Physics 727: Assignment 2

(to be submitted by Tuesday, February 27, 2024)

1. In class, we considered the quantum rigid rotor (discussed in §4.4.4 of Kennett's book). The Hamiltonian for the spherically symmetric case is
$$\hat{H} = \frac{1}{2I}\hat{\mathbf{J}} \cdot \hat{\mathbf{J}} = \frac{1}{2I}\hat{J}^2.$$
Here, I is the rotor's moment of inertia, and $\hat{\mathbf{J}} = (\hat{J}_x, \hat{J}_y, \hat{J}_z)$ is the vector of angular momentum operators. The states $|j, m\rangle$ are simulataneous eigenstates of $\hat{J}^2$ and $\hat{J}_z$, viz.,
$$\hat{J}^2|j,m\rangle = \hbar^2 j(j+1)|j,m\rangle \text{ with } j = 0, 1, 2, ...,$$
$$\text{and } \hat{J}_z|j,m\rangle = \hbar m|j,m\rangle \text{ with } m = -j, -j+1, \ldots, 0, \ldots, j-1, j.$$

   (a) The corresponding partition function can be expressed as
$$Z = \operatorname{tr} e^{-\beta \hat{H}} = \sum_{j=0}^{\infty} g_j e^{-\beta h_j \varepsilon_0}.$$
   Reproduce the derivation in detail, and show that that $g_j = 2j + 1$, $h_j = j(j+1)$, and $\varepsilon_0 = \hbar^2/2I$.

   (b) Plot the internal energy $U = -Z^{-1}dZ/d\beta$ and heat capacity $C_V = dU/dT$ of this system. For simplicity, work in units where $\varepsilon_0 = k_B = 1$. Note that there is no closed-from solution for the infinite sum in the partition function, so it is necessary to apply a cutoff, e.g., $\sum_{j=0}^{\infty} \approx \sum_{j=0}^{1000}$. Suggest a criterion for selecting the cutoff scale.

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Z = Sum[(2 j + 1) Exp[-j (j + 1) \[Beta]], {j, 0, 1000}];
U = -D[Z, \[Beta]]/Z;
Plot[U /. \[Beta] -> 1/T, {T, 0, 1}]
CV = D[U /. \[Beta] -> 1/T, T];
Plot[CV, {T, 0.001, 3}, PlotRange -> All]
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   Comment on the shape of the C_V plot. (The peak is analogous to the Schottky anomaly in solids.)

   (c) Integrate the ratio of specific heat to temperature, according to
$$S = \int_0^T dT' \, \frac{C_V(T')}{T'},$$
   to obtain the entropy as a function of temperature. You will have to carry out the integral numerically for a mesh of T values. Comment on the resulting plot.

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Table[NIntegrate[CV/T, {T, 0, Tmax}], {Tmax, 0.1*Range[30]}];
ListPlot[%]
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2. A quantum system is defined by the Hamiltonian
$$\hat{H}/\varepsilon_0 = -|1\rangle\langle 2| - |2\rangle\langle 1| + |2\rangle\langle 3| + |3\rangle\langle 2| + \sum_{j=1}^{3} j|j\rangle\langle j|.$$
Suppose that this system has reached equilibrium in contact with a heat bath of inverse temperature β.

   (a) Compute the partition function $Z = \operatorname{tr} \exp(-\beta \hat{H})$. You should be able to show that
$$Z = e^{-2\beta\varepsilon_0}\left[1 + 2\cosh\sqrt{3}\beta\varepsilon_0\right].$$

(b) Find the Helmholtz free energy F.

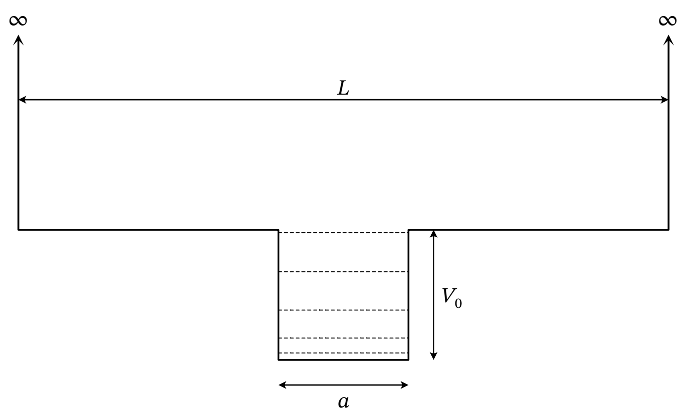
(c) Find the internal energy U. Demonstrate that $U \to (2-\sqrt{3})\varepsilon_0$ at low temperature and $U \to 2\varepsilon_0$ at high temperature.

(d) Find the entropy S. Demonstrate that $S \to 0$ at low temperature and $S \to k_B \ln 3$ at high temperature.

3. The Hamiltonian for a one-electron system consists of a free-kinetic-energy term plus a finite-square-well potential that is $a = 0.5$ nm wide and $V_0 = 25$ eV deep. For these parameters, the finite well produces five bound states at the following energies (measured with respect to the energy zero at the lip of the well).

$$\begin{aligned} \varepsilon_1 &= -23.877\,\text{eV} \\ \varepsilon_2 &= -20.539\,\text{eV} \\ \varepsilon_3 &= -15.095\,\text{eV} \\ \varepsilon_4 &= -7.838\,\text{eV} \\ \varepsilon_5 &= -0.218\,\text{eV} \end{aligned}$$

Suppose that the finite square well is itself centered within an infinite square well of width $L \gg a$. The remaining eigenstates (countably infinite, of energy $\varepsilon_6, \varepsilon_7, \varepsilon_8, \dots$) exhibit energy levels quantized by the confinement to L.



(a) Produce simple analytical estimates for the energy levels in the two regimes, $\varepsilon_1, \dots, \varepsilon_5$ and $\varepsilon_6, \varepsilon_7, \dots$.

(b) Show that the partition function can be reliably approximated by

$$Z = \sum_{j=1}^{5} e^{-\beta\varepsilon_j} + \frac{L}{\hbar}\sqrt{\frac{m_e}{2\pi\beta}}.$$

(c) Show that the specific heat is just $C_V = k_B/2$ in the macroscopic ($L \to \infty$) limit. Explain why levels $\varepsilon_1, \dots, \varepsilon_5$ make no contribution.

(d) Suppose that, instead of having a single width-a, depth-V_0 well (an a-well) at its centre, the bottom of the width-L, infinite-depth well (L-well) is randomly sprinkled with a-wells. If b is average separation between a-wells, then $n = L/(a+b)$ is the total number of a-wells within the L-well, and $\eta = 1/(a+b) = n/L$ is their linear density. Argue that

$$Z \approx n \sum_{j=1}^{5} e^{-\varepsilon_j/k_B T} + \frac{L}{h}\sqrt{2\pi m_e k_B T}$$

is a reasonable approximation in the regime $a \ll b \ll L$.

(e) Show that

$$C_V = k_B \frac{d}{d(k_B T)} \left[\frac{\sum_{j=1}^{5} \varepsilon_j e^{-\varepsilon_j / k_B T} + k_B T (k_B T / E(b))^{1/2}}{\sum_{j=1}^{5} e^{-\varepsilon_j / k_B T} + (k_B T / E(b))^{1/2}} \right]$$

where

$$E(b) = \frac{0.4789\,\mathrm{eV\,nm}^2}{(0.5\,\mathrm{nm} + b)^2}$$

is an energy scale set by the average separation of the a-wells. You may find it helpful to note that $m_e c^2 = 0.511\,\mathrm{MeV}$ and $hc = 1240\,\mathrm{eV\,nm}$.

(f) Suppose that $b = 15\,\mathrm{nm}$. Plot the internal energy U and the heat capacity $C = dU/dT$ as a function of $k_B T$ over the domain $0.1\,\mathrm{eV} < k_B T < 50\,\mathrm{eV}$. Identify where the Dulong-Petit law sets in. Compare this to the room temperature value, $k_B T_{\mathrm{room}} = 25.8\,\mathrm{meV}$.

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Ewell[b_] = 0.4789/(0.5 + b)^2
\[Epsilon] = { -23.877, -20.539, -15.095, -7.838, -0.218 }
Z0 = Sum[Exp[-\[Epsilon][[i]]/kT], {i, 1, 5}]
Z1 = Sum[\[Epsilon][[i]] Exp[-\[Epsilon][[i]]/kT], {i, 1, 5}]
E0 = Ewell[15]
U = (Z1 + kT (kT/E0)^(1/2))/(Z0 + (kT/E0)^(1/2))
Plot[U, {kT, 0.1, 50}, PlotRange -> All]
Plot[CV, {kT, 0.1, 50}, PlotRange -> All]
```