Statistical Mechanics

Problem Sheet 2

Magnets and Oscillators

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Magnets and oscillators

2.1

(i) The energy levels are given by:

$$E_{\pm} = \pm \mu_B B \tag{1}$$

The single particle partition function is:

$$Z_1 = e^{-\beta \mu_B B} + e^{\beta \mu_B B} = 2\cosh\left(\beta \mu_B B\right) \tag{2}$$

(ii) The partition function for N non-interacting particles is:

$$Z = Z_1^N = \left[2\cosh\left(\beta \mu_B B\right)\right]^N \tag{3}$$

so that the internal energy is:

$$\begin{aligned} U &= -\frac{\partial \ln Z}{\partial \beta} \\ &= -N\frac{\partial \ln\left[2\cosh\left(\beta \mu_B B\right)\right]}{\partial \beta} \\ &= -N\mu_B B \tanh\left(\beta \mu_B B\right) \end{aligned} \tag{4}$$

The heat capacity is:

$$C_B = \left(\frac{\partial U}{\partial T}\right)_B = Nk_B\left(\frac{\theta}{T}\right)^2 \frac{1}{\cosh^2\left(\theta/T\right)} \tag{5}$$

where we identify the temperature scale:

$$\theta \equiv \frac{\mu_B B}{k_B} \tag{6}$$

The maximum of C_B can be derived by setting the derivative to zero. Denoting $x = \theta/T$, we have:

$$\begin{aligned} \frac{\partial C_B}{\partial x} &\propto -2x^2\frac{\sinh x}{\cosh^3 x} + 2x\frac{1}{\cosh^2 x} \\ &= 2x\frac{1 - x\tanh x}{\cosh^2 x} \end{aligned} \tag{7}$$

Thus, the maximum of C_B occurs at $x = \tanh x$, which is approximately $x = 1.20$. Therefore, the maximum of C_B occurs at:

$$T_{\text{peak}} = \frac{\theta}{1.20} = 0.83\frac{\mu_B B}{k_B} \tag{8}$$

(iii) With $B = 2\,\mathrm{T}$ and $\mu_B = 9.27 \times 10^{-24}\,\mathrm{J/T}$, we have:

$$T_{\text{peak}} = 1.119\,\mathrm{K} \tag{9}$$

at which the heat capacity of the system is significant.

(iv) At high T, we have $\theta/T \ll 1$, so that $\cosh(\theta/T) \approx 1$ and $C_B \propto T^{-2}$. At low T, we have $\theta/T \gg 1$, so that:

$$C_B \propto \frac{1}{T^2}\frac{e^{\theta/T}}{e^{2\theta/T}} \propto \frac{e^{-\theta/T}}{T^2} \tag{10}$$

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2.2

The partition function for a single particle in a harmonic oscillator potential is:

$$Z_1 = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+1/2)} = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} = \frac{1}{2\sinh(\beta\hbar\omega/2)} \tag{11}$$

The partition function for N non-interacting particles is:

$$Z = Z_1^N = \frac{1}{\left[2\sinh(\beta\hbar\omega/2)\right]^N} \tag{12}$$

The internal energy is:

$$\begin{aligned} U &= -\left(\frac{\partial \ln Z}{\partial \beta}\right)_V \\ &= \frac{N\hbar\omega}{2} + \frac{N\hbar\omega}{\exp(\beta\hbar\omega) - 1} \end{aligned} \tag{13}$$

so that the specific heat is:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = Nk_B \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{\exp(\beta\hbar\omega)}{\left[\exp(\beta\hbar\omega) - 1\right]^2} = Nk_B \left[\frac{\beta\hbar\omega/2}{\sinh(\beta\hbar\omega/2)}\right]^2 \tag{14}$$

In high temperature limit, we have $\beta\hbar\omega \ll 1$, so that $C_V \to Nk_B$. In low temperature limit, we have $\beta\hbar\omega \gg 1$, so that $C_V \to 0$.

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2.3

The free energy of a single particle in a harmonic oscillator potential is:

$$F_1 = -k_B T \ln Z_1 = -k_B T \ln\left[\frac{1}{2\sinh(\beta\hbar\omega/2)}\right] \tag{15}$$

so that the entropy (scaled by k_B) is:

$$\frac{S_1}{k_B} = -\frac{1}{k_B}\left(\frac{\partial F_1}{\partial T}\right)_V = \ln\left[\frac{1}{2\sinh(\theta/T)}\right] + \frac{\theta}{T}\frac{\cosh(\theta/T)}{\sinh(\theta/T)} \tag{16}$$

where we define the temperature scale $\theta \equiv \hbar\omega/2k_B$.

We require the internal energy of system, defined as:

$$U = -\left(\frac{\partial \ln Z_1}{\partial \beta}\right)_V = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{\exp(2\theta/T) - 1} \tag{17}$$

to equal $(m + 1/2)\hbar\omega$.

This puts a constraint on the temperature:

$$\frac{1}{\exp(2\theta/T) - 1} = m \tag{18}$$

or equivalently $e^{2\theta/T} = 1 + 1/m$.

Substituting this into the entropy expression, we have:

$$\begin{aligned}\frac{S_1}{k_B} &= -\ln\left(\sqrt{1+1/m} - \frac{1}{\sqrt{1+1/m}}\right) + (1+2m)\ln\sqrt{1+1/m} \\ &= -\ln\left(\frac{1}{\sqrt{m^2+m}}\right) + (1+2m)\ln\sqrt{1+1/m} \\ &= (m+1)\ln(m+1) - m\ln m\end{aligned} \tag{19}$$

which is the desired result.

When $m \to 0$, we have $S_1 \to 0$. This means that the entropy is zero (which is an arbitrary reference value) when every particle is in the ground state.

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2.4

(i) The single particle partition function is:

$$\begin{aligned} Z_M &= \sum_{k=-J}^{J} \exp\left(\beta k g_J \mu_B B\right) \\ &= \sum_{k=-J}^{J} \exp\left(kC\right) \\ &= \frac{e^{-JC} - e^{(J+1)C}}{1 - e^{C}} \\ &= \frac{\sinh\left[(J+1/2)C\right]}{\sinh\left(C/2\right)} \end{aligned} \tag{20}$$

where $C \equiv g_J \mu_B B / k_B T$.

(ii) Consider the free energy for $\mathcal{N} = NV$ particles:

$$F = \mathcal{N} F_1 = -\mathcal{N} k_B T \ln Z_M \tag{21}$$

The total magnetic moment is:

$$m = -\mathcal{N} \left(\frac{\partial F_1}{\partial B}\right)_T \tag{22}$$

so that the magnetization is:

$$
\begin{aligned}
M &= \frac{m}{V} \\
&= -N\left(\frac{\partial F_1}{\partial B}\right)_T \\
&= -N\frac{g_J\mu_B}{k_BT}\left(\frac{\partial F_1}{\partial C}\right)_T \\
&= Ng_J\mu_B\left[\frac{J+1/2}{\tanh\left[(J+1/2)C\right]} - \frac{1/2}{\tanh\left(C/2\right)}\right] \\
&= Ng_J\mu_B\frac{1}{C}\left[\frac{(J+1/2)C}{\tanh\left[(J+1/2)C\right]} - \frac{C/2}{\tanh\left(C/2\right)}\right]
\end{aligned}
\tag{23}
$$

Thus, the susceptibility can be taken as:

$$
\begin{aligned}
\chi &= \frac{\mu_0 M}{B} \\
&= \frac{\mu_0 N g_J^2\mu_B^2}{k_BT}\frac{1}{C^2}\left[\frac{(J+1/2)C}{\tanh\left[(J+1/2)C\right]} - \frac{C/2}{\tanh\left(C/2\right)}\right] \\
&\approx \frac{\mu_0 N g_J^2\mu_B^2}{k_BT}\frac{1}{C^2}\left(\frac{\left[(J+1/2)C\right]^2}{3} - \frac{C^2/4}{3}\right) \\
&= \frac{\mu_0 N g_J^2\mu_B^2}{3k_BT}J(J+1)
\end{aligned}
\tag{24}
$$

which reduces to the Curie law for $J = 1/2$.

(iii) Define the partition function for a harmonic oscillator as:

$$
Z_{\text{SHO}}(\hbar\omega) = \frac{1}{2\sinh\left(\beta\hbar\omega/2\right)} \tag{25}
$$

We can check that Z_M is a ratio of two partition functions:

$$
Z_M = \frac{Z_{\text{SHO}}(g_J\mu_B B)}{Z_{\text{SHO}}[(2J+1)g_J\mu_B B]} \tag{26}
$$

Consider the logarithm of $-Z_M$:

$$
-\ln Z_M = -\ln Z_{\text{SHO}}(g_J\mu_B B) + \ln Z_{\text{SHO}}[(2J+1)g_J\mu_B B] \tag{27}
$$

This means that the free energy is that of a harmonic oscillator with frequency $g_J\mu_B B$ minus that of a harmonic oscillator with frequency $(2J+1)g_J\mu_B B$.

(iv) Given the form of Z_M as a ratio of harmonic oscillator partition functions, we can write the internal energy as:

$$\begin{aligned}
U &= -\left(\frac{\partial \ln Z_M}{\partial \beta}\right)_V \\
&= -\left(\frac{\partial \ln Z_{\text{SHO}}(g_J \mu_B B)}{\partial \beta}\right)_V + \left(\frac{\partial \ln Z_{\text{SHO}}[(2J+1) g_J \mu_B B]}{\partial \beta}\right)_V \\
&= U_{\text{SHO}}(g_J \mu_B B) - U_{\text{SHO}}[(2J+1) g_J \mu_B B]
\end{aligned} \tag{28}$$

This implies that the heat capacity can be written as a difference of those for the two harmonic oscillators:

$$\begin{aligned}
C_V &= \left(\frac{\partial U}{\partial T}\right)_V \\
&= C_{V,\text{SHO}}(g_J \mu_B B) - C_{V,\text{SHO}}[(2J+1) g_J \mu_B B] \\
&= k_B \left[\frac{\beta \hbar \omega_1/2}{\sinh(\beta \hbar \omega_1/2)}\right]^2 - k_B \left[\frac{\beta \hbar \omega_2/2}{\sinh(\beta \hbar \omega_2/2)}\right]^2
\end{aligned} \tag{29}$$

where for simplicity we define the frequencies:

$$\hbar \omega_1 \equiv g_J \mu_B B \qquad \hbar \omega_2 \equiv (2J+1) g_J \mu_B B \tag{30}$$

We can define the temperature scale:

$$\phi \equiv \frac{\hbar \omega}{k_B} = \frac{g_J \mu_B B}{k_B} \tag{31}$$

so that the heat capacity becomes:

$$C_V = k_B \left[\frac{\phi/2}{\sinh(\phi/2)}\right]^2 - k_B \left[\frac{(2J+1)\phi/2}{\sinh[(2J+1)\phi/2]}\right]^2 \tag{32}$$

As shown in the figures, higher J shifts the maximum of the heat capacity towards lower temperatures. In the limit $J \to \infty$, the heat capacity peaks at $T = 0$. Therefore, it is possible to plot the heat capacity as a function of T for a given system and determine J from the position of the peak.

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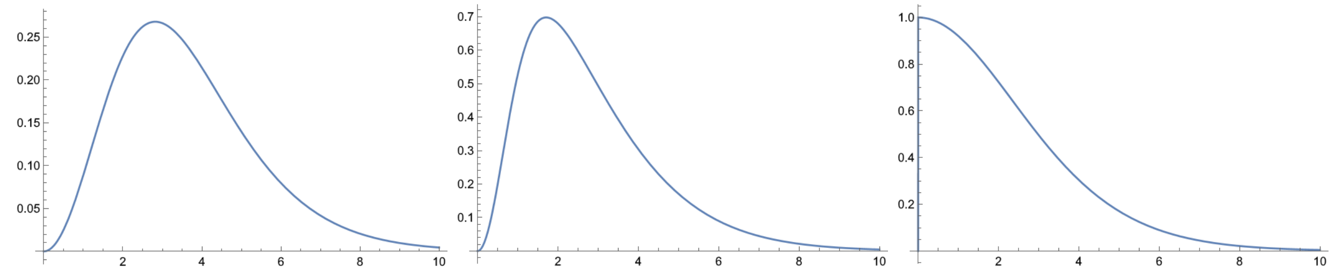

Figure 1: Heat capacity for $J = 1/2$, $J = 3/2$ and $J \to \infty$.

2.5

(i) Consider a single three-dimensional harmonic oscillator with characteristic frequencies ω_i, $i = 1, 2, 3$. The energy levels are given by:

$$E_{n_1,n_2,n_3} = \hbar\omega_1\left(n_1 + \frac{1}{2}\right) + \hbar\omega_2\left(n_2 + \frac{1}{2}\right) + \hbar\omega_3\left(n_3 + \frac{1}{2}\right) \tag{33}$$

The single particle partition function, denoted $Z_1^{(3)}$, is:

$$\begin{aligned} Z_1^{(3)} &= \sum_{n_1,n_2,n_3} e^{-\beta E_{n_1,n_2,n_3}} \\ &= \sum_{n_1} e^{-\beta\hbar\omega_1\left(n_1+\frac{1}{2}\right)} \sum_{n_2} e^{-\beta\hbar\omega_2\left(n_2+\frac{1}{2}\right)} \sum_{n_3} e^{-\beta\hbar\omega_3\left(n_3+\frac{1}{2}\right)} \\ &= Z_{1,x}Z_{1,y}Z_{1,z} \end{aligned} \tag{34}$$

Assuming identical frequencies $\omega_i = \omega$, we have:

$$Z_1^{(3)} = Z_1^3 \tag{35}$$

Then the partition function for N non-interacting three-dimensional harmonic oscillators is:

$$Z^{(3)} = (Z_1^{(3)})^N = (Z_1^3)^N = Z_1^{3N} \tag{36}$$

Since the partition function contains all information about the thermodynamics of the system, N non-interacting three-dimensional harmonic oscillators is equivalent to $3N$ one-dimensional harmonic oscillators.

(ii) Given $\omega = 2\pi\nu = 3.3 \times 10^{13}\,\text{rads}^{-1}$, we have the specific heat:

$$C_V = 3Nk_B\left[\frac{\beta\hbar\omega/2}{\sinh\left(\beta\hbar\omega/2\right)}\right]^2 \tag{37}$$

Defining the temperature scale $\theta \equiv \hbar\omega/2k_B = 124.8\,\mathrm{K}$, we have:

$$C_V = 3Nk_B \left[\frac{\theta/T}{\sinh(\theta/T)}\right]^2 \tag{38}$$

The function $x^2/\sinh^2 x$ has a maximum of unity at $x = 0$, so the maximum of C_V is $3Nk_B$ as $T \to \infty$. At room temperature (taken as $T_{\mathrm{room}} = 298\,\mathrm{K}$), we have:

$$\frac{C_V}{3Nk_B} = \left[\frac{\theta/T_{\mathrm{room}}}{\sinh(\theta/T_{\mathrm{room}})}\right]^2 \approx 0.94 \tag{39}$$

This means that the specific heat of the system is already significant at room temperature.

(iii) We make the change to temperature scale:

$$\theta = \frac{\hbar\omega}{2k_B} = 748.7\,\mathrm{K} \tag{40}$$

The new fraction for the heat capacity is:

$$\frac{C_V}{3Nk_B} = \left[\frac{\theta/T_{\mathrm{room}}}{\sinh(\theta/T_{\mathrm{room}})}\right]^2 \approx 0.017 \tag{41}$$

which is significantly smaller due to a higher temperature scale.

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2.6

(i) Suppose that out of the total N particles, rN are the in the higher energy state E_+ and $(1-r)N$ are in the lower energy state E_-. We assume $r > 0.5$. We could write the entropy as:

$$S = -k_B \sum_{-,+} p_i \ln p_i = -k_B \left[r \ln r + (1-r)\ln(1-r)\right] \tag{42}$$

and the internal energy:

$$U = rNE_+ + (1-r)NE_- \tag{43}$$

But the temperature is defined via the entropy as:

$$
\begin{aligned}
T &= -\left(\frac{\partial U}{\partial S}\right)_V \\
&= -\left(\frac{\partial U}{\partial r}\right)_V \left(\frac{\partial r}{\partial S}\right)_V \\
&= \frac{N(E_+ - E_-)}{k_B[\ln r - \ln(1-r)]}
\end{aligned} \tag{44}
$$

Since $r > 1 - r$ and both quantities are less than unity, we have $\ln r - \ln(1-r) < 0$. Therefore, the effective temperature is negative, which shows that the system cannot be in equilibrium.

Note the second derivative of the entropy with respect to U:

$$
\begin{aligned}
\left(\frac{\partial^2 S}{\partial U^2}\right)_V &= -\left[\frac{\partial(1/T)}{\partial U}\right]_V \\
&= -\left[\frac{\partial(1/T)}{\partial r}\right]_V \left(\frac{\partial r}{\partial U}\right)_V \\
&= -\frac{k_B}{N^2(E_+ - E_-)^2}\left(\frac{1}{r} + \frac{1}{1-r}\right)
\end{aligned} \tag{45}
$$

Since this is a negative quantity, the system is still in equilibrium, i.e., $C_V > 0$.

(ii) The swapping operation is equivalent to the exchange of the ratios r and $1 - r$, i.e., the substitution $r \to 1 - r$. The entropy is invariant under this operation, but the temperature changes sign:

$$
T \to \frac{E_+ - E_-}{k_B[\ln(1-r) - \ln r]} \tag{46}
$$

(iii) Taking instead the limit $r \to 1$, we have $\ln r \to 0$ and $\ln(1-r) \to -\infty$, so that the temperature tends to zero:

$$
T \to -\frac{E_+ - E_-}{k_B \ln(1-r)} \to 0 \tag{47}
$$

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