Solutions to Problem Set 3

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3.1 Boundary Conditions

(a) We have the energy of N point particles with periodic Boundary Conditions (BCs) given by

$$E = \frac{2\hbar^2\pi^2}{mL^3}\sum_{i=1}^{N}(n_{x_i}^2 + n_{y_i}^2 + n_{z_i}^2).$$

Now $n_{x_i}, n_{y_i}, n_{z_i} \in \mathbb{Z}$, therefore the number of states with an energy less than E is given by the "volume" of a $3N$ dimensional sphere.

$$R = \sqrt{\frac{EmL^2}{2\hbar^2\pi^2}}$$

thus we have the number of states with energy less than E, $\Phi(E)$

$$\begin{aligned}\Phi(E) &= V_{3N}(R) \\ &= \frac{\pi^{3N/2}R^{3N}}{\Gamma\left(\frac{3N}{2}+1\right)}\end{aligned}$$

where we've used the volume of the $3N$-dimensional sphere derived in class.

Using Stirling's approximation we see:

$$\begin{aligned}\Phi(E) &\approx \pi^{3N/2}\left(\frac{EmL^2}{2\hbar^2\pi^2}\right)^{3N/2}\left(\frac{3N}{2}\right)^{-3N/2}e^{3N/2}\sqrt{2\pi\frac{3N}{2}} \\ &= \sqrt{3\pi N}\left(\frac{EmL^2e}{3\hbar^2\pi N}\right)^{3N/2}\end{aligned}$$

We want the number of states between energy E and $E+\delta E$. This should be the volume of the shell between the corresponding radii, ie the hypersurface area times the width of the shell:

$$\begin{aligned}\Omega_P(E) &= \frac{d\Phi}{dR}\delta R = \frac{d\Phi}{dE}\delta E \\ &= \frac{3N}{2}\sqrt{3\pi N}\left(\frac{EmL^2e}{3\hbar^2\pi N}\right)^{3N/2-1}\frac{mL^2e}{3\hbar^2\pi N}\delta E\end{aligned}$$

which gives

$$\boxed{\Omega_P(E) = \frac{3N}{2E}\sqrt{3\pi N}\left(\frac{EmL^2e}{3\hbar^2\pi N}\right)^{3N/2}} \tag{1}$$

The number of states for the Dirichlet Boundary Conditions can be inferred from comparing the energies of the different systems. We see that

$$E_D = 4E_P \Rightarrow R_D = 2R_P \tag{2}$$

Noting the factor of 2^{-3N} that limits the volume considered to the positive "quadrant" of the $3N$sphere, we see

$$\boxed{\Omega_D(E) = 2^{-3N}\Omega_P(E)\left(\frac{R_D}{R_P}\right)^{3N} = \Omega_P(E)} \tag{3}$$

Thus the number of states with the periodic boundary conditions is the same as the number of states with Dirichlet boundary conditions.

(b) The Neumann boundary conditions require that the derivative of the wavefunction be zero at the boundaries. This yields a cosine like solution (Dirichlet boundary conditions lead to a sine like solution). Both the Dirichlet and the Neumann solutions have the same wavelength, and thus the same energies in corresponding states. Thus the number of states for the Neumann boundary conditions must be the same as the number for the Dirichlet boundary conditions.

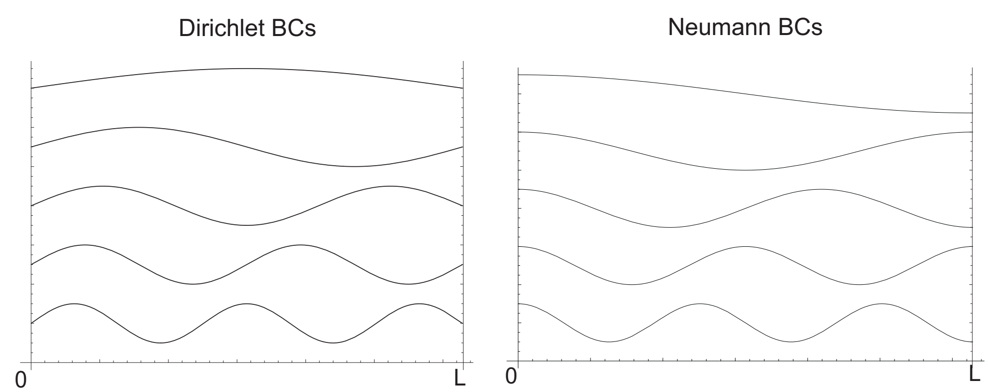

Figure 1: The solution to the Dirichlet boundary conditions have the same wavelengths and energies as the solutions to the Neumann boundary conditions, thus there will be the same number of states with energy less than E in both cases.

□

3.2 Magnetization with Temperature

Reif §3.2: Consider a system of N localized weakly interacting particles, each of spin $\frac{1}{2}$ and magnetic moment μ, located in an external magnetic field H. This system was already discussed in Problem 2.4.

(a) Using the expression for $\ln \Omega(E)$ calculated in Problem 2.4b and the definition $\beta = \partial \ln \Omega / \partial E$, find the relation between the absolute temperature T and the total energy E of this system.

(b) Under what circumstances is T negative?

(c) The total magnetic moment M of this system is related to its energy E. Use result of part (a) to find M as a function of H and the absolute temperature T.

(a) Recall the result of problem 2.4(a), $\ln \Omega(E)$ of the system is

$$\ln \Omega(E) = N \ln N - \ln 2\mu H - \frac{N - E/\mu H}{2} \ln \frac{N - E/\mu H}{2} - \frac{N + E/\mu H}{2} \ln \frac{N + E/\mu H}{2}$$

Using the definition of β,

$$\begin{aligned}
\beta &= \frac{\partial \ln \Omega(E)}{\partial E} \\
&= \frac{1}{2\mu H} \ln \frac{N - E/\mu H}{2} - \frac{N/2 - E/2\mu H}{N/2 - E/2\mu H}\left(-\frac{1}{2\mu H}\right) \\
&\quad - \frac{-1}{2\mu H} \ln \frac{N + E/\mu H}{2} - \frac{N/2 + E/2\mu H}{N/2 + E/2\mu H} \frac{1}{2\mu H} \\
&= \frac{1}{2\mu H} \ln \frac{N\mu H - E}{N\mu H + E}
\end{aligned}$$

Since $\beta = \frac{1}{k_B T}$ this is, $\frac{2\mu H}{k_B T} = \ln \frac{N\mu H - E}{N\mu H + E}$. If we write E in terms of T,

$$\begin{aligned}
e^{\frac{2\mu H}{k_B T}} &= \frac{N\mu H - E}{N\mu H + E} \\
\frac{E}{N\mu H}\left(1 + e^{\frac{2\mu H}{k_B T}}\right) &= 1 - e^{\frac{2\mu H}{k_B T}} \\
\frac{E}{N\mu H} &= \frac{1 - e^{\frac{2\mu H}{k_B T}}}{1 + e^{\frac{2\mu H}{k_B T}}} = -\tanh \frac{\mu H}{k_B T}.
\end{aligned} \tag{4}$$

(b) Using the result of (a), this problem is straight forward. Since $\beta = \frac{1}{2\mu H} \ln \frac{N\mu H - E}{N\mu H + E} = \frac{1}{k_B T}$, we require $\beta < 0$ for $T < 0$. μ and H being positive, we have $\frac{N\mu H - E}{N\mu H + E} < 1$ which gives us $E > 0$.

(c) For the spin model, $E = -(n_1 - n_2)\mu H$ whereas $M = (n_1 - n_2)\mu$. Thus, $M = -\frac{E}{H}$. Use the result of part (a), we get

$$M = N\mu \tanh \frac{\mu H}{k_B T}.$$

□

3.3 Spin Systems in a Magnetic Field

Reif §3.3: Consider two spin systems A and A' placed in an ecternal field H. System A consists of N weakly interacting localized particles of spin $\frac{1}{2}$ and magnetic moment μ. Similarly, system A' consists of N' weakly interacting localized particles of spin $\frac{1}{2}$ and magnetic moment μ'. The two systems are initially isolated with respective total energies $bN\mu H$ and $b'N\mu' H$. They are then placed in thermal contact with each other. Suppose that $|b| \ll 1$ and $|b'| \ll 1$ so that the simple expressions of problem 2.4c can be used for the densities of states of the two systems.

(a) In the most probably sistuation corresponding to the final thermal equilibrium, how is the energy $\tilde{E}$ of the system A related to the energy $\tilde{E}'$ of system A'?

(b) What is the value of the energy $\tilde{E}$ of system A?

(c) What is the heat Q absorbed by system A in going from the initial situation to the final situation when it is in equilibrium with A'?

(d) What is the probability $P(E)dE$ that A has its final energy in the range between E and $E + dE$.

(e) What is the dispersion $(\Delta * E)^2 \equiv \overline{(E - \tilde{E})^2}$ of the energy E of system A in the final equilibrium situation?

(f) What is the value of the relative energy spread $|\Delta * E/\tilde{E}|$ in the case when $N' \gg N'$?

From section we know that the number of states in such a system from problem 2.4 in Reif is

$$\Omega(E) = \frac{\delta E}{\sqrt{2\pi\mu^2 H^2 N}} e^{-\frac{E^2}{2\mu^2 H^2 N}}$$

(a) At equilibrium the total entropy is maximized, such that the temperatures (and therefore

β must be equal in the two systems

$$\begin{aligned}
\frac{\partial \ln \Omega}{\partial E} &= \frac{\partial \ln \Omega'}{\partial E'} \\
\frac{\partial}{\partial E}\frac{-E^2}{2\mu^2 H^2 N} &= \frac{\partial}{\partial E'}\frac{-E'^2}{2\mu'^2 H^2 N'} \\
\frac{\tilde{E}}{\mu^2 N} &= \frac{\tilde{E}'}{\mu'^2 N'} \\
\Rightarrow \tilde{E} &= \tilde{E}'\frac{\mu^2 N}{\mu'^2 N'}
\end{aligned}$$

(b) Noting that the total energy is conserved we have

$$\begin{aligned}
\tilde{E} &= E_{tot} - \tilde{E}' \\
\tilde{E} &= H(bN\mu + b'N'\mu') - \tilde{E}\frac{\mu'^2 N'}{\mu^2 N} \\
\Rightarrow \tilde{E} &= \frac{H(bN\mu + b'N'u')}{1 + \mu'^2 N'/\mu^2 N}
\end{aligned}$$

Hence

$$\boxed{\tilde{E} = \frac{\mu^2 N H(bN\mu + b'N'\mu')}{\mu^2 N + \mu'^2 N'}} \tag{5}$$

(c) Since the system is siolated and only in thermal contact with each other all the energy transferred must be heat, therefore

$$\begin{aligned}
Q &= \Delta E \\
&= \frac{H(bN\mu + b'N'u')}{1 + \mu'^2 N'/\mu^2 N} - bN\mu H
\end{aligned}$$

$$\boxed{Q = \frac{NN'H(b'\mu'\mu^2 - b\mu'^2\mu)}{\mu^2 N + \mu'^2 N'}} \tag{6}$$

(d) We have

$$\Omega(E) \propto \delta E \exp[-\frac{E^2}{2\mu^2 H^2 N}] \qquad \Omega'(E') \propto \exp[-\frac{E'^2}{2\mu'^2 H^2 N'}]$$

The probability for system A to be in a state with energy between E and $E + dE$ is

$$\begin{aligned}
P_A(E) &\propto \Omega(E)\Omega'(E^(o) - E) \\
&= \delta E \exp[-\frac{E^2}{2\mu^2 H^2 N} - \frac{(E^(o) - E)^2}{2\mu'^2 H^2 N'}] \\
&= \delta E \exp[-\frac{\mu' N' E^2 + \mu^2 N(E^(o) - E)^2}{2\mu^2\mu'^2 H^2 N N'}] \\
&= \delta E \exp[-\frac{E^2(\mu'^2 N' + \mu^2 N) - 2\tilde{E}E(\mu'^2 N' + \mu^2 N)}{2\mu^2\mu'^2 H^2 N N'}] \exp[-\frac{\mu^2 N(E^(o))^2}{2\mu^2\mu'^2 H^2 N N'}]
\end{aligned}$$

Since $E^(o)$ and $\tilde{E}$ are constants we can mulitply by exponentials of them and still maintain proportionality, thus dropping the $(E^(o))^2$ term and completin the square with $\tilde{E}$:

$$P_A(E) \propto \delta E \exp[-\frac{(E^2 - 2\tilde{E}E - E^2)(\mu^2 N + \mu'^2 N')}{2\mu^2\mu'^2 N N' H^2}]$$

Normalizing we see:

$$\boxed{P_A(E) = \frac{\delta E}{\sqrt{2\pi}\sigma} e^{-(E-\tilde{E})^2/2\sigma^2}}$$

where $\sigma^2 \equiv \frac{\mu^2\mu'^2 H^2 N N'}{\mu^2 N + \mu'^2 N'}$.

(e) As we can see in the formulation above, the probability $P_A(E)$ is a gaussian, with variance σ^2 as defined above.

(f) Using the results from above we see

$$\begin{aligned}
\left|\frac{\Delta * E}{\tilde{E}}\right| &= \frac{\mu\mu' H \left(\frac{NN'}{\mu^2 N + \mu'^2 N'}\right)^{1/2}}{\frac{\mu^2 N H (bN\mu + b'N'\mu'}{\mu^2 N + \mu'^2 N'}} \\
&= \frac{\mu\mu' H (NN')^{1/2}}{\mu'^2 N H [bN\mu + b'N'\mu']} (\mu^2 N + \mu'^2 N')^{1/2} \\
&\approx \frac{\mu'}{\mu b' N^{1/2}}
\end{aligned}$$

□

3.4 Mixture of Ideal Gases

Reif §3.5: A system consists of N_1 molecules of type 1 and N_2 molecules of type 2 confined within a box of volume V. The molecules are supposed to interact very weakly so that they constitute an ideal gas mixture.

(a) How doe the total number of states $\Omega(E)$ in the range between E and $E + \delta E$ depend on the volume V of this system? You may treat the problem classically.

(b) Use this result to find the equation of state of this system, i.e., to find its mean pressure $\bar{p}$ as a function of V and T.

(a) According to Reif §2.5.14, the total number of states has the following dependence on V:

$$\boxed{\Omega(E) \propto V^{N_1+N_2}}$$

(b) We have

$$\begin{aligned}\bar{p} &= \frac{1}{\beta}\frac{\partial \ln \Omega}{\partial V} \\ &= \frac{1}{\beta}\frac{\partial}{\partial V}[(N_1 + N_2)\ln V] \\ &= \frac{1}{\beta}\frac{N_1 + N_2}{V}\end{aligned} \tag{7}$$

Hence we have the equation of state:

$$\boxed{\bar{p} = \frac{N_1 + N_2}{V} kT}$$

□