

# Assignment 9

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PC2135

Thermodynamics and Statistical Mechanics

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## Problem 1

[13 pts] In class, we have discussed the probability to find a state in a system that has a fixed temperature  $T$ , and this probability is given by  $e^{-\beta E}/Z$ , where  $\beta = 1/(kT)$ ,  $E$  is the energy of this state and  $Z = \sum e^{-\beta E}$  is the partition function. In this problem, we discuss this probability distribution in more detail. In particular, we would like to understand the fluctuations of energy around its average value.

(1) (2 points) Denote the energy of the system by  $U$ . Show that the average value of  $U^n$  is given by

$$\overline{U^n} = \frac{(-1)^n \partial^n Z}{Z \partial \beta^n} \quad (1)$$

(2) (2 points) The fluctuations of the energy around its average value can be characterised by the standard deviation,  $\sigma_U$ , which is determined by  $\sigma_U^2 = \overline{(U - \overline{U})^2}$ . Show that

$$\sigma_U^2 = \overline{U^2} - (\overline{U})^2 \quad (2)$$

Namely, the standard deviation squared is the average of the square minus the square of the average.

(3) (6 points) Show that the standard deviation of energy can be related to  $C = \frac{\partial \overline{U}}{\partial T}$ , the heat capacity of the system under constant volume and particle number, via

$$\sigma_U = kT \sqrt{C/k} \quad (3)$$

(4) (3 points) How do the heat capacity  $C$  and energy  $\overline{U}$  scale with the number of particles in all systems we have examined so far, which is denoted by  $N$ ? Namely, if  $C \sim N^{\alpha_C}$  and  $\overline{U} \sim N^{\alpha_U}$ , what are  $\alpha_C$  and  $\alpha_U$ ? How does the relative deviation of energy scale with the particle number? Namely, if  $\sigma_U/\overline{U} \sim N^\alpha$ , what is  $\alpha$ ?

## Solution

### Part (1): Generating-function identity for $\overline{U^n}$

The partition function is  $Z = \sum_s e^{-\beta E_s}$ , where the sum runs over all microstates  $s$ . Taking the  $n$ -th derivative with respect to  $\beta$ :

$$\frac{\partial^n Z}{\partial \beta^n} = \sum_s (-E_s)^n e^{-\beta E_s} = (-1)^n \sum_s E_s^n e^{-\beta E_s} \quad (4)$$

The thermal average of  $U^n$  is

$$\overline{U^n} = \frac{1}{Z} \sum_s E_s^n e^{-\beta E_s} \quad (5)$$

Comparing with Equation 4 immediately gives

$$\overline{U^n} = \frac{(-1)^n \partial^n Z}{Z \partial \beta^n} \quad (6)$$

So  $Z$  essentially acts as a moment-generating function: each derivative with respect to  $\beta$  pulls down a factor of  $(-E)$ .

### Part (2): Variance identity

Expanding the definition of the variance:

$$\sigma_U^2 = \overline{(U - \overline{U})^2} = \overline{U^2 - 2U\overline{U} + (\overline{U})^2} \quad (7)$$

Since  $\overline{U}$  is a constant (the thermal average), it factors out of the averaging:

$$\sigma_U^2 = \overline{U^2} - 2\overline{U} \cdot \overline{U} + (\overline{U})^2 = \overline{U^2} - (\overline{U})^2 \quad (8)$$

### Part (3): Relating $\sigma_U$ to the heat capacity

From part (1) with  $n = 1$ :

$$\overline{U} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta} \quad (9)$$

Differentiating Equation 9 with respect to  $\beta$ :

$$\frac{\partial \overline{U}}{\partial \beta} = -\frac{\partial^2 \ln Z}{\partial \beta^2} \quad (10)$$

The second derivative of  $\ln Z$  can be evaluated directly:

$$\frac{\partial^2 \ln Z}{\partial \beta^2} = \frac{\partial}{\partial \beta} \left( \frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \left( \frac{1}{Z} \frac{\partial Z}{\partial \beta} \right)^2 = \overline{U^2} - (\overline{U})^2 = \sigma_U^2 \quad (11)$$

Therefore from Equation 10:

$$\sigma_U^2 = -\frac{\partial \overline{U}}{\partial \beta} \quad (12)$$

Now we convert to a temperature derivative. Since  $\beta = 1/(kT)$ :

$$\frac{d\beta}{dT} = -\frac{1}{kT^2} \quad (13)$$

By the chain rule:

$$\frac{\partial \overline{U}}{\partial \beta} = \frac{\partial \overline{U}}{\partial T} \frac{dT}{d\beta} = C \cdot (-kT^2) \quad (14)$$

Substituting Equation 14 into Equation 12:

$$\sigma_U^2 = CkT^2 \quad (15)$$

Taking the square root:

$$\sigma_U = kT \sqrt{\frac{C}{k}} \quad (16)$$

### Part (4): Scaling with particle number

In every system studied so far (ideal gas, Einstein solid, paramagnets, diatomic molecules), both the energy and heat capacity are extensive quantities, meaning they are proportional to the number of particles:

$$\begin{aligned}\bar{U} \propto N &\implies \alpha_U = 1 \\ C \propto N &\implies \alpha_C = 1\end{aligned}\tag{17}$$

From Equation 3, the standard deviation scales as

$$\sigma_U = kT\sqrt{C/k} \propto \sqrt{N}\tag{18}$$

so the relative fluctuation is

$$\frac{\sigma_U}{\bar{U}} \propto \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}} \implies \alpha = -\frac{1}{2}\tag{19}$$

For a macroscopic system with  $N \sim 10^{23}$ , the relative energy fluctuation is of order  $10^{-12}$ , which is completely negligible. This is why the canonical ensemble (fixed  $T$ ) and the microcanonical ensemble (fixed  $U$ ) give the same thermodynamic predictions for large systems.

## Problem 2

[14 pts] In class, we have discussed diatomic molecules made of two different atoms. In this problem, we will discuss diatomic molecules made of two identical atoms. In particular, we will investigate the behaviour of ordinary hydrogen,  $\text{H}_2$ , at low temperatures. The rotational energy of a hydrogen molecule is given by  $E(j) = \varepsilon j(j+1)$ , where the constant  $\varepsilon$  is 0.0076 eV and  $j$  is the orbital angular momentum. For each  $j$ , there are  $2j+1$  states. The set of allowed  $j$  values is determined by the spin configuration of the two atomic nuclei. There are four independent spin configurations, classified as a single “singlet” state and three “triplet” states. The time required for a molecule to convert between the singlet and triplet configurations is ordinarily quite long, so the properties of the two types of molecules can be studied independently. The singlet molecules are known as parahydrogen while the triplet molecules are known as orthohydrogen.

(1) (3 points) For parahydrogen, only the rotational states with even values of  $j$  are allowed. Use a computer to calculate the rotational partition function, average energy, and heat capacity of a parahydrogen molecule. Sketch the heat capacity as a function of  $kT/\varepsilon$ . When you calculate the partition function by a computer, you will need to truncate  $j$  at some appropriate value. You should determine the cutoff of  $j$  and numerically verify that ignoring the contributions from larger  $j$ 's does not induce a sizable error in the partition function.

(2) (3 points) For orthohydrogen, only the rotational states with odd values of  $j$  are allowed. Repeat part (1) for orthohydrogen.

(3) (3 points) At high temperatures, a sample of hydrogen gas will ordinarily consist of a mixture of 1/4 parahydrogen and 3/4 orthohydrogen. A mixture with these proportions is called normal hydrogen. Suppose that normal hydrogen is cooled to low temperature without allowing the spin configurations of the molecules to change. Sketch the rotational heat capacity of this mixture as a function of temperature. At what temperature does the rotational heat capacity fall to half its high-temperature value (i.e., to  $k/2$  per molecule)?

(4) (3 points) Suppose now that some hydrogen is cooled in the presence of a catalyst that allows the nuclear spins to frequently change alignment. In this case all values of  $j$  are allowed, but the odd- $j$  terms should be counted three times each because of the nuclear spin degeneracy. Calculate the rotational partition function, average energy, and heat capacity of this system, and plot the heat capacity as a function of  $kT/\varepsilon$ .

(5) (2 points) A deuterium molecule,  $\text{D}_2$ , has nine independent nuclear spin configurations, of which six are “symmetric” and three are “antisymmetric.” The rule for nomenclature is that the variety with more independent states gets called “ortho-,” while the other gets called “para-.” For orthodeuterium only even- $j$  rotational states are allowed, while for paradeuterium only odd- $j$  states are allowed. Suppose, then, that a sample of  $\text{D}_2$  gas, consisting of a normal equilibrium mixture of 2/3 ortho and 1/3 para, is cooled without allowing the nuclear spin configurations to change. Calculate and plot the rotational heat capacity of this system as a function of temperature.

### Solution

The rotational energy levels are  $E(j) = \varepsilon j(j+1)$  with degeneracy  $2j+1$ . Define the dimensionless temperature  $x = kT/\varepsilon$ , so  $\beta\varepsilon = 1/x$ . The partition function for a given set of allowed  $j$  values is

$$Z = \sum_j (2j+1) e^{-j(j+1)/x} \quad (20)$$

The average energy and heat capacity follow from

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta} = \varepsilon x^2 \frac{d \ln Z}{dx} \quad (21)$$

$$C = \frac{\partial \bar{E}}{\partial T} = kx^2 \frac{d}{dx} \left( x^2 \frac{d \ln Z}{dx} \right)$$

or equivalently from the fluctuation formula  $C = (\overline{E^2} - \bar{E}^2)/(kT^2)$ .

All sums are truncated at  $j_{\max} = 20$ , which gives  $E(20) = 420\varepsilon$ . The Boltzmann factor  $e^{-420/x}$  is negligible ( $< 10^{-180}$ ) even at the highest plotted temperature  $x = 10$ , so this cutoff is more than sufficient.

### Part (1): Parahydrogen (even $j$ )

For parahydrogen, the sum in Equation 20 runs over  $j = 0, 2, 4, \dots$ :

$$Z_{\text{para}} = \sum_{j \text{ even}} (2j+1)e^{-j(j+1)/x} = 1 + 5e^{-6/x} + 9e^{-20/x} + \dots \quad (22)$$

At low temperature ( $x \rightarrow 0$ ), the  $j = 0$  ground state dominates, so  $Z_{\text{para}} \rightarrow 1$  and  $C \rightarrow 0$ . At high temperature ( $x \gg 1$ ), many rotational levels are populated and  $C \rightarrow k$  (the classical rotational heat capacity for two degrees of freedom). In between,  $C$  actually overshoots  $k$  before settling down, which is typical of systems with a discrete energy gap.

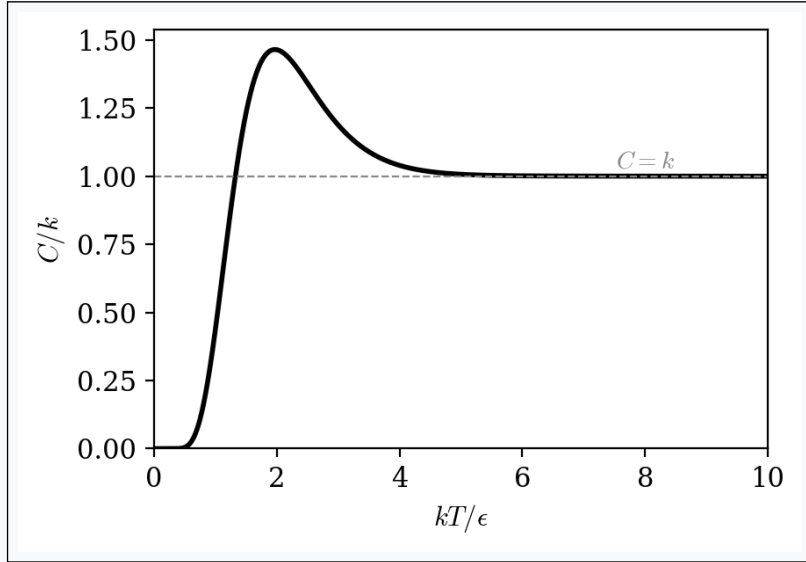


Figure 1: Heat capacity of parahydrogen (even  $j$  only) as a function of  $kT/\varepsilon$ . The peak near  $kT/\varepsilon \approx 2$  exceeds the classical limit  $k$  before settling to it at high temperatures.

### Part (2): Orthohydrogen (odd $j$ )

For orthohydrogen, the sum runs over  $j = 1, 3, 5, \dots$ :

$$Z_{\text{ortho}} = \sum_{j \text{ odd}} (2j+1)e^{-j(j+1)/x} = 3e^{-2/x} + 7e^{-12/x} + 11e^{-30/x} + \dots \quad (23)$$

At low temperature, the  $j = 1$  level dominates. The heat capacity again approaches zero as  $T \rightarrow 0$  and approaches  $k$  at high temperature, but the peak position and shape differ from the para case because the ground state has a finite energy  $2\varepsilon$ .

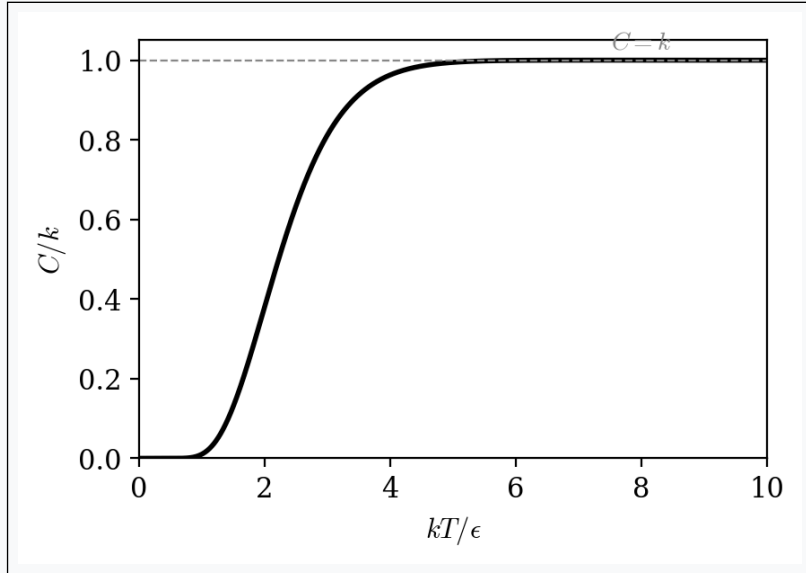


Figure 2: Heat capacity of orthohydrogen (odd  $j$  only) as a function of  $kT/\epsilon$ . The curve approaches zero at low  $T$  and the classical value  $k$  at high  $T$ .

### Part (3): Normal hydrogen

Normal hydrogen is a frozen mixture of  $1/4$  parahydrogen and  $3/4$  orthohydrogen (the high-temperature equilibrium ratio). Since the two species do not interconvert on the timescale of the cooling, the heat capacity of the mixture is simply the weighted sum:

$$C_{\text{normal}} = \frac{1}{4}C_{\text{para}} + \frac{3}{4}C_{\text{ortho}} \quad (24)$$

At high temperature, both species contribute  $C = k$ , so  $C_{\text{normal}} \rightarrow k$ . At low temperature, the ortho contribution dominates the approach to zero because its gap ( $2\epsilon$ ) is smaller than the para gap ( $6\epsilon$ ).

The temperature at which  $C_{\text{normal}} = k/2$  is found numerically to be  $kT/\epsilon \approx 1.67$ , i.e.,  $T \approx 1.67\epsilon/k \approx 147$  K.

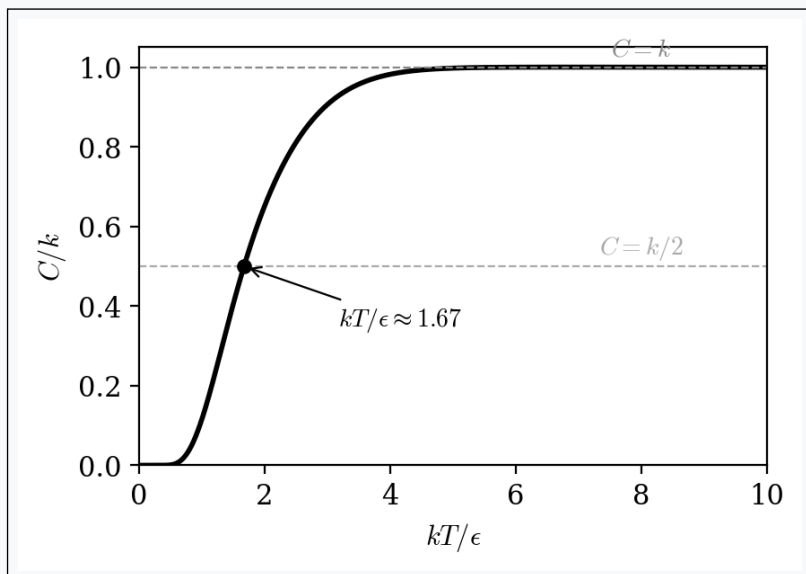


Figure 3: Heat capacity of normal hydrogen ( $1/4$  para +  $3/4$  ortho) as a function of  $kT/\epsilon$ . The dashed line marks  $C = k/2$ ; the crossing occurs near  $kT/\epsilon \approx 1.67$ .

#### Part (4): Equilibrium hydrogen with catalyst

When a catalyst allows free interconversion, the system explores all  $j$  values, but odd- $j$  states carry an additional degeneracy factor of 3 from the triplet nuclear-spin configuration (even- $j$  states have only the singlet, weight 1). The partition function is

$$Z_{\text{eq}} = \sum_{j \text{ even}} (2j+1)e^{-j(j+1)/x} + 3 \sum_{j \text{ odd}} (2j+1)e^{-j(j+1)/x} = Z_{\text{para}} + 3Z_{\text{ortho}} \quad (25)$$

The average energy and heat capacity are computed from Equation 21 using this combined partition function. This is *not* the same as a simple weighted sum of  $C_{\text{para}}$  and  $C_{\text{ortho}}$ , because we sum the partition function before differentiating, so the nuclear spin degeneracy changes the relative Boltzmann weights.

At high temperature,  $C \rightarrow k$  as usual. At low temperature, the  $j = 0$  ground state (para, weight 1) dominates and  $C \rightarrow 0$ . The interesting feature is the sharp Schottky-like peak at low temperature: it comes from the competition between the  $j = 0$  state (weight 1) and the  $j = 1$  state (weight  $3 \times 3 = 9$ ), which are close enough in energy for the spin degeneracy to matter.

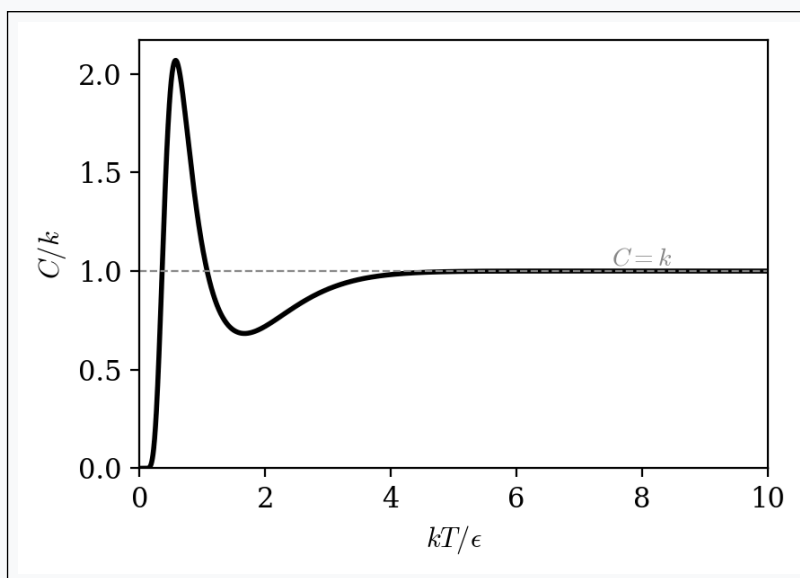


Figure 4: Heat capacity of equilibrium hydrogen (catalyst-assisted interconversion) as a function of  $kT/\epsilon$ . The sharp low-temperature peak arises from the nuclear-spin degeneracy of odd- $j$  states.

#### Part (5): Normal deuterium

For deuterium ( $D_2$ ):

- Orthodeuterium (6 symmetric spin states): even- $j$  rotational states
- Paradeuterium (3 antisymmetric spin states): odd- $j$  rotational states

At high temperature, the equilibrium mixture is  $6/9 = 2/3$  ortho and  $1/3$  para. Cooling without interconversion gives:

$$C_{\text{normal } D_2} = \frac{2}{3}C_{\text{ortho-}D_2} + \frac{1}{3}C_{\text{para-}D_2} \quad (26)$$

where  $C_{\text{ortho-}D_2}$  uses even- $j$  states (same functional form as parahydrogen) and  $C_{\text{para-}D_2}$  uses odd- $j$  states (same functional form as orthohydrogen). The actual rotational constant  $\epsilon$  for  $D_2$  is half that of  $H_2$  because of the doubled reduced mass, but since we plot as a function of  $kT/\epsilon$ , the functional form in reduced units is the same and only the mixture fractions change.

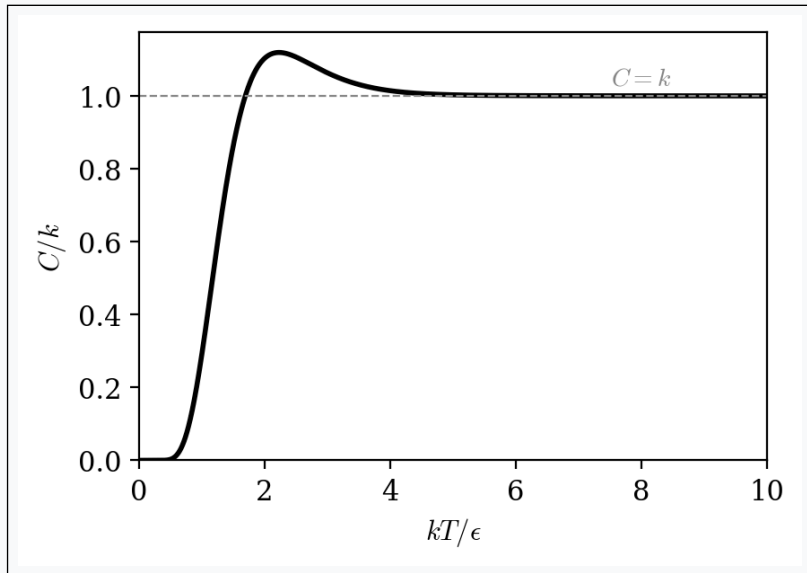


Figure 5: Heat capacity of normal deuterium ( $2/3$  ortho  $+1/3$  para) as a function of  $kT/\epsilon$ . The larger ortho fraction (even  $j$ , with its  $j = 0$  ground state) causes a steeper drop at low temperature compared to normal hydrogen.

### Problem 3

[13 pts] In this course, we have encountered the equipartition theorem in the first week, seen its manifestation in many examples, and learnt its proof. In this problem, we apply the equipartition theorem to a simple pendulum, which consists of a mass  $m$  that is attached to a massless string with length  $L$  (see figure below). Suppose the pendulum is in an environment with temperature  $T$ . We would like to discuss the effect of the thermal fluctuations on the position of this pendulum.

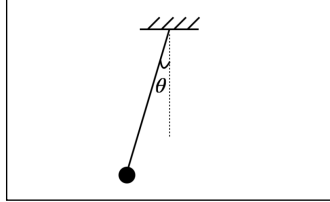


Figure 6: A simple pendulum consists of a mass  $m$  attached to a massless string of length  $L$ .

(1) (4 points) Suppose the mass  $m$  slightly moves away from its equilibrium position, so that the angle between the string and the vertical direction is  $\theta$  and the angular velocity is  $\omega$  (namely,  $\omega = d\theta/dt$  where  $t$  is time). What is the total energy of the pendulum, which includes both the kinetic energy and gravitational energy? Denote the gravitational acceleration by  $g$ , and assume  $\theta$  is small in order to simplify the result.

(2) (5 points) In thermal equilibrium at temperature  $T$ , what is  $\bar{\theta}$ , the average value of  $\theta$ ? What is  $\sigma_\theta$ , the standard deviation of  $\theta$ ? Similar to Problem 1, here the standard deviation of  $\theta$  is defined as  $\sigma_\theta = \sqrt{\overline{\theta^2} - (\bar{\theta})^2}$ .

(3) (4 points) Suppose  $T = 300$  K,  $L = 0.5$  m,  $m = 0.1$  kg and  $g = 10$  m/s<sup>2</sup>. What is the value of  $\sigma_\theta$ ? Is the assumption of a small  $\theta$  valid?

### Solution

#### Part (1): Energy of the pendulum

The mass  $m$  moves on a circular arc of radius  $L$ . Its velocity along the arc is  $v = L\omega$ , so the kinetic energy is

$$K = \frac{1}{2}mv^2 = \frac{1}{2}mL^2\omega^2 \quad (27)$$

The gravitational potential energy, measured from the lowest point of the swing, is

$$U = mgL(1 - \cos \theta) \quad (28)$$

For small  $\theta$ , we use  $\cos \theta \approx 1 - \theta^2/2$ , giving

$$U \approx \frac{1}{2}mgL\theta^2 \quad (29)$$

The total energy is therefore

$$E = \frac{1}{2}mL^2\omega^2 + \frac{1}{2}mgL\theta^2 \quad (30)$$

This has the form of two independent quadratic degrees of freedom: one kinetic ( $\omega$ ) and one potential ( $\theta$ ).

#### Part (2): Thermal averages

**Average angle:** The Boltzmann weight  $e^{-\beta E}$  with the energy in Equation 30 is an even function of  $\theta$  (the potential  $\propto \theta^2$ ). Therefore the probability distribution  $P(\theta) \propto e^{-\beta mgL\theta^2/2}$  is symmetric about  $\theta = 0$ , and

$$\bar{\theta} = 0 \quad (31)$$

**Standard deviation:** The energy Equation 30 consists of two independent quadratic terms. By the equipartition theorem, each quadratic degree of freedom carries an average energy of  $kT/2$ :

$$\overline{\frac{1}{2}mgL\theta^2} = \frac{1}{2}kT \implies \overline{\theta^2} = \frac{kT}{mgL} \quad (32)$$

Since  $\bar{\theta} = 0$ :

$$\sigma_\theta = \sqrt{\overline{\theta^2} - (\bar{\theta})^2} = \sqrt{\overline{\theta^2}} = \sqrt{\frac{kT}{mgL}} \quad (33)$$

This makes sense physically: a heavier mass or longer pendulum has a larger restoring torque  $mgL$ , so it resists thermal fluctuations more, while a higher temperature increases them.

### Part (3): Numerical evaluation

Substituting the given values into Equation 33:

$$\sigma_\theta = \sqrt{\frac{1.381 \times 10^{-23} \times 300}{0.1 \times 10 \times 0.5}} = \sqrt{\frac{4.14 \times 10^{-21}}{0.5}} = \sqrt{8.29 \times 10^{-21}} \quad (34)$$

$$\sigma_\theta \approx 9.1 \times 10^{-11} \text{ rad} \quad (35)$$

This is an extraordinarily small angle, about  $10^{-10}$  radians or roughly  $5 \times 10^{-9}$  degrees. The small-angle approximation  $\sin \theta \approx \theta$  has a relative error of order  $\theta^2/6 \sim 10^{-21}$ , so the assumption of small  $\theta$  is completely justified.

The point is that a macroscopic pendulum is so massive compared to the thermal energy scale  $kT$  that the thermal fluctuations are negligible. The restoring force  $mg$  is enormous compared to random thermal kicks.