Statistical Thermodynamics Second Homework Assignment

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One end of a flexible polymer consisting of 10^{20} *monomers is fixed from a ceiling so that the polymer is allowed to hang, and a* $4 \times 10^{-10}\,\mathrm{g}$ *weight is attached to the other end. The length of a single monomer is* $2\,\mathrm{nm}$ *and the temperature is fixed at* $300\,\mathrm{K}$. *Calculate the average potential energy of the weight. How much heat does the polymer exchange with its surroundings if the mass of the weight is doubled?*

Parameters

- $a = 2 \times 10^{-9}\,\mathrm{m}$, the length of a monomer
- $N = 10^{20}$, the total number of monomers
- $T = 300\,\mathrm{K}$, the absolute temperature
- $m = 4 \times 10^{-13}\,\mathrm{kg}$, the mass of the weight

Solution: Part 1

Note: Because the absolute temperature and pressure are fixed, the monomers form a canonical ensemble that is formally best described in terms of Gibbs free energy G and enthalpy H. However, I have used the more common quantities Helmholtz free energy F and internal energy E.

The energy contribution E of an individual monomer oriented at a polar angle θ and the average total energy of the system, respectively, are

$$E = -mga\cos\theta \qquad \text{and} \qquad \langle E \rangle = \langle Nmga\cos\theta \rangle = Nmga\,\langle \cos\theta \rangle$$

where

$$\langle \cos\theta \rangle = \int_\Gamma \cos\theta \rho(E)\,\mathrm{d}\Gamma$$

The probability $\rho(E)$ of a microstate with energy E is

$$\rho(E) = e^{-\beta(E-F)} = \frac{e^{-\beta E}}{Z_c}$$

The expression for $\langle \cos\theta \rangle$ thus becomes

$$\begin{aligned}\langle \cos\theta \rangle &= \int_\Gamma \cos\theta \left(\frac{e^{-\beta E}}{Z_c}\right) \mathrm{d}\Gamma = \frac{1}{Z_c}\int_\Gamma \cos\theta e^{-\beta E}\,\mathrm{d}\Gamma \\ &= \frac{1}{Z_c}\int_\Gamma \cos\theta e^{\beta mga\cos\theta}\,\mathrm{d}\Gamma = \frac{1}{Z_c}\int_\Gamma \cos\theta e^{\alpha\cos\theta}\,\mathrm{d}\Gamma\end{aligned}$$

where we define the constant $\alpha \equiv \beta mga$ for shorthand. The partition function Z_c is given by:

$$Z_c = e^{-\beta F} = \int_\Gamma e^{-\beta E}\,\mathrm{d}\Gamma = \int_\Gamma e^{\beta mga\cos\theta}\,\mathrm{d}\Gamma = \int_\Gamma e^{\alpha\cos\theta}\,\mathrm{d}\Gamma$$

The value $\langle \cos\theta \rangle$ is thus

$$\langle \cos\theta \rangle = \frac{\int_\Gamma \cos\theta e^{\alpha\cos\theta}\,\mathrm{d}\Gamma}{\int_\Gamma e^{\alpha\cos\theta}\,\mathrm{d}\Gamma}$$

In spherical coordinates, in terms of the element of solid angle $\mathrm{d}\Omega = \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$, the expression becomes

$$\langle \cos\theta \rangle = \frac{\int_\Gamma \cos\theta e^{\alpha\cos\theta}\,\mathrm{d}\Omega}{\int_\Gamma e^{\alpha\cos\theta}\,\mathrm{d}\Omega}$$

Formally, in spherical coordinates, the elements of the phase space are r, θ, and ϕ; however, only the polar angle θ is relevant to our problem since it is the only term contributing to a monomer's energy $E = -mga\cos\theta$. With this simplification, the average polar angle becomes

$$\langle \cos\theta \rangle = \frac{\int_0^\pi \cos\theta e^{\alpha\cos\theta}\sin\theta\,\mathrm{d}\theta}{\int_0^\pi e^{\alpha\cos\theta}\sin\theta\,\mathrm{d}\theta}$$

With the change of variables

$$u = \cos\theta \qquad \mathrm{d}u = -\sin\theta\,\mathrm{d}\theta \qquad u(0) = 1 \qquad u(\pi) = -1$$

the integrals become

$$\langle \cos\theta \rangle = \frac{\int_{-1}^1 u e^{\alpha u}\,\mathrm{d}u}{\int_{-1}^1 e^{\alpha u}\,\mathrm{d}u} = \frac{\cosh\alpha - \frac{1}{\alpha}\sinh\alpha}{\sinh\alpha} = \coth\alpha - \frac{1}{\alpha} = L(\alpha)$$

where $L(\alpha)$ denotes the Langevin function $\coth\alpha - \frac{1}{\alpha}$. The average energy is thus

$$\langle E \rangle = Nmga\,\langle \cos\theta \rangle = (Nmga)L(\alpha)$$

The value of the dimensionless constant α is

$$\alpha = \beta mga = \frac{mga}{k_B T} = \frac{(4 \times 10^{-13}\,\mathrm{kg})(9.8\,\mathrm{m\cdot s^{-2}})(2 \times 10^{-9}\,\mathrm{m})}{(300\,\mathrm{K})(1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}})}$$
$$= 1.89$$

The numerical value of the average energy is

$$\begin{aligned}
\langle E \rangle &= (Nmga)L(\alpha) = (Nmga)\left(\coth(\alpha) + \frac{1}{\alpha}\right) \\
&= \left[(10^{20})(4 \times 10^{-13}\,\mathrm{kg})(9.8\,\mathrm{m\cdot s^{-2}})(2 \times 10^{-9}\,\mathrm{m})\right]\left(\coth(1.89) + \frac{1}{1.89}\right) \\
&= (0.784\,\mathrm{J})\,(1.047 + 0.529) \\
&= 1.23\,\mathrm{J}
\end{aligned}$$

Solution: Part 2

We find the heat Q exchanged by the polymer with its surroundings in terms of the entropy change ΔS.

$$Q = T\Delta S = T\Delta\left(\frac{\langle E \rangle - F}{T}\right) = \Delta\big(\langle E \rangle - F\big)$$

The average energy and partition functions were already found to be

$$\langle E \rangle = (Nmga)L(\alpha)$$
$$Z_c = \int_0^{\pi} e^{\alpha\cos\theta}\sin(\theta)\,\mathrm{d}\theta = \frac{1}{\alpha}(e^{\alpha} - e^{-\alpha}) = \frac{2}{\alpha}\sinh\alpha$$

The Helmholtz free energy F is given

$$Z_c = e^{-\beta F} \quad\Longrightarrow\quad F = -\frac{1}{\beta}\ln(Z_c) = -\frac{1}{\beta}\ln\!\left(\frac{2}{\alpha}\sinh\alpha\right)$$

We then have

$$Q = \langle E \rangle_2 - F_2 - \big[\langle E \rangle_1 - F_1\big] = \langle E \rangle_2 - \langle E \rangle_1 + F_1 - F_2$$

where

$$\langle E \rangle_1 = (Nm_1ga)L(\alpha_1) \qquad \langle E \rangle_2 = (Nm_2ga)L(\alpha_2)$$
$$F_1 = -\frac{1}{\beta}\ln\!\left(\frac{2}{\alpha_1}\sinh\alpha_1\right) \qquad F_2 = -\frac{1}{\beta}\ln\!\left(\frac{2}{\alpha_2}\sinh\alpha_2\right)$$

Let $m_1 = 4 \times 10^{-13}\,\text{kg}$ be the original mass, and let $m_2 = 2m_1$ be the doubled mass. Reusing calculations from the previous part, we get the following numerical values:

$$\alpha_1 = \beta m_1 g a = 1.89 \qquad \alpha_2 = \beta m_2 g a = 2\alpha_1 = 3.78$$

$$N m_1 g a = 0.784\,\text{J} \qquad N m_2 g a = 2N m_1 g a = 1.568\,\text{J}$$

The energy contributions to the exchanged heat are:

$$\langle E \rangle_1 = (N m_1 g a) L(\alpha_1) = (0.784\,\text{J}) \left(\coth(1.89) + \frac{1}{1.89} \right) = 1.23\,\text{J}$$

$$\langle E \rangle_2 = (N m_2 g a) L(\alpha_2) = (1.568\,\text{J}) \left(\coth(3.78) + \frac{1}{3.78} \right) = 1.98\,\text{J}$$

$$F_1 = -\frac{1}{\beta} \ln\!\left(\frac{2}{\alpha_1} \sinh \alpha_1 \right) = (4.14 \times 10^{-21}\,\text{J}) \ln\!\left(\frac{2}{1.89} \sinh(1.89) \right) \approx 0\,\text{J}$$

$$G_2 = -\frac{1}{\beta} \ln\!\left(\frac{2}{\alpha_2} \sinh \alpha_2 \right) = (4.14 \times 10^{-21}\,\text{J}) \ln\!\left(\frac{2}{3.78} \sinh(3.78) \right) \approx 0\,\text{J}$$

Because the factor contributed by the thermodynamic beta is of the order 10^{-21}, the values of F_1 and F_2 are negligible compared to $\langle E \rangle_1$ and $\langle E \rangle_2$. The result for the heat exchanged by the polymer with its surroundings when the weight's mass is doubled is:

$$\begin{aligned} Q &= \langle E \rangle_2 - \langle E \rangle_1 + F_1 - F_2 \approx \langle E \rangle_2 - \langle E \rangle_1 \\ &= 1.98\,\text{J} - 1.23\,\text{J} \\ &= 0.75\,\text{J} \end{aligned}$$