

Phys 150 HW 6 solutions

Nelson, Problem 6.2, pg 239 (8 pts)

a) Because the boxes are isolated from the rest of the world, their total energy doesn't change and the sum of their temperatures doesn't change

$$E_{i,total} = E_{f,total} \quad (1)$$

$$E_{i,1} + E_{i,2} = E_{f,1} + E_{f,2} \quad (2)$$

$$N \frac{3}{2} k_B (T_{i,1} + T_{i,2}) = N \frac{3}{2} k_B (T_{f,1} + T_{f,2}) \quad (3)$$

$$(T_{i,1} + T_{i,2}) = (T_{f,1} + T_{f,2}) \quad (4)$$

Knowing that they come to the same final temperature $T_{f,1} = T_{f,2} = T_f$, this means

$$(T_{i,1} + T_{i,2}) = 2T_f \quad (5)$$

$$T_f = \frac{1}{2}(T_{i,1} + T_{i,2}) \quad (6)$$

b) The entropy of an ideal gas is given by the Sakur-Tetrode formula (see Nelson, p.201). In the case under consideration N and V are constant for both systems, so the entropy formula becomes

$$S = N \frac{3}{2} k_B \ln E + \text{const.} \quad (7)$$

To find the total change of total entropy, take the difference

$$\Delta S_{tot} = S_{f,tot} - S_{i,tot} \quad (8)$$

$$= S_{f,1} + S_{f,2} - S_{i,1} - S_{i,2} \quad (9)$$

$$= N \frac{3}{2} k_B (\ln E_{f,1} + \ln E_{f,2} - \ln E_{i,1} - \ln E_{i,2}) \quad (10)$$

$$= N \frac{3}{2} k_B \ln \frac{E_{f,1} E_{f,2}}{E_{i,1} E_{i,2}} = N \frac{3}{2} k_B \ln \frac{T_{f,1} T_{f,2}}{T_{i,1} T_{i,2}} = N \frac{3}{2} k_B \ln \frac{T_f^2}{T_{i,1} T_{i,2}} = N \frac{3}{2} k_B \ln \frac{(T_{i,1} + T_{i,2})^2}{4 T_{i,1} T_{i,2}} \quad (11)$$

c) Dividing the numerator and denominator in the argument of the logarithm above by $T_{i,2}^2$ gives

$$\Delta S_{tot} = N \frac{3}{2} k_B \ln \frac{(T_{i,1}/T_{i,2} + 1)^2}{4 T_{i,1}/T_{i,2}} \quad (12)$$

and substituting $X = T_{i,1}/T_{i,2}$ yields

$$\Delta S_{tot} = N \frac{3}{2} k_B \ln \frac{(X + 1)^2}{4X}. \quad (13)$$

To determine that $\Delta S_{tot} \geq 0$ it suffices to show that the argument in the logarithm $g(X) = (X + 1)^2/(4X) \geq 1$. Taking the first and second derivatives

$$g(X) = \frac{(X + 1)^2}{4X} = \frac{X}{4} + \frac{1}{2} + \frac{1}{4X} \quad (14)$$

$$g'(X) = \frac{1}{4} - \frac{1}{4X^2} \quad (15)$$

$$g''(X) = \frac{1}{2X^3} \quad (16)$$

$$(17)$$

and noting that $X \geq 0$, we see that $g''(X) > 0$ and that $g'(X) = 0$ when (and only when) $X = 1$. Therefore, $g(X) \geq 1$.

d) ΔS_{tot} will be zero only when $T_{i,1} = T_{i,2}$ because no heat flows when two systems at the same temperature come into contact.

Nelson, Problem 6.4, pg 239 (6 pts)

a) Let d_1 be the distance the ball moves as the spring relaxes upon reduction of the external force from f to f_1 . Note that, after it is “suddenly reduced”, the external force is constant. Therefore, the “work done against the external force” is simply $W_{\text{useful}} = f_1 d_1$. To determine d_1 , we note that it is the difference between the position at which the spring force balanced the initial force $x_i = f/k$ and the position at which the spring force balances the reduced force $x_f = f_1/k$. Therefore,

$$d_1 = f_1/k - f/k = (f_1 - f)/k < 0, \quad (18)$$

where the sign indicates that the displacement took place in a direction that reduced the compression/extension of the spring, and

$$W_{\text{useful}} = f_1 d_1 = f_1(f_1 - f)/k = (f_1^2 - f_1 f)/k. \quad (19)$$

b) To maximize W_{useful} with respect to f_1 , set the derivative equal to zero and solve for f_1

$$\frac{dW_{\text{useful}}}{df_1} = (2f_1 - f)/k = 0 \rightarrow f_1 = f/2. \quad (20)$$

When $f_1 = f/2$,

$$W_{\text{useful}} = (f_1^2 - f_1 f)/k = (f^2/4 - f^2/2)/k = -f^2/4k, \quad (21)$$

where the sign is consistent with work having been done “against” the external force.

c) The process would be most efficient if the force were reduced by a factor of 2 with every step.

Nelson, Problem 6.6 pg 240 (3 pts)

Discher found $\sqrt{\langle(\Delta x)^2\rangle} = 35 \text{ nm}$. The average energy stored in the “springiness” of the polymer network along the x-direction is therefore $k(\Delta x)^2/2$. EQUIPARTITION! When the potential energy of a subsystem in contact with a thermal reservoir can be written as the sum of terms of the form kx^2 , then each of the displacement variables shares average thermal energy $\frac{1}{2}k_B T$ in equilibrium. (See Your Turn 6F on Nelson, p. 219.) Therefore,

$$\frac{1}{2}k(\Delta x)^2 = \frac{1}{2}k_B T \rightarrow k = \frac{k_B T}{(\Delta x)^2} = \frac{4.1 \text{ pN} \cdot \text{nm}}{(35 \text{ nm})^2} = 3.3 \cdot 10^{-3} \text{ pN nm}^{-1}. \quad (22)$$

Nelson, Problem C.6.11, pg 586 (4 pts)

EQUIPARTITION AGAIN! When the potential energy of a subsystem in contact with a thermal reservoir can be written as the sum of terms of the form kx^2 , then each of the displacement variables shares average thermal energy $\frac{1}{2}k_B T$ in equilibrium. (See Your Turn 6F on Nelson, p. 219.) The kinetic energy $\frac{1}{2}mv^2$ has the right form. To determine the form of the potential energy, consider how the vertical displacement of the point mass, Δz depends on its mean-square displacement from equilibrium in the horizontal plane Δr . For small displacements, $\Delta z = \Delta r \tan \theta$, where θ is the angle the pendulum makes with the vertical axis. Draw a figure to convince yourself that $\tan \theta = (\Delta r)/L$, where L is the length of the pendulum. Therefore, the gravitational potential energy of the pendulum has the right form as well: $mg\Delta z = mg\Delta r \tan \theta = mg(\Delta r)^2/L$.

So equipartition applies, and there will be $\frac{1}{2}k_B T$ of energy in each degree of freedom. Note that there are effectively only three degrees of freedom: two kinetic (velocity in the vertical direction is “frozen out” because it is opposed by the force of gravity) and one potential (gravitational potential energy is not a function of θ , only r). Therefore, the mean translational energy of the pendulum is

$$\frac{1}{2}m\langle v_x \rangle^2 + \frac{1}{2}m\langle v_y \rangle^2 = k_B T = 4.1 \text{ pN nm} = 4.1 \cdot 10^{-12} \cdot 10^{-9} \text{ J} = 4.1 \cdot 10^{-21} \text{ J}. \quad (23)$$

and the mean square displacement of the pendulum is

$$\frac{mg\langle \Delta r \rangle^2}{L} = \frac{1}{2}k_B T \quad (24)$$

$$\langle \Delta r \rangle^2 = \frac{Lk_B T}{2mg} = \frac{1.2 \text{ m} \cdot 4.1 \cdot 10^{-21} \text{ J}}{2 \cdot 0.4 \text{ kg} \cdot 9.8 \text{ m s}^{-2}} = 0.63 \cdot 10^{-21} \text{ m}^2. \quad (25)$$

which is about eleven orders of magnitude smaller than the size of an atom!

Nelson, Problem C.6.12, pg 587 (6 pts)

a) The protein diffuses (*i.e.*, undergoes a one-dimensional random walk) along the DNA. It's position as a function of time is described by a probability distribution that evolves from a delta-function at $t = 0$ into a spreading, Gaussian profile (see Nelson, Section 4.6.5):

$$P(x, t) = \frac{1}{\sqrt{4\pi Dt}} e^{-x^2/(2Dt)} \quad (26)$$

Given D , the probability of finding the protein a distance of 34 nm from where it started after a time t is

$$2 \cdot P(34 \text{ nm}, t) dx = \frac{0.34 \text{ nm}}{\sqrt{\pi Dt}} e^{-1156 \text{ nm}^2/(2Dt)} \quad (27)$$

where the factor of 2 comes from the fact that either direction satisfies the condition.

b) The probability that the protein will diffuse a distance greater than 100 basepairs from its starting point in a time t is 1 minus the probability that it diffuses a distance less than 100 basepairs:

$$\int_{-\infty}^{-34 \text{ nm}} P(x, t) dx + \int_{34 \text{ nm}}^{\infty} P(x, t) dx = 1 - \int_{-34 \text{ nm}}^{34 \text{ nm}} P(x, t) dx \quad (28)$$

c) While it is bound to the DNA, the protein isn't diffusing, so the mean-square displacement of the protein will be reduced. If the protein spends only a fraction α of the time t unbound, the probability distribution of its displacement will be given by $P(x, \alpha t)$ instead of $P(x, t)$.

The fraction α will be a function of the difference in free energy, $\Delta G = G_{\text{unbound}} - G_{\text{bound}}$ (see Nelson, p. 219):

$$\frac{P_{\text{unbound}}}{P_{\text{bound}}} = \frac{\alpha}{1 - \alpha} = \frac{e^{-G_{\text{unbound}}/k_B T}}{e^{-G_{\text{bound}}/k_B T}} = e^{-\Delta G/k_B T}. \quad (29)$$

Solving for α

$$\alpha = (1 - \alpha) e^{-\Delta G/k_B T} \quad (30)$$

$$\alpha(1 + e^{-\Delta G/k_B T}) = e^{-\Delta G/k_B T} \quad (31)$$

$$\alpha = \frac{e^{-\Delta G/k_B T}}{1 + e^{-\Delta G/k_B T}} = \frac{1}{e^{\Delta G/k_B T} + 1} \quad (32)$$

Therefore, the protein's mean-square displacement will be

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 P(x, \alpha t) dx = \frac{1}{\sqrt{4\pi D\alpha t}} \int_{-\infty}^{\infty} x^2 e^{-x^2/(2D\alpha t)} dx = 2D\alpha t = \frac{2Dt}{e^{\Delta G/k_B T} + 1} \quad (33)$$

and, since the denominator is always greater than 1, this value will always be less than in the absence of binding.

Nelson, Your Turn 6C, pg 212 (4 pts) We wish to compute the change in the gas's entropy in the case where the temperature is fixed and then find the value of L that maximizes the entropy. The key is that, when temperature is fixed, the kinetic energy of the ideal gas does not change. From the Sakur-Tetrode formula, we see that the entropy is then a strictly increasing function of L . Therefore, the equilibrium location will be the one that maximizes L . This answer makes sense because the thermal reservoir can supply all the energy required for the gas to expand.

Nelson, Your Turn 6G, pg 224 (4 pts)

$$F_a = \langle E_a \rangle - TS_a = \sum_j P_j E_j - T(-k_B \sum_j P_j \ln P_j) \quad (34)$$

$$= \sum_j P_j E_j - T(-k_B \sum_j P_j \ln e^{-E_j/k_B T}) \quad (35)$$

$$= \sum_j P_j E_j + k_B T \sum_j P_j (-E_j)/(k_B T) \quad (36)$$

$$= \sum_j P_j E_j + \sum_j P_j (-E_j) = 0 \quad (37)$$