Chapter 7- Answers to selected exercises

1. Show that the entropy in the grand canonical ensemble can be written as

$$S = -k_B \sum_j P_j \ln P_j,$$

with probability P_j given by,

$$P_j = \Xi^{-1} \exp\left(-\beta E_j + \beta \mu N_j\right).$$

Show that this same form of entropy still holds in the pressure ensemble (with a suitable probability distribution).

2. Consider a classical ultrarelativistic gas of particles, given by the Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N} c \left| \vec{p_i} \right|,$$

where c is a positive constant, inside a container of volume V, in contact with a reservoir of heat and particles (at temperature T and chemical potential μ). Obtain the grand partition function and the grand thermodynamic potential. From a Legendre transformation of the grand potential, write an expression for the Helmholtz free energy of this system. To check your result, use the integral in equation (??) for obtaining an asymptotic form for the canonical partition function.

 $\ast\ast\ast$ As we have already calculated in a previous exercise, the canonical partition function is given by

$$Z_N = \frac{1}{N!} \left[\frac{8\pi V}{\left(h\beta c\right)^3} \right]^N.$$

Using this expression, we obtain the grand canonical partition function,

$$\Xi = \sum_{N=0}^{\infty} \exp(\beta \mu N) Z_N = \exp\left\{\frac{8\pi V}{\left(h\beta c\right)^3} \exp\left(\beta \mu\right)\right\},\,$$

from which we have the grand potential,

$$\Phi = -rac{1}{eta} rac{8\pi V}{\left(heta c
ight)^3} \exp\left(eta \mu
ight).$$

If we write $\exp(\beta\mu) = z$, the canonical partition function is given by

$$Z = \frac{1}{2\pi i} \oint \frac{\Xi\left(\beta, z, V\right)}{z^{N+1}} dz \sim \frac{1}{2\pi i} \oint \exp\left[Nf\left(z\right)\right] dz,$$

with

$$f(z) = \frac{8\pi v}{\left(h\beta c\right)^3} z - \ln z,$$

where v = V/N. From a saddle-point integration (see Appendix), we have

$$\frac{1}{N}\ln Z \sim f(z_o) = 1 - \ln \frac{(h\beta c)^3}{8\pi v}$$

It is interesting to note that the same expression comes from the asymptotic form

$$\frac{1}{N}\ln Z_N = \frac{1}{N}\ln\left\{\frac{1}{N!}\left[\frac{8\pi V}{(h\beta c)^3}\right]^N\right\}.$$

3. Obtain the grand partition function of a classical system of particles, inside a container of volume V, given by the Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N} \left[\frac{1}{2m} \vec{p}_i^2 + u\left(\vec{r}_i \right) \right].$$

Write the equations of state in the representation of the grand potential. For all reasonable forms of the single-particle potential $u(\vec{r})$, show that the energy and the pressure obey typical equations of an ideal gas.

4. Show that the average quadratic deviation of the number of particles in the grand canonical ensemble may be written as

$$\left\langle \left(\Delta N\right)^2 \right\rangle = \left\langle N_j^2 \right\rangle - \left\langle N_j \right\rangle^2 = z \frac{\partial}{\partial z} \left[z \frac{\partial}{\partial z} \ln \Xi \left(\beta, z\right) \right].$$

Obtain an expression for the relative deviation $\sqrt{\langle (\Delta N)^2 \rangle} / \langle N_j \rangle$ of an ideal gas of classical monatomic particles.

*** For a classical ideal gas of monatomic particles, we have

$$\langle N \rangle = z \frac{\partial}{\partial z} \ln \Xi \left(\beta, z \right) = \frac{zV}{h^3} \left(\frac{2\pi m}{\beta} \right)^{3/2}$$

and

$$\left\langle \left(\Delta N\right)^2 \right\rangle = z \frac{\partial}{\partial z} \left[z \frac{\partial}{\partial z} \ln \Xi \left(\beta, z\right) \right] = \frac{zV}{h^3} \left(\frac{2\pi m}{\beta} \right)^{3/2} = \left\langle N \right\rangle.$$

The relative deviation is thus of order $1/\sqrt{N}$.

5. Show that the average quadratic deviation of energy in the grand canonical ensemble may be written as

$$\left\langle \left(\Delta E\right)^2 \right\rangle = \left\langle E_j^2 \right\rangle - \left\langle E_j \right\rangle^2 = -\left(\frac{\partial U}{\partial \beta}\right)_{z,V},$$

where $U = \langle E_j \rangle$ is the thermodynamic internal energy in terms of β , z, and V. Hence, show that we may also write

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$$\left\langle \left(\Delta E\right)^2 \right\rangle = k_B T^2 \left[\left(\frac{\partial U}{\partial T}\right)_{\mu,V} + \frac{\mu}{T} \left(\frac{\partial U}{\partial \mu}\right)_{T,V} \right]$$

(you may use the Jacobian transformations of Appendix A.5). From this last expression, show that

$$\left\langle (\Delta E)^2 \right\rangle = \left\langle (\Delta E)^2 \right\rangle_{can} + k_B T^2 \left[\left(\frac{\partial U}{\partial N} \right)_{T,V} \left(\frac{\partial N}{\partial T} \right)_{V,\mu} \right. \\ \left. + \frac{\mu}{T} \left(\frac{\partial U}{\partial N} \right)_{T,V} \left(\frac{\partial N}{\partial \mu} \right)_{T,V} \right],$$

where

$$\left\langle \left(\Delta E\right)^2 \right\rangle_{can} = Nk_B T^2 c_V$$

is the average quadratic deviation of energy in the canonical ensemble. Finally, show that

$$\begin{bmatrix} \left(\frac{\partial U}{\partial N}\right)_{T,V} \left(\frac{\partial N}{\partial T}\right)_{V,\mu} + \frac{\mu}{T} \left(\frac{\partial U}{\partial N}\right)_{T,V} \left(\frac{\partial N}{\partial \mu}\right)_{T,V} \end{bmatrix}^2$$
$$= \frac{1}{T} \left(\frac{\partial N}{\partial \mu}\right)_{T,V} \left[\left(\frac{\partial U}{\partial N}\right)_{T,V} \right]^2 > 0,$$

since

$$\left\langle (\Delta N)^2 \right\rangle = k_B T \left(\frac{\partial N}{\partial \mu} \right)_{T,V} > 0.$$

6. At a given temperature T, a surface with N_o adsorption centers has $N \leq N_o$ adsorbed molecules. Suppose that there are no interactions between molecules. Show that the chemical potential of the adsorbed gas is given by

$$\mu = k_B T \ln \frac{N}{\left(N_o - N\right) a\left(T\right)}.$$

What is the meaning of the function a(T)?

*** Suppose an adsorbed particle has energy $-\epsilon$. We then write the canonical partition function

$$Z = \frac{N_o!}{N! (N_o - N)!} \exp\left(\beta \epsilon N\right).$$

Now we can use the grand-canonical formalism to write

$$\Xi = \sum_{N} \frac{N_o!}{N! (N_o - N)!} \exp(\beta \epsilon N) z^N = [z \exp(\beta \epsilon) + 1]^{N_o},$$

from which we have

$$N = \frac{N_o z}{z + \exp\left(-\beta\epsilon\right)},$$

and the expression for the chemical potential with $a = \exp(\beta \epsilon)$.

7. The grand partition function for a simplified statistical model is given by the expression

$$\Xi(z,V) = (1+z)^V \left(1+z^{\alpha V}\right),\,$$

where α is a positive constant. Write parametric forms of the equation of state. Sketch an isotherm of pressure versus specific volume (draw a graph to eliminate the variable z). Show that this system displays a (first-order) phase transition. Obtain the specific volumes of the coexisting phases at this transition. Find the zeros of the polynomial $\Xi(z, V)$ in the complex z plane, and show that there is a zero at z = 1 in the limit $V \to \infty$.

*** Note the structures of zeroes at z = -1 and $z = \exp \left[i\pi \left(2n+1\right)/(\alpha V)\right]$, for $n = 0, \pm 1, \dots$

Also, note the thermodynamic limit,

$$\frac{1}{V}\ln\Xi \to \ln(1+z) + \alpha\ln z, \quad \text{for} \quad z > 1$$

and

$$\frac{1}{V}\ln\Xi \rightarrow \ln\left(1+z\right), \quad \text{for} \quad z<1.$$

For z > 1, we have the equations of state

$$\frac{p}{k_B T} = \ln\left(1+z\right) + \alpha \ln z, \quad \text{and} \quad \frac{1}{v} = \frac{z^2 + \alpha \left(1+z\right)}{z \left(1+z\right)}$$

For z < 1, we have

$$\frac{p}{k_B T} = \ln(1+z)$$
, and $\frac{1}{v} = \frac{z}{1+z}$.

There is a first-order transition $\left[\Delta v = 4\alpha/(1+2\alpha)\right]$ at z = 1.