

1 A transfer of 4×10^{-3} J of heat at 300 K adds $\Delta S = \frac{4}{3} \times 10^{-5}$ J/K to the entropy and $\frac{\Delta S}{k_B} \simeq 10^{18}$ to $\log \Omega$, since $k_B = \frac{R}{N_A} \simeq \frac{8 \text{ J/K}}{6 \times 10^{23}} = \frac{4}{3} \times 10^{-23}$ J/K. Accordingly, the number of microstates is increased by a factor of about $e^{10^{18}}$, which is colossal.

2

(a) Upon writing $E_k = \sum_{j=1}^N E_0 s_j$ with $s_j = 0$ or 1 for the energy of the k th configuration, specified by the values of s_1, s_2, \dots, s_n , we have

$$\begin{aligned} Q(\beta, N) &= \sum_k e^{-\beta E_k} = \sum_{\text{all } s_j} e^{-\beta E_0 \sum_j s_j} \\ &= \left(\sum_{s=0,1} e^{-\beta E_0 s} \right)^N = \left(1 + e^{-\beta E_0} \right)^N \end{aligned}$$

for the canonical partition function and, then,

$$S = -k_B \sum_k p_k \log p_k \Big|_{p_k = Q^{-1} e^{-\beta E_k}} = k_B \log Q + k_B \beta \langle E_k \rangle$$

with

$$\langle E_k \rangle = \sum_k p_k e^{-\beta E_k} = - \left(\frac{\partial \log Q}{\partial \beta} \right)_N = \frac{N E_0}{e^{\beta E_0} + 1}.$$

Accordingly, we find

$$S(\beta, N) = k_B N \log \left(1 + e^{-\beta E_0} \right) + k_B N \frac{\beta E_0}{e^{\beta E_0} + 1}.$$

(b) Since the average energy is E_0 times the average number of molecules with energy $E_b = E_0$, the average number of molecules with energy $E_a = 0$ is

$$N - \frac{\langle E_k \rangle}{E_0} = \frac{N}{1 + e^{-\beta E_0}}.$$

(c) In a configuration with energy E , there are E/E_0 molecules with energy E_0 and $N - E/E_0$ molecules with energy 0. The count of such configurations is

$$\Omega(E, N) = \frac{N!}{(E/E_0)! (N - E/E_0)!}$$

and

$$S(E, N) = k_B \left(\frac{E}{E_0} \log \frac{NE_0}{E} + \frac{NE_0 - E}{E_0} \log \frac{NE_0}{NE_0 - E} \right)$$

is the resulting entropy. Upon identifying E with $\langle E_k \rangle$, this $S(E, N)$ becomes $S(\beta, N)$ of part (a).

- (d) The average length is ℓ_a times the average number of molecules with energy E_a plus ℓ_b times the average number of molecules with energy E_b , that is

$$L(T, N) = \ell_a \frac{N}{1 + e^{-\beta E_0}} + \ell_b \frac{N}{e^{\beta E_0} + 1} = N \frac{\ell_a e^{\beta E_0} + \ell_b}{e^{\beta E_0} + 1}.$$

When the temperature increases (and $e^{\beta E_0}$ decreases) the fraction of molecules in the excited state increases, and since $\ell_b < \ell_a$ the length of the rubber band decreases.

At high temperatures ($e^{\beta E_0} \rightarrow 1$), we have $L = \frac{1}{2}N(\ell_a + \ell_b)$, consistent with the expectation that the molecules should be equally distributed over the two states. At low temperatures ($e^{\beta E_0} \rightarrow \infty$), we have $L = N\ell_a$, consistent with the expectation that all molecules are in the energetic ground state.

3

- (a) Since $N = z \left(\frac{\partial \log Z}{\partial z} \right)_{\beta, V} = \log Z = \beta PV$, it follows that PV is constant for isothermal changes, that is: when N and β are constant.

- (b) Since

$$\frac{S}{k_B} = -\beta^2 \left(\frac{\partial \beta^{-1} \log Z}{\partial \beta} \right)_{N, z} - N \log z = (\kappa + 1) \log Z - N \log z = (\kappa + 1 - \log z)N,$$

the fugacity z is constant for isentropic changes. Then $\beta^{-\kappa} V = \text{constant}$ implies $\beta^{-\kappa} \propto V^{-1}$ and $P \propto \beta^{-\kappa-1} \propto V^{-1-1/\kappa}$. It follows that $PV^{1+1/\kappa} = \text{constant}$ for isentropic changes. For $\kappa = \frac{3}{2}$, this gives $PV^{\frac{5}{3}} = \text{constant}$, as it should.

Alternatively, we can use $U = \langle E \rangle = - \left(\frac{\partial \log Z}{\partial \beta} \right)_{V, z} = \frac{\kappa}{\beta} Z = \kappa PV$ and $dU = -PdV$ for isentropic changes ($dS = 0$ and $dN = 0$). Together, they establish $(1 + \kappa)PdV + \kappa VdP = 0$ or $P^\kappa V^{1+\kappa} = \text{constant}$ for isentropic changes.

- (c) In view of

$$Z(\beta, V, z) = \exp \left((k_B T_0 \beta)^{-\kappa} \frac{Vz}{V_0} \right) = \sum_{N=0}^{\infty} z^N Q(\beta, V, N),$$

the canonical partition function is

$$e^{-\beta F} = Q(\beta, V, N) = \frac{1}{N!} \left((k_B T_0 \beta)^{-\kappa} \frac{V}{V_0} \right)^N = e^N \left((k_B T_0 \beta)^{-\kappa} \frac{V}{NV_0} \right)^N$$

and so we find

$$F(T, V, N) = -Nk_B T \left(1 + \kappa \log \frac{T}{T_0} + \log \frac{V}{NV_0} \right).$$

In the Legendre transformation $U = F + TS$, we need to solve

$$S = - \left(\frac{\partial F}{\partial T} \right)_{V, N} = -\frac{F}{T} + Nk_B \kappa = Nk_B \left(\kappa + 1 + \kappa \log \frac{T}{T_0} + \log \frac{V}{NV_0} \right)$$

for T , which gives

$$T = T_0 \left(\frac{V}{NV_0} \right)^{-1/\kappa} e^{\frac{S}{\kappa k_B N} - \frac{\kappa+1}{\kappa}}.$$

So, $U = F + TS = N\kappa k_B T$ reads

$$U(S, V, N) = N\kappa k_B T_0 \left(\frac{V}{NV_0} \right)^{-1/\kappa} e^{\frac{S}{\kappa k_B N} - \frac{\kappa+1}{\kappa}}.$$

- (d) The equations of state are exactly those of a classical ideal gas with adiabatic index $\gamma = 1 + 1/\kappa$. Therefore, we have $C_P - C_V = Nk_B$ and $C_P = \gamma C_V$, which imply $C_V = \kappa Nk_B$ and $C_P = (\kappa + 1)Nk_B$.

4

- (a) Here we have a standard Ising chain, for which

$$F(K, 0, N) = -\frac{N}{\beta} \log(2 \cosh(K)).$$

- (b) Here we have two standard Ising chains, each with $\frac{1}{2}N$ sites and a next-neighbor interaction energy J' , for which

$$F(0, K', N) = 2F(K', 0, \frac{1}{2}N) = -\frac{N}{\beta} \log(2 \cosh(K')).$$

(c) With $s_j s_{j+1} = q_j$, we have

$$\begin{aligned} Q(K, K', N) &= \sum_{\text{all } s_j} e^{K \sum_j s_j s_{j+1} + K' \sum_j s_{j-1} s_{j+1}} \\ &= 2 \sum_{\text{all } q_j} e^{K \sum_j q_j + K' \sum_j q_j q_{j+1}}, \end{aligned}$$

where the factor of 2 accounts for the degeneracy associated with a global sign change (all s_j to $-s_j$). The q_j expression is that of a standard Ising chain with next-neighbor interaction energy J' and on-site energy $-2J$, so that

$$Q(K, K', N) = 2 \left(e^{K'} \cosh(K) + \sqrt{e^{2K'} \sinh(K)^2 + e^{-2K'}} \right)^N$$

where we use λ_+ of (4.2.36) with the replacements $\beta E_0 \rightarrow -2K$ and $\beta J \rightarrow K'$. The resulting free energy is

$$F(K, K', N) = -\frac{N}{\beta} \log \left(e^{K'} \cosh(K) + \sqrt{e^{2K'} \sinh(K)^2 + e^{-2K'}} \right).$$

For $K' = 0$ or $K = 0$, we get the expressions of parts (a) and (b), as we should.

(d) We have

$$\begin{aligned} \frac{C}{k_B N} &= -\frac{1}{k_B N} T \left(\frac{\partial^2 F}{\partial T^2} \right)_{V, N} = -\beta^2 \left(\frac{\partial^2 (\beta F / N)}{\partial \beta^2} \right)_{V, N} \\ &= \left(K^2 \frac{\partial^2}{K^2} + 2KK' \frac{\partial}{\partial K} \frac{\partial}{\partial K'} + K'^2 \frac{\partial^2}{K'^2} \right) \log \left(\text{as above} \right), \end{aligned}$$

where the argument of the logarithm is

$$e^{K'} \cosh(K) + \sqrt{e^{2K'} \sinh(K)^2 + e^{-2K'}} \cong 2 \cosh(K) \left(1 + \tanh(K)^2 K' \right)$$

to first-order in K' . This yields

$$\begin{aligned} \frac{C}{k_B N} &\cong \left(K^2 \frac{\partial^2}{K^2} + 2KK' \frac{\partial}{\partial K} \frac{\partial}{\partial K'} \right) \left(\log(2 \cosh(K)) + \tanh(K)^2 K' \right) \\ &= \frac{K^2}{\cosh(K)^2} + \frac{2K^2 K'}{\cosh(K)^2} \left(1 - 3 \tanh(K)^2 \right) + \frac{4KK'}{\cosh(K)^2} \tanh(K). \end{aligned}$$