{dilute} + \mu_i^{excess} = k_B T \ln(\gamma_i x_i) + z_i e\phi = k_B T \ln(f_i c_i) + z_i e\phi$

where γ_i and f_i are activity coefficients.

[Note]

$$x_i = \frac{\# \text{ particles } i}{\# \text{ sites}} = \frac{N_i}{N_s} = \frac{N_i/V}{N_s/V} = \frac{C_i}{\rho_s}$$

$$C_i = \frac{N_i}{V} = \text{concentration}(M) \quad \rho_s = \frac{N_s}{V} = \text{SiteDensity}$$

$$a_i = \gamma_i x_i = f_i c_i: \text{Absolute activity}$$

In dilute electrolytes, the dominant non-ideality comes from the electrostatic attractions between opposite charge ions in the neutral bulk solution, which tend to lower the total free energy. Later in the class, we will use the dilute solution theory of electrolytes to derive the Debye-Huckel formula

$$\ln(\gamma_i) = -\frac{Z_i^2 A \sqrt{I}}{1 + B \sqrt{I}}$$

where $I = \sum_i z_i^2 x_i$ is dimensionless ionic strength (a measure of the salt concentration). The excess chemical potential decreases like the square root of the ionic strength at low concentration and saturates at high concentration.

4. Concentrated Solutions

At high concentrations, more complicated expressions for the activity coefficient arises because of the various short-range interactions in addition to long-range electrostatic interactions.

A) Lattice gas (or solid)

$$\gamma_i = \frac{1}{x_0}, \text{ where } x_0 = 1 - \sum_{i=1}^M x_i = 1 - \Phi$$

where Φ is the total filling fraction. The excess chemical potential in this case¹

$$\frac{\mu_i^{\text{excess}}}{k_B T} = \ln \gamma_i = -\ln(1 - \Phi) \sim \Phi \text{ as } \Phi \rightarrow 0$$

diverges at close packing and has a linear dependence at low volume fraction. The latter dependence is a direct proportionality since each particle on a lattice excludes only its own volume.

B) Hard spheres of identical size as a model for short range repulsion in a liquid

This excess chemical potential is well approximated by the Carnahan-Starling EOS (equation of state) up to roughly 0.55 total volume fraction²

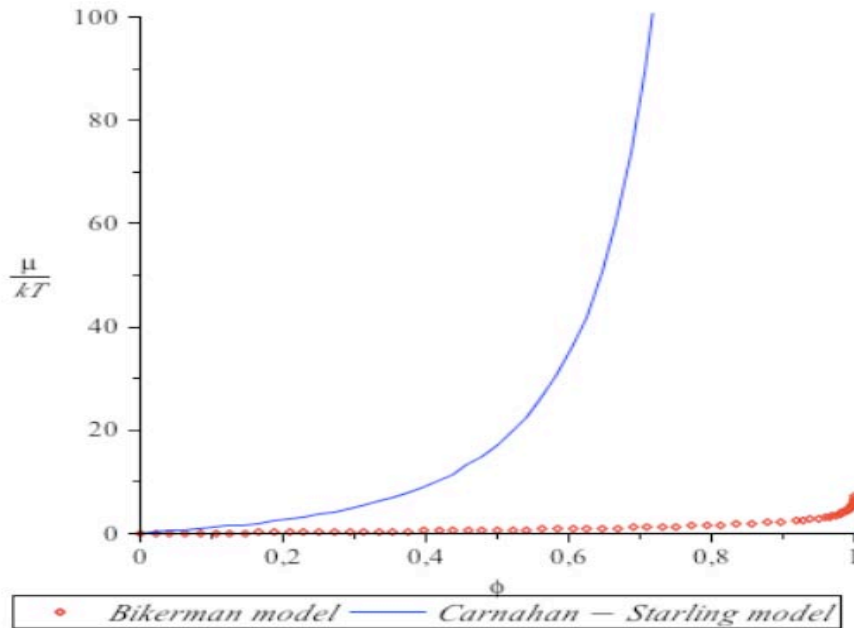
$$\frac{\mu_i^{\text{excess}}}{k_B T} = \ln \gamma_i = \frac{\Phi(8 - 9\Phi + 3\Phi^2)}{(1 - \Phi)^3} \sim 8\Phi \text{ as } \Phi \rightarrow 0$$

The expansion at low volume fraction shows that the contribution to excess chemical potential for hard spheres is 8 times that of a lattice gas, which expresses the geometrical fact that a sphere excluded 8 times its own volume for other identical spheres. The plot below shows

¹ The application of this model to describe finite-sized charged particles was proposed by Grimley and Mott (1947) for ionic crystals, leading to a continuum theory equivalent to that of Bikerman (1942), which we will cover later in the class. It has also recently been used to model ionic liquids (Kornyshev 2007) and dilute electrolytes subjected to large voltages (Kilic, Bazant, Ajdari 2007), where the large electric field leads to crowding near a highly charged surface.

² This model has been applied to electrolyte by Lue et 1999 and other recent authors. It neglects non-local correlation effects, but captures some features of highly concentrated electrolytes. For a review see Bazant, Kilic, Storey, Ajdari, *Advances in Colloid and Interface Science* (2009).

that excluded volume effects are much larger for hard spheres, not only at low volume fraction, but even more so at high volume fraction. The CS approximation breaks down, however, above roughly 0.55. Since it diverges only at 1.0, it is clear that it does not capture the jamming/glass transition of randomly packed hard spheres, around 0.63, or the maximum crystal volume fraction (for the face-centered-cubic lattice) at 0.74.



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Figure 2. Excess chemical potential (dimensionless) as a function of packing fraction [1]

[Appendix: Derivation of Stirling's formula]

A systematic way to derive Stirling's formula starts with the following definite equation

$$N! = \Gamma(N+1) = \int_0^{\infty} t^N e^{-t} dt$$

Consider the integrand $F(t) = t^N e^{-t}$ when N is large. Then t^N is a rapidly increasing function of t , while e^{-t} is a rapidly decreasing function of t . Hence, the product F exhibits a sharp maximum for some value $t=t_0$. To find this maximum,

$$\frac{d \ln F(t)}{dt} = \frac{N}{t} - 1 = 0$$

Therefore, $t_0=N$. However, only values of t in the vicinity of $t_0=N$ contributes to the above integral because F has the sharp maximum. To find an expression for F near $t_0=N$, write $t=N+x$ ($x \ll N$) and expand $\ln F$ by using a Taylor expansion around $t_0=N$.

$$\ln F(t) = N \ln t - t = N \ln(N+x) - (N+x)$$

$$\text{And, } \ln(N+x) = \ln N + \ln\left(1 + \frac{x}{N}\right) = \ln N + \frac{x}{N} - \frac{1}{2}\left(\frac{x}{N}\right)^2 + \mathcal{O}\left(\frac{x}{N}\right)^3$$

$$\text{Hence, } \ln F(t) = N \ln N - N - \frac{1}{2}\left(\frac{x}{N}\right)^2 \quad \text{Or } F(t) = N^N e^{-N} e^{-\frac{1}{2}\left(\frac{x}{N}\right)^2}$$

Put this integrand into the integral,

$$N! = \Gamma(N+1) = \int_0^{\infty} N^N e^{-N} e^{-\frac{1}{2}\left(\frac{x}{N}\right)^2} dt = N^N e^{-N} \int_0^{\infty} e^{-\frac{1}{2}\left(\frac{x}{N}\right)^2} dt = N^N e^{-N} \sqrt{2\pi N}$$

This is the Stirling's formula. $\ln N! = N \ln N - N + \frac{1}{2} \ln(2\pi N)$

If N is very large, $\ln N \ll N$. (For example, $N = N_A = 6 \times 10^{23}$, Avogadro's number, then $\ln N = 55$)

Thus, in the thermodynamic limit, $\ln N! = N \ln N - N$

[References]

1. MIT Student and Martin Z Bazant. Lecture 3, 10.95 Scribed Notes, 2009

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10.626 / 10.462 Electrochemical Energy Systems
Spring 2011

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