5.6: Problems

5.5 Decoupling quantal Hamiltonians

Prove the “decoupling Hamilton implies factoring partition function” theorem of section 5.1.2 for quantal systems.

5.6 Schottky anomaly

A molecule can be accurately modeled by a quantal two-state system with ground state energy 0 and excited state energy ϵ. Show that the internal specific heat is

$$c_V^{\text{int}}(T) = k_B\left(\frac{\epsilon}{k_BT}\right)^2 \frac{e^{-\epsilon/k_BT}}{\left(1+e^{-\epsilon/k_LT}\right)^2} \tag{5.6.1}$$

Sketch this specific heat as a function of k_B/ϵ. How does the function behave when $k_BT \ll \epsilon$ and $k_BT \gg \epsilon$?

5.7 Simple harmonic oscillator

Suppose a molecule can be accurately modeled as a harmonic oscillator of natural frequency ω.

a. Find the expected internal energy of one such molecule, written as a sum of the ground state energy plus a temperature-dependent part.

b. Show that the internal specific heat is

$$c_V^{\text{int}}(T) = k_B\left(\frac{\hbar\omega}{k_BT}\right)^2 \frac{e^{-\hbar\omega/k_BT}}{\left(1-e^{-\hbar\omega/k_HT}\right)^2}. \tag{5.6.2}$$

c. Show that at low temperatures $(k_BT \ll \hbar\omega)$,

$$c_V^{\text{int}}(T) \approx k_B\left(\frac{\hbar\omega}{k_BT}\right)^2 e^{-\hbar\omega/k_BT} \tag{5.6.3}$$

whereas at high temperatures (k_BT\rr$\hbar\omega$),

$$c_V^{\text{int}}(T) \approx k_B. \tag{5.6.4}$$

d. (Optional.) Show that the leading quantal correction to the high-temperature specific heat is

$$c_V^{\text{int}}(T) = k_B\left[1-\frac{1}{12}x^2+\mathcal{O}\left(x^3\right)\right], \quad \text{where} \quad x=\frac{\hbar\omega}{k_BT}. \tag{5.6.5}$$

e. Sketch the internal specific heat as a function of $k_BT/\hbar\omega$.

5.8 Simple harmonic oscillator — entropy

I was speaking with someone who claimed that thermodynamics didn’t apply to systems of interacting atoms, or to living things, or to anything other than the ideal gas. He challenged me “What’s the entropy of a pendulum? The answer is that entropy doesn’t apply to a pendulum!” Answer his question for a pendulum in the simple harmonic oscillator approximation, with natural frequency ω and temperature *T*.

5.9 Kinetic energy in air

What is the kinetic energy is a cubic liter of air (mostly nitrogen and oxygen) at one atmosphere pressure and room temperature? At one atmosphere pressure and temperature 600 K? Use classical mechanics, and express your answer both in Joules and in the commercial unit kilowatt-hours. (Clue: If you calculate the average kinetic energy of one molecule, you’re working way too hard.) Why doesn’t anyone exploit all this valuable energy lying around in every cubic meter of air?

5.10 Conceptual comparison

a. Explain qualitatively why the results of the two previous problems are parallel at low temperatures.

b. (Harder.) Explain qualitatively both high temperature results. (Clue: At high temperatures, the average energy per particle in the Schottky case approaches $\epsilon/2$. Why?)

5.11 Compressibility of a diatomic gas

Find the isothermal compressibility κ_T for an ideal diatomic gas, where each molecule is modeled as a dumbbell with moment of inertia I.

5.12 Systems with a small number of states

(This problem requires *no calculation*! All the answers can be found in your head.) A collection of non-interacting particles is in thermal equilibrium. Each particle has only three energy eigenvalues, namely 0, ϵ, and 4ϵ.

a. What is the criterion for "high temperature" in this situation?

b. Suppose there are three non-degenerate energy eigenstates. At high temperatures, what is the average energy of each particle? (Clue: The answer is not 4ϵ.)

c. Now suppose that the lower two energy eigenstates are non-degenerate, but that there are two independent states with energy 4ϵ. What is the average energy per particle at high temperatures in this case?

5.13 Anharmonic oscillator

The energy eigenvalues of a simple harmonic oscillator are equally spaced, and we have explored the consequences of this for the heat capacity of a collection of harmonic oscillators. Suppose an anharmonic oscillator is approximately harmonic (with natural frequency ω_0) for small energies, but that for large energies (greater than, say, E_x) the eigenvalues become more closely spaced as energy increases. At temperatures greater than E_x/k_B, will the heat capacity of a collection of such anharmonic oscillators be greater than or less than that of a collection of harmonic oscillators with the same natural frequency ω_0? Why?

5.14 Descriptive features of models

(This problem is stolen from a GRE Physics test.)

Two possible models for a diatomic ideal gas are the rigid dumbbell (model R; two point particles connected by a rigid rod) and the springy dumbbell (model S; two point particles connected by a spring). In classical statistical mechanics, which of the following statements is true?

a. Model R has a specific heat $c_V = \frac{3}{2} k_B$.

b. Model S has a smaller specific heat than model R.

c. Model S is always correct.

d. Model R is always correct.

e. The choice between models R and S depends on the temperature.

5.15 An n-state system, qualitatively

A model molecule has n equally-spaced energy levels, all of them non-degenerate, with energy spacing ϵ. Thus as n varies from 2 to ∞ this model interpolates between the Schottky system of problem 5.6 and the simple harmonic oscillator of problem 5.7.

a. Find a low-temperature approximation for the specific heat that is independent of n.

b. At high temperatures, the specific heat approaches zero. What is the criterion for "high temperature"?

c. At high temperatures, what is the expected energy of this model?

d. There is a theorem stating that at any fixed positive temperature, the specific heat must increase with increasing n. Assume this theorem and use it to prove that as n increases, the maximum in the specific heat versus temperature curve becomes higher.

5.16 An n-state system, quantitatively

Show that the system of the previous problem has internal specific heat

$$c_V^{\text{int}}(T) = k_B \left[\left(\frac{\epsilon}{k_B T} \right)^2 \frac{e^{-\epsilon/k_B T}}{\left(1 - e^{-\epsilon/k_B T}\right)^2} - \left(\frac{n\epsilon}{k_B T} \right)^2 \frac{e^{-n\epsilon/k_B T}}{\left(1 - e^{-n\epsilon/k_B T}\right)^2} \right]. \tag{5.6.6}$$

Does this expression have the proper limits when $n = 2$ and when $n \to \infty$?