10.40 Thermodynamics **Fall 2003**
Problem Set 8

Problem 2

Show that the standard deviation or square root of the variance of the distribution of particle densities, σ_ρ, for a pure fluid varies as $(\langle N \rangle)^{-1/2}$ for a fixed volume system. For typical thermodynamic systems, what happens to the value of $\sigma_\rho / \langle \rho \rangle$ at low densities and at the critical point?

Solution:

$$\sigma_\rho^2 = \overline{\left(\rho - \langle \rho \rangle\right)^2} \qquad \text{where } \rho = \frac{N}{\underline{V}} \tag{1}$$

For a fixed volume system, $\underline{V}$ is constant, so that

$$\sigma_\rho^2 = \overline{\left(\frac{N}{\underline{V}} - \left\langle \frac{N}{\underline{V}} \right\rangle\right)^2} = \frac{1}{\underline{V}}\overline{\left(N - \langle N \rangle\right)^2} = \frac{\sigma_N^2}{\underline{V}} \tag{2}$$

So what we are really looking for is σ_N^2. The derivation of σ_N^2 is analogous to the derivation of $\sigma_{\underline{E}}^2$ developed in class, but instead of working in the canonical ensemble (N, $\underline{V}$, T), we must use the grand canonical ensemble (μ, $\underline{V}$, T) in order to derive σ_N^2. First, we must expand the expression:

$$\sigma_N^2 = \overline{\left(N - \langle N \rangle\right)^2} = \overline{N^2 - 2N\langle N \rangle + \langle N \rangle^2} \tag{3}$$

where the overbar indicates that the variance is equal to the average of the expression on the right hand side. Since the average of a summation of terms is equal to the sum of the average of each term, we can break the right hand side up into its individual terms and take the average of each term in the sum:

$$\begin{aligned} \sigma_N^2 &= \overline{N^2} - \overline{2N\langle N \rangle} + \overline{\langle N \rangle^2} = \langle N^2 \rangle - 2\langle N \rangle^2 + \langle N \rangle^2 \\ \sigma_N^2 &= \langle N^2 \rangle - \langle N \rangle^2 \end{aligned} \tag{4}$$

We now turn to the grand canonical ensemble to determine the expressions for $\langle N \rangle^2$ and $\langle N^2 \rangle$. By performing a Legendre transform for a one component system from $y^{(0)} = \underline{S} = f(\underline{U}, N, \underline{V}) \rightarrow y^{(2)} = P\underline{V}/T = f(1/T, \mu/T, \underline{V})$, and then substituting Equation (10-57) into the expression

$$\left(\frac{\partial y^{(2)}}{\partial \mu}\right)_{\underline{V},T} = \left(\frac{\partial\left(P\underline{V}/T\right)}{\partial \mu}\right)_{\underline{V},T} \tag{5}$$

the result is Equation (10-58):

$$\langle N\rangle = kT\left(\frac{\partial \ln \Xi}{\partial \mu}\right)_{\underline{V},T} = \frac{1}{\beta\Xi}\left(\frac{\partial \Xi}{\partial \mu}\right)_{\underline{V},T} \tag{10-58}$$

where $\Xi\left(T,\underline{V},\mu\right) = \sum_{N=0}^{\infty}\lambda^N Q_N\left(T,\underline{V}\right) = \sum_{N=0}^{\infty} e^{\beta\mu N} Q_N\left(T,\underline{V}\right)$ (10-31)

$<N^2>$ can be determined by using the probability density function, Equation (10-10)

$$\langle N^2\rangle = \sum_N N^2 P(N) = \frac{\sum_N N^2 e^{N\beta\mu} Q_N\left(\underline{V},T\right)}{\Xi\left(\mu,\underline{V},T\right)} \tag{6}$$

We want some expression for $<N^2>$ that does not involve a summation. Noting that for each term in the summation of Equation (10-31):

$$\left(\frac{\partial^2\left(e^{N\beta\mu}Q_N\left(T,\underline{V}\right)\right)}{\partial \mu^2}\right)_{T,\underline{V}} = Q_N\left(\frac{\partial^2\left(e^{N\beta\mu}\right)}{\partial \mu^2}\right)_{T,\underline{V}} = \left(N\beta\right)^2 e^{N\beta\mu} Q_N \tag{7}$$

We can say that

$$\Xi\langle N^2\rangle = \frac{1}{\beta^2}\left(\frac{\partial^2\left(\sum_{N=0}^{\infty} e^{\beta\mu N} Q_N\right)}{\partial \mu^2}\right)_{T,\underline{V}} = \frac{1}{\beta^2}\left(\frac{\partial^2 \Xi}{\partial \mu^2}\right)_{T,\underline{V}} \tag{8}$$

Using the chain rule on Equation (10-58), we also see that

$$\left(\frac{\partial^2 \Xi}{\partial \mu^2}\right)_{T,\underline{V}} = \left(\frac{\partial}{\partial \mu}\left(\frac{\partial \Xi}{\partial \mu}\right)\right)_{\underline{V},T} = \left(\frac{\partial}{\partial \mu}\left(\beta\Xi\langle N\rangle\right)\right)_{\underline{V},T} \tag{9}$$

$$\left(\frac{\partial^2 \Xi}{\partial \mu^2}\right)_{T,\underline{V}} = \beta\left[\langle N\rangle\left(\frac{\partial \Xi}{\partial \mu}\right)_{\underline{V},T} + \Xi\left(\frac{\partial\langle N\rangle}{\partial \mu}\right)_{\underline{V},T}\right] = \beta^2\Xi\langle N\rangle^2 + \beta\Xi\left(\frac{\partial\langle N\rangle}{\partial \mu}\right)_{\underline{V},T} \tag{10}$$

Plugging this into Equation (8) gives

$$\langle N^2\rangle = \langle N\rangle^2 + \frac{1}{\beta}\left(\frac{\partial\langle N\rangle}{\partial \mu}\right)_{\underline{V},T} \tag{11}$$

Now we can substitute Equation (11) into Equation (4) to give

$$\sigma_N^2 = \langle N \rangle^2 + \frac{1}{\beta}\left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{\underline{V},T} - \langle N \rangle^2 = kT\left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{\underline{V},T} \tag{12}$$

Or, from Equation (2)

$$\sigma_\rho^2 = \frac{\sigma_N^2}{\underline{V}^2} = \frac{kT}{\left(V\langle N \rangle\right)^2}\left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{\underline{V},T} = -\frac{kT}{V^2}\left(\frac{\partial \left(1/\langle N \rangle\right)}{\partial \mu}\right)_{\underline{V},T} \tag{13}$$

From Equation (13), since *k, T,* μ and *V* are not functions of *N*, then it is obvious that $\sigma_\rho \propto N^{-1/2}$. Also, from Table 7.1 in the text, we see that $(\partial N/\partial\mu)_{T,\underline{V}} = A_{NN}^{-1}$ approaches infinity at the critical point. Conversely, $-kT/V^2$ approaches zero as *V* approaches infinity, which is the case for an ideal gas. This can also be shown by expressing Equation (13) in terms of the isothermal compressibility, κ_T:

From the Gibb's Duhem equation for a pure fluid at constant temperature:

$$0 = -\cancel{\underline{S}dT} + \underline{V}dP - Nd\mu \tag{14}$$

Taking the derivative with respect to *N* at constant *T* and $\underline{V}$:

$$\underline{V}\left(\frac{\partial P}{\partial N}\right)_{T,\underline{V}} = N\left(\frac{\partial \mu}{\partial N}\right)_{T,\underline{V}} \tag{15}$$

Next, noting that the isothermal compressibility can be expressed as:

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{N}{\underline{V}}\left(\frac{\partial \left(\underline{V}/N\right)}{\partial P}\right)_T = \frac{1}{N}\left(\frac{\partial N}{\partial P}\right)_{T,\underline{V}} \tag{16}$$

Substituting Equations (15) and (16) into Equation (13):

$$\sigma_\rho^2 = \frac{kT}{\underline{V}(V)^2}\kappa_T = \frac{kT}{\langle N \rangle (V)^3}\kappa_T \tag{17}$$

From Equation (17), it can be seen that $\sigma_\rho \propto N^{-1/2}$, that at the critical point, the fluctuations go to infinite since κ_T goes to infinite, and that at low densities, for an ideal gas:

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial \left(kT/P\right)}{\partial P}\right)_T = -\frac{1}{P} \tag{18}$$

and Equation (17) goes to zero at low densities, since *V* goes to infinity.