NAME :

Quiz 15

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Prof. Garima's talk yesterday had an interesting statement: *Excluded volume leads to an increase in free energy.* Let us see if we can show this for a simple non-interacting gas with an excluded volume. Such a gas has an internal energy and equation of state given by

$$U = C_V T \qquad \text{and} \qquad P(V - Nb) = Nk_B T. \tag{1}$$

(a) We will first try to find $S(T, V)$ for such a system. Use the differential form of the first law to show

(i) $\left(\frac{\partial U}{\partial T}\right)_{V,N} = T\left(\frac{\partial S}{\partial T}\right)_{V,N}$, and consequently that $\left(\frac{\partial S}{\partial T}\right)_{V,N} = \frac{C_V}{T}$. [3]

(ii) Next, show that $\left(\frac{\partial S}{\partial V}\right)_{T,N} = \frac{P}{T} = \frac{Nk_B}{V - Nb}$. [3]

(b) Use the above two results to show that [2]

$$S(T,V) = S_0 + C_V \log T + N k_B \log(V - Nb), \tag{2}$$

where S_0 is an unimportant constant. **Hint:** Use the fact that $\mathrm{d}S(T,V) = \left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V$.

(c) Using the fact that $F(T,V,N) = U - TS$, find F for the given system. Now, suppose $Nb \ll V$: show that in this case, we can write

$$F(T,V,N) \approx F_{\text{ideal gas}}(T,V,N) + k_B T\left(\frac{N^2 b}{V}\right). \tag{3}$$

In other words, if we take into account the "excluded" volume of a real gas, its free energy is *higher* than that of an ideal gas. [2]