10.40 Thermodynamics **Fall 2003**
Exam 2

Problem 3

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3. (15 points) In terms of the grand partition function, Ξ, the *PVT* equation of state is expressed explicitly in molecular units in Equation (10-57) as $P\underline{V} = kT\ln\Xi$. Recalling our discussion in class of the Virial equation of state, develop an analysis to determine under what conditions Eq(10-57) would reduce to the ideal gas equation of state for a range of densities. Describe the nature of the intermolecular interactions that exist that will yield this result.

Solution:
For an ideal gas, $PV = NkT$. Therefore, it would appear that we must show the circumstances under which $\ln\Xi = N$. Going through the discussion for the Virial Equation of State in Section 10.4, from Equation (10-105) we see that:

$$\ln\Xi = \frac{P\underline{V}}{kT} = \underline{V}\sum_{j=1}^{\infty} b_j\rho_o^j \qquad (10\text{-}105)$$

The values of b_j are described by Equation (10-106):

$$\begin{aligned} b_1 &= \frac{1}{1!\underline{V}} Z_1^* = 1 \\ b_2 &= \frac{1}{2!\underline{V}}\left(Z_2^* - Z_1^{*2}\right) \\ b_3 &= \frac{1}{3!\underline{V}}\left(Z_3^* - 3Z_2^*Z_1^* - 2Z_1^{*3}\right) \\ &\vdots \end{aligned} \qquad (10\text{-}106)$$

Each is related to configurational integral(s) Z_1^*, …, Z_j^*, described by Equation (10-112). For the configurational integrals, Z_1^* depends only on a particle interacting with itself, Z_2^* depends on binary interactions, Z_3^* depends only on three-way particle interactions, etc.

$$Z_1^* = \int d\mathbf{r}_1 = \underline{V}$$

$$Z_2^* = \int\int e^{-\Phi_2/kT} d\mathbf{r}_1 d\mathbf{r}_2$$

$$Z_3^* = \int\int e^{-\Phi_3/kT} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3, \quad \text{etc.}$$

We know that an ideal gas is a gas in which it is assumed that the molecules have no volume and do not interact with any other molecules in the gas. If this is true, then we would expect that the contribution from Z_j^* for $j > 1$, which account for binary interactions, ternary interactions, etc., to be negligible. For this to be true, the intermolecular interaction potentials must be zero, $\Phi_j = 0$, for *all* values of **r**. It should be stressed again that $\Phi_j = 0$ for all values of **r**, from zero to infinity. This means that there is no hard sphere repulsion assumption, or that it is assumed that the molecules have zero volume.

For the case where $\Phi_j = 0$ and there is no interaction potential, Equation (10-112) shows that all $Z_j^* = \underline{V}^j$. Plugging these back into Equation (10-106), we see that $b_1 = 1$ and all other $b_j = 0$ for $j \geq 2$. Also, Equation (10-108) shows that $\rho_o = a_1\rho + a_2\rho^2 + a_3\rho^3 + ... = \rho$ for the assumptions we have made here. Plugging all this into Equation (10-105), we see that:

$$\ln \Xi = \frac{P\underline{V}}{kT} = \underline{V}\sum_{j=1}^{\infty} b_j \rho_o^j = \underline{V}\left(1 \cdot \rho\right) = N$$

or $P\underline{V} = NkT$! Thus under the conditions that the intermolecular interaction potential is zero for all values of **r**, $P\underline{V} = kT \ln \Xi$ reduces to the ideal gas equation of state. These conditions imply that 1.) the molecules in the gas do not interact with each other and 2.) the molecules do not have any volume (ie. no hard sphere interaction).

There are several ways that we could have come to this conclusion. One could have equally started from Equation (10-109) in the discussion on the Virial Equation of state:

$$\frac{P}{kT} = \rho + B\left(T\right)\rho^2 + C\left(T\right)\rho^3 + ... \tag{10-109}$$

We can immediately see that we get the ideal gas equation of state for the case where $B(T) = 0$, $C(T) = 0$, etc, where $B(T)$ accounts for secondary interactions, $C(T)$ accounts for ternary interactions, etc. Scanning down to Equation (10-112), we see that this is the case when all $\Phi_j = 0$ for all **r**, or in words, that there is no interaction between the molecules, neither in the form of attractive intermolecular potentials or repulsive hard sphere interactions.

Likewise, one could start with Equation (10-159):

$$P\underline{V} = NkT + \tfrac{1}{3} < \sum_i \sum_j \mathbf{F}_{ij}\left(r_{ij}\right) r_{ij} > \tag{10-159}$$

and then point out that for the case where the forces between the molecules (for all *i-j* interactions) are zero for all values of *r*, the result is the ideal gas equation of state. This implies that there are no intermolecular forces between the particles for an ideal gas.