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

(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 $s_1$, $s_2$, $\ldots$, $s_n$, we have

$$Q(\beta, N) = \sum_k e^{-\beta E_k} = \sum_{\text{all } s_j} e^{-\beta E_0} \sum_{s_j}$$

$$= \left( \sum_{s=0,1} e^{-\beta E_0 s} \right)^N = \left( 1 + e^{-\beta E_0} \right)^N$$

for the canonical partition function and, then,

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

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 $E_k = E_0$, 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

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

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and 

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

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 \( \ell_a \) times the average number of molecules with energy \( E_a \) plus \( \ell_b \) times the average number of molecules with energy \( E_b \), that is

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

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 \( (e^{\beta E_0} \to 1) \), 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 \( (e^{\beta E_0} \to \infty) \), 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 \( \beta \) 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 \( P \propto \beta^{-\kappa - 1} \propto V^{-1-1/\kappa} \). If follows that \( PV^{1+1/\kappa} = \text{constant for isentropic changes. For } \kappa = \frac{3}{2}, \text{ this gives } PV^2 = \text{constant, as it should.} \)

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 \( (dS = 0 \text{ and } dN = 0) \). Together, they establish \( (1 + \kappa)PdV + \kappa VdP = 0 \) or \( P^{\kappa} V^{1+\kappa} = \text{constant for isentropic changes.} \)

(c) In view of

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

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the canonical partition function is

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

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

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

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

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

(b) 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 \( C_V = \kappa N k_B \) and \( C_P = (\kappa + 1) N k_B \).

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

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

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

$$Q(K, K', N) = \sum_{all \ s_j} e^K \sum_j s_j s_{j+1} + K' \sum_j s_{j-1} s_{j+1}$$

$$= 2 \sum_{all \ q_j} e^K \sum_j q_j + K' \sum_j q_j q_{j+1},$$

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 $\lambda_+$ of (4.2.36) with the replacements $\beta E_0 \to -2K$ and $\beta J \to K'$. 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

$$\frac{C}{k_B N} = -\frac{1}{k_B N} T \left( \frac{\partial^2 F}{\partial T^2} \right)_{V,N} = -\beta^2 \left( \frac{\partial^2 (\beta F/N)}{\partial \beta^2} \right)_{V,N}$$

$$= \left( K^2 \frac{\partial^2}{K^2} + 2KK' \frac{\partial}{\partial K} \frac{\partial}{\partial K'} + K'^2 \frac{\partial^2}{K'^2} \right) \log \left( \text{as above} \right),$$

where the argument of the logarithm is

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

to first-order in $K'$. This yields

$$\frac{C}{k_B N} \approx \left( K^2 \frac{\partial^2}{K^2} + 2KK' \frac{\partial}{\partial K} \frac{\partial}{\partial K'} \right) \left( \log (2 \cosh(K)) + \tanh(K)^2 K' \right)$$

$$= \frac{K^2}{\cosh(K)^2} + \frac{2K^2 K'}{\cosh(K)^2} \left( 1 - 3 \tanh(K)^2 \right) + \frac{4KK'}{\cosh(K)^2} \tanh(K).$$

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