10.40 Thermodynamics **Fall 2003**
Exam 2

Problem 6

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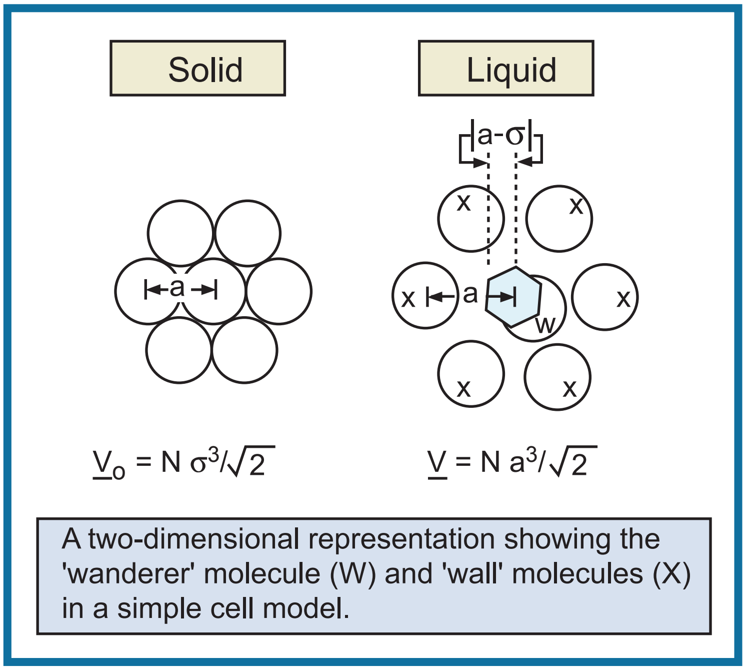
6. (15 points) The direct evaluation of the partition function for a liquid is difficult to achieve in practice. Fortunately a range of approximations are available. In the simple cell model for liquids, a unit cell is envisioned to be composed of a single molecule "engaged" inside a rigid lattice formed by the nearest neighbor molecules surrounding the trapped molecule. This entrapped molecule is allowed to wander inside the cell volume (see figure below). Although it is not possible to characterize the interaction energy of the wandering molecule by a single value, the mean field approximation and free volume concepts can be applied. If we bring N molecules together from infinite mutual separations to form a lattice, the system loses potential energy due to attractive forces which can be equated to the "lattice energy" = Φ_L. Now we assume that all molecules are at fixed locations in the lattice, except for the wandering molecule which is assumed to preferentially want to locate at the cell center. Thus, on a per molecule basis the attractive part of the potential energy is Φ_L/N. In general, Φ_L depends on lattice spacing and hence on the volume. Note that while all molecules have the same size described by spheres of diameter σ, the lattice on the other hand has characteristic nearest neighbor distance of a as shown in the figure below.

   (a) (8 points) Develop an expression for the configurational integral for the cell in the liquid model.

   (b) (7 points) If Φ_L/N can be approximated by $\Phi_L = -a/V$, *where* $a = a(T)$ is only a function of temperature, develop a pressure-explicit EOS form in terms of $P = f(T, V, V_o, a(T))$.



A two-dimensional representation showing the 'wanderer' molecule (W) and 'wall' molecules (X) in a simple cell model.

Image by MIT OCW.

Solution:

a.

$$Z^* \equiv \int \dots \int \exp\left[\frac{-\Phi\left(\underset{\sim}{r}^N\right)}{kT}\right] d\underset{\sim}{r}^N \tag{10-76}$$

Applying the mean field approximation to (10-76),

$$Z^* = \left(\exp\left[\frac{-|\Phi|}{kT}\right]\right)^N \int \dots \int d\underset{\sim}{r}^N$$

$\exp\left[\frac{-|\Phi|}{kT}\right]$ can be pulled out of the integral since $|\Phi|$, the mean potential is independent of $\underset{\sim}{r}^N$

In this problem, $|\Phi| = \Phi_L$, the total, N-particle interaction potential

$$Z^* = \left(\exp\left[\frac{-\Phi_L}{kT}\right]\right)^N \underbrace{\int_\sigma^a \dots \int_\sigma^a d\underset{\sim}{r}^N}_{(\text{Free Volume})^N}$$

Where the free volume = total system volume (V) - volume excluded by the finite size of the molecules ($\underline{V}_0$)

$$\boxed{Z^* = \left(\exp\left[\frac{-\Phi_L N}{kT}\right]\right)\left(\underline{V} - \underline{V}_0\right)^N = \left(\exp\left[\frac{-\Phi_L N}{kT}\right]\right)\left(\frac{N}{\sqrt{2}}\left(a^3 - \sigma^3\right)\right)^N} \tag{1}$$

b.

We are given that $\Phi_L = -\frac{a(T)}{V} = -\frac{a(T)N}{\underline{V}}$ (2)

Plugging (2) into (1) yields,

$$Z^* = \left(\exp\left[\frac{a(T)N^2}{\underline{V}kT}\right]\right)\left(\underline{V} - \underline{V}_0\right)^N \tag{3}$$

To obtain a pressure-explicit equation of state, we plug (3) into

$$P = kT\left(\frac{\partial \ln Z^*}{\partial \underline{V}}\right)_{T,N} \tag{10-77}$$

to obtain

$$P = kT\left(\frac{\partial\left(\frac{aN^2}{kT}\frac{1}{\underline{V}} + N\ln\left(\underline{V}-\underline{V}_0\right)\right)}{\partial\underline{V}}\right)_{T,N}$$

$$P = \frac{kTN}{\underline{V}-\underline{V}_0} - \frac{aN^2}{\underline{V}^2}$$

$$\boxed{P = \frac{kT}{V-V_0} - \frac{a}{V^2}}$$

Our final answer is the van der Waals equation of state on a per molecule basis with $V_0 = b$.