

DYLAN J. TEMPLES: CHAPTER 4

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Classical Mechanics and Thermodynamics - Garrod
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1 Garrod 4.7: One-Dimensional Crystal Lattice.

Shown in Figure 1 (Garrod Fig. 4.10) is a simple model of a one-dimensional crystal. The springs all have spring constant k and, at equilibrium, the particles are all separated by length ℓ . Let x_n be the deviation from equilibrium of the n th particle.

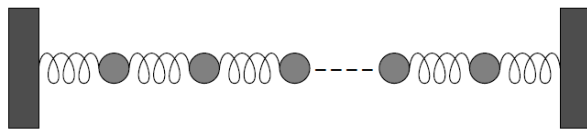


Figure 1: Diagram of the crystal structure (Garrod Figure 4.10)

1.1 Equations of Motion.

Let us consider the n th particle in the crystal, which if it only interacts with the springs directly attached to it has the Lagrangian

$$\mathcal{L} = \frac{1}{2}m\ddot{x}_n^2 - \frac{1}{2}k(x_{n+1} - x_n)^2 - \frac{1}{2}k(x_{n-1} - x_n)^2 \quad (1)$$

$$= \frac{1}{2}m\ddot{x}_n^2 - \frac{1}{2}k(x_{n+1}^2 + x_n^2 - 2x_{n+1}x_n + x_{n-1}^2 + x_n^2 - 2x_{n-1}x_n), \quad (2)$$

which gives the Euler-Lagrange equation

$$m\ddot{x}_n = -\frac{1}{2}k[4x_n - 2x_{n+1} - 2x_{n-1}] = k(x_{n+1} + x_{n-1} - 2x_n), \quad (3)$$

where $n = 1, \dots, N$. Let us impose that x_0 and x_{N+1} are defined to be zero for all t .

1.2 Solutions to Equation of Motion.

To solve this coupled system of differential equations would involve dealing with and diagonalizing a $N \times N$ matrix, which I do not believe to be the point of this exercise. The general solution to differential equations is¹

$$x_n(t) = A \cos(\theta n) \cos(\omega t) + B \cos(\theta n) \sin(\omega t) + C \sin(\theta n) \cos(\omega t) + D \sin(\theta n) \sin(\omega t), \quad (4)$$

where A, B, C, D, θ are arbitrary constants, which we can constrain using some boundary conditions. If we know that x_0 must be zero for all t , we can write

$$x_0(t) = 0 = A \cos(\theta n) \cos(\omega t) + B \cos(\theta n) \sin(\omega t) + C \sin(0) \cos(\omega t) + D \sin(0) \sin(\omega t), \quad (5)$$

which is only true for any time is $A = B = 0$. Similarly, we can investigate the $x_{N+1} = 0$ solution,

$$x_{N+1}(t) = 0 = C \sin(\theta(N+1)) \cos(\omega t) + D \sin(\theta(N+1)) \sin(\omega t), \quad (6)$$

which is satisfied for all time if

$$\sin(\theta(N+1)) = 0 \quad \text{so} \quad \theta(N+1) = K\pi, \quad (7)$$

¹David Morin, Harvard University. [Normal Modes](#), pg 12.

where K is an integer from 1 to N . We can limit the range of K to this because the sine will have the same value for $K > N$ as it did for one of the $K < N$, it will just acquire a phase, which will be unimportant when calculating frequencies (additionally, the ω are normal mode frequencies, and for N particles, there are only N normal modes). This implies there are N solutions to each differential equation for x_n , each of the form

$$x_n(t) = \alpha \sin\left(\pi \frac{K}{N+1} n\right) \cos(\omega_K t + \delta), \quad (8)$$

where we have incorporated the constants C and D in the amplitude α and the arbitrary phase δ , which we will set to zero.

We can solve for the normal modes of the system by inserting the solution above back into the differential equation. First note the second derivative of x_n with respect to time is

$$\ddot{x}_n = -\alpha \omega_K^2 \sin\left(\pi \frac{K}{N+1} n\right) \cos(\omega_K t). \quad (9)$$

We can notice immediately that each term will have factors of $\alpha \cos(\omega_K t)$, so we can substitute our solutions into Equation 3 and divide through by this factor to get

$$-\left(\frac{\omega_K}{\omega_0}\right)^2 \sin(\eta n) = \sin(\eta(n+1)) + \sin(\eta(n-1)) - 2 \sin(\eta n), \quad (10)$$

where $\omega_0 = \sqrt{k/m}$ and $\eta = \pi K/(N+1)$. We simplify the sines with sums in their arguments to

$$\sin(\eta n) \cos(\eta) + \cos(\eta n) \sin(\eta) + \sin(\eta n) \cos(\eta) - \cos(\eta n) \sin(\eta), \quad (11)$$

of which the second and fourth terms cancel, and the first and third sum. If we substitute this in to Equation 10, and divide through by $\sin(\eta n)$, we find

$$-\left(\frac{\omega_K}{\omega_0}\right)^2 = 2 \cos(\eta) - 2, \quad (12)$$

which gives the normal mode frequencies to be

$$\omega_K^2 = 2\omega_0^2 \left[1 - \cos\left(\pi \frac{K}{N+1}\right)\right] = 4\omega_0^2 \sin^2\left(\pi \frac{K}{N+1}\right). \quad (13)$$

1.3 Thermal Energy.

Treating the system quantum mechanically, the thermal energy of the crystal is given by Garrod Equation 4.23. The thermal energy is the energy at temperature T relative to the ground state energy. We begin by defining a variable k as the argument of the sine in the normal mode frequencies, which, for large N , has the range $0, < k < \pi$. We can rewrite the sum in the thermal energy over the index K as an integral over k by noting $dk = \pi/(N+1)dK$, so

$$E(T) = \int_0^\pi \frac{N+1}{\pi} dk \left[\frac{2\hbar\omega_0 \sin(k)}{\exp[2\hbar\omega_0 \sin(k)/k_B T] - 1} \right], \quad (14)$$

where k_B is the Boltzmann constant. If we are in the large N limit, we can say $N+1 \rightarrow N$ in the above expression. So a simplified form of the thermal energy is

$$E(T) = \frac{2\hbar\omega_0 N}{\pi} \int_0^\pi \left[\frac{\sin(k)}{\exp\left[\frac{2\hbar\omega_0}{k_B T} \sin(k)\right] - 1} \right] dk. \quad (15)$$

1.4 Dulong-Petit Value.

The exponential may be expanded in a power series of Planck's constant; terms higher than linear order in \hbar will have negligible contributions to the integral. For small x , $\exp[x] \sim 1 + x + \frac{1}{2}x^2$, so the thermal energy can be approximated to linear order as

$$E(T) = \frac{2\hbar\omega_0 N}{\pi} \int_0^\pi \left[\frac{\sin(k)}{\frac{2\hbar\omega_0}{k_B T} \sin(k)} + \mathcal{O}(\hbar^2) \right] dk = \frac{2\hbar\omega_0 N}{\pi} \int_0^\pi \frac{k_B T}{2\hbar\omega_0} dk = Nk_B T, \quad (16)$$

which is the classical thermal energy, the Dulong-Petit value.

1.5 Quantum Mechanical Correction.

If we kept the quadratic term in \hbar from the power series, we find that

$$E(T) = \frac{2\hbar\omega_0 N}{\pi} \int_0^\pi \left[\frac{\sin(k)}{\frac{2\hbar\omega_0}{k_B T} \sin(k) + \frac{2\hbar^2\omega_0^2}{k_B^2 T^2} \sin^2(k)} + \mathcal{O}(\hbar^3) \right] dk \quad (17)$$

$$= \frac{Nk_B T}{\pi} \int_0^\pi \left[\frac{1}{1 + \frac{\hbar\omega_0}{k_B T} \sin(k)} \right] dk. \quad (18)$$

We can again use a Taylor expansion in \hbar to approximate the integrand as

$$\frac{1}{1 + \frac{\hbar\omega_0}{k_B T} \sin(k)} = 1 - \frac{\hbar\omega_0}{k_B T} \sin(k) + \mathcal{O}(\hbar^2), \quad (19)$$

which can be evaluated yielding,

$$E(T) = \frac{Nk_B T}{\pi} \int_0^\pi \left[1 - \frac{\hbar\omega_0}{k_B T} \sin(k) \right] dk = \frac{Nk_B T}{\pi} \left(\pi - 2 \frac{\hbar\omega_0}{k_B T} \right). \quad (20)$$

Let us define the ratio of the quantum correction term to the classical value term from the expansion,

$$\rho = 2 \frac{\hbar\omega_0}{k_B T} \frac{1}{\pi} = . \quad (21)$$

If we take $\omega_0 = \sqrt{k/m} = 10^{13}$ rad/sec (a reasonable value for real crystals) and $T = 300$ K, we find that

$$\rho = 0.1531506307, \quad (22)$$

so the quantum correction contributes 15% of the total thermal energy, which is not a negligible effect.

2 Garrod 4.15: Two-Dimensional Crystal.

In Figure 3 (Garrod Fig. 4.11) is shown the surface or upper boundary of a two-dimensional square crystal. In this solid-on-solid model, we assume that there are no overhangs (filled lattice sites that lie above empty ones). The configuration of the surface can then be defined by N integer height variables y_1, y_2, \dots, y_N . (In the figure, $y_1 = 0$ and $y_2 = -1$.) The surface energy is assumed to be proportional to the length of the surface. If we assign zero energy to the straight surface, then $E = \epsilon \sum_{n=1}^N |y_n - y_{n-1}|$, where $y_0 = 0$. The canonical partition for the system is

$$Z(N, \beta) = \sum_{y_1} \dots \sum_{y_N} \exp \left[-\beta \epsilon \sum |y_n - y_{n-1}| \right]. \quad (23)$$

2.1 Transformation of Variables.

By a transformation of variables, $u_n = y_n - y_{n-1}$, evaluate $Z(N, \beta)$.

Using the specified transformation of variables, it is easy to see

$$Z(N, \beta) = \sum_{u_1=-\infty}^{\infty} \dots \sum_{u_N=-\infty}^{\infty} \exp \left[-\beta \epsilon \sum |u_n| \right], \quad (24)$$

where the sums over y_n can be transformed to over u_n by noting that $y_n - y_{n-1}$ and u_n take the same range of values. If we expand the sum in the exponential, we can write this as a product of single-term exponentials. Then each term is over a single u_n , so we can distribute the exponential to the corresponding summation, i.e.

$$Z(N, \beta) = \left[\sum_{u_1=-\infty}^{\infty} e^{-\beta \epsilon |u_1|} \right] \dots \left[\sum_{u_N=-\infty}^{\infty} e^{-\beta \epsilon |u_N|} \right] = \left[\sum_{u=-\infty}^{\infty} e^{-\beta \epsilon |u|} \right]^N, \quad (25)$$

because this results in N terms that are exactly the same. We can change the range of summation from $(-\infty, \infty)$ to $[0, \infty)$ to remove the absolute value, but we must subtract one, so we are not double-counting the $u = 0$ term. Then the partition function is

$$Z(N, \beta) = \left[2 \sum_{u=0}^{\infty} e^{-\beta \epsilon u} - 1 \right]^N = \left[2 \sum_{u=0}^{\infty} (e^{-\beta \epsilon})^u - 1 \right]^N, \quad (26)$$

so we may use the geometric series to write this as

$$Z(N, \beta) = \left[\frac{2}{1 - e^{-\beta \epsilon}} - 1 \right]^N = \coth^N \frac{\beta \epsilon}{2} = \left[\frac{e^{\beta \epsilon} + 1}{e^{\beta \epsilon} - 1} \right]^N, \quad (27)$$

by MATHEMATICA.

2.2 Probability Distribution.

Determine the probability distribution for the step height u_n . It should be independent of n .

We are interested on the probability of the n th step having a height of x , so we must integrate over all the other u_k (for $k \neq n$). This integration is really just the sum given by the partition function but not including the n th particle,

$$Z' = \prod_{i=1}^N \sum_{u_i=-\infty}^{\infty} \left(\exp \left[-\beta\epsilon \sum |u_i| \right] (1 - \delta_{in}) \right), \quad (28)$$

where δ_{in} is the Kronecker delta function and is 0 for $n = i$, so the product excludes this term. From the analysis in section 1.1, we see

$$Z' = \left[\frac{e^{\beta\epsilon} + 1}{e^{\beta\epsilon} - 1} \right]^{N-1}, \quad (29)$$

so the probability of the n th step having a height x is

$$P(u_n = x) = \frac{e^{-\beta\epsilon|u_n|}}{Z} Z' = e^{-\beta\epsilon|x|} \left[\frac{e^{\beta\epsilon} + 1}{e^{\beta\epsilon} - 1} \right]^{-N} \left[\frac{e^{\beta\epsilon} + 1}{e^{\beta\epsilon} - 1} \right]^{N-1} = e^{-\beta\epsilon|x|} \left[\frac{e^{\beta\epsilon} - 1}{e^{\beta\epsilon} + 1} \right], \quad (30)$$

this distribution is shown in Figure 2, and has a maximum value of $(e^{\beta\epsilon} - 1)/(e^{\beta\epsilon} + 1)$.

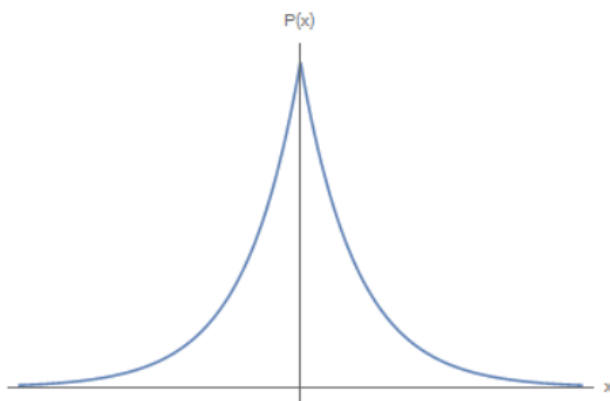


Figure 2: Probability distribution of the n th step having a height of x . Clearly, we see the most probable height is zero, with the maximum defined by (β, ϵ) : $P(0) = \tanh \beta\epsilon$. Note we have set $\beta\epsilon = 1$, because only the functional form matters.

2.3 Central Limit Theorem.

Using the central limit theorem, determine the probability distribution for the coordinate of the last step, y_N .

We will follow the treatment in Garrod section 1.14 and Appendix A.1. We have the sum of our independent variables:

$$U = \sum_{n=1}^N u_n = \sum_{n=1}^N (y_n - y_{n-1}) = (y_1 - 0) + (y_2 - y_1) + (y_3 - y_2) + \dots + (y_N - y_{N-1}) = y_N, \quad (31)$$

we must note the central limit theorem is concerned with the average value of some set of independent variables, while we are interested only in the sum, so we will use our $U = NX$ (where X is

the average of the sum of independent variables, see section Garrod 1.14), i.e. when the book uses dx , we will use du/N , therefore

$$P(u)du = P_X(x)dx = \frac{1}{N}P_X\left(\frac{u}{N}\right)du . \quad (32)$$

Using this, Garrod Equation A.16 becomes

$$P(u) = \frac{1}{N} \sqrt{\frac{N}{2\pi a^2}} \exp\left[-N \left(\frac{u}{N}\right)^2 / 2a^2\right] = (2\pi N a^2)^{-1/2} \exp\left[-\frac{u^2}{2N a^2}\right] , \quad (33)$$

where a is the mean square uncertainty (Garrod Equation 1.58). Each of our independent variables u_n , has the same uncertainty, so our a^2 is simply Δu^2 , given by

$$a^2 = \Delta u^2 = \langle u^2 \rangle - \langle u \rangle^2 . \quad (34)$$

We have previously shown (Equation 30 and Figure 2) that the most probable step height is zero, so $\langle u \rangle = 0$. The expectation value of u^2 is

$$\langle u^2 \rangle = \sum_{u=-\infty}^{\infty} u^2 P(u) = \sum_{u=-\infty}^{\infty} u^2 \frac{Z'}{Z} = 2 \left[\frac{e^{\beta\epsilon} - 1}{e^{\beta\epsilon} + 1} \right] \sum_{u=0}^{\infty} u^2 e^{-\beta\epsilon u} , \quad (35)$$

note we do not need to subtract one for double counting because for $u = 0$ the term in the sum is zero. The expectation value (and uncertainty), then, is

$$\Delta u^2 = \langle u^2 \rangle = 2 \left[\frac{e^{\beta\epsilon} - 1}{e^{\beta\epsilon} + 1} \right] \left(\frac{e^{\beta\epsilon} (e^{\beta\epsilon} + 1)}{(e^{\beta\epsilon} - 1)^3} \right) = \frac{2e^{\beta\epsilon}}{(e^{\beta\epsilon} - 1)^2} = \frac{1}{\cosh(\beta\epsilon) - 1} , \quad (36)$$

using MATHEMATICA to compute the sum, and simplify. We now see the probability of the last particle (because the sum of our independent variables is our parameter of interest) to be a height x on the right wall is

$$P(y_N = x) = \sqrt{\frac{\cosh(\beta\epsilon) - 1}{2\pi N}} \exp\left[-\frac{x^2(\cosh \beta\epsilon - 1)}{2N}\right] , \quad (37)$$

which again is maximized for $x = 0$, as expected.

3 Garrod 4.16: Two-Dimensional Crystal - Alternate Model.

Another model of the surface of a two-dimensional crystal is shown in Figure 4 (Garrod Fig. 4.12). A configuration of the surface can be described by a sequence of N variables $\sigma_1, \dots, \sigma_n$ that take the values $\sigma = \pm 1$ according to the scheme shown in the figure. The y coordinate of the right-hand end (in appropriate units) is $y = \sum \sigma_n$. If there is an interaction between the crystal particles and the right-hand wall, then it is reasonable to assume that the energy is given by $E = \epsilon y$, where $\epsilon < 0$ for an attractive interaction and $\epsilon > 0$ for a repulsive one.

3.1 Canonical Potential.

Calculate the canonical potential, ψ , as a function of N , β , and ϵ .

We begin by writing the partition function, combining the definition of energy and the y position,

$$Z = \sum_{\Omega} \exp \left[-\beta \epsilon \sum_{n=1}^N \sigma_i \right] , \quad (38)$$

where the sum is over all possible microstates. We note that each σ_i may take one of two values and the combination of all of these possibilities can be written as

$$Z = \sum_{\sigma_1=\pm 1} \sum_{\sigma_2=\pm 1} \dots \sum_{\sigma_N=\pm 1} \exp [-\beta \epsilon (\sigma_1 + \sigma_2 + \dots + \sigma_N)] . \quad (39)$$

As done in section 1, we can write the exponential of a sum as a product of exponential terms and associate each one with its corresponding sum

$$Z = \left[\sum_{\sigma=\pm 1} e^{-\beta \epsilon \sigma} \right]^N = \left[e^{\beta \epsilon} + e^{-\beta \epsilon} \right]^N = [2 \cosh(\beta \epsilon)]^N . \quad (40)$$

Using the definition (Garrod Equation 4.45), we find the canonical potential is given by

$$\phi(N, \beta, \epsilon) = \log Z = N \log [2 \cosh(\beta \epsilon)] . \quad (41)$$

3.2 Expectation Value of y .

Show that $\langle y \rangle = \partial \phi / \partial \epsilon$ and calculate $\langle y \rangle$ as a function of N , β , and ϵ .

Using the definition of energy, we find $\langle E \rangle = \epsilon \langle y \rangle$, with the expectation value of energy given by

$$\langle E \rangle = \epsilon \langle y \rangle = -\frac{\partial \phi}{\partial \beta} = -N \epsilon \tanh[\beta \epsilon] , \quad (42)$$

so that the expectation value of the height of the crystal on the right hand wall is

$$\langle y \rangle = -N \tanh[\beta \epsilon] , \quad (43)$$

which for an attractive wall ($-\epsilon$), the expected y is positive (hyperbolic tangent is symmetric about the origin), which is expected. Similarly for a repulsive interaction, the expected y is positive. The attractive potential would mean more particles are attempting to pile up on the right wall while a

repulsive one makes the particles crowd up on the left hand wall.

We can find the expected value of y using the formula given by Garrod,

$$\langle y \rangle = \frac{\partial \phi}{\partial \epsilon} = N\beta \tanh[\beta\epsilon] , \quad (44)$$

which is not consistent with the result found previously. Silly Garrod, consistency is for kids. Evidently, we are trying to prove that

$$\langle y \rangle = -\frac{1}{\epsilon} \frac{\partial \phi}{\partial \beta} = \frac{\partial \phi}{\partial \epsilon} , \quad (45)$$

which cannot be the case because both of the parameters we are differentiating to are in the argument of the hyperbolic tangent. For this to be consistent, we would have to have

$$-\frac{1}{\epsilon} \frac{\partial \phi}{\partial \beta} = -\frac{1}{\beta} \frac{\partial \phi}{\partial \epsilon} , \quad (46)$$

which makes more sense from a purely aesthetic view.

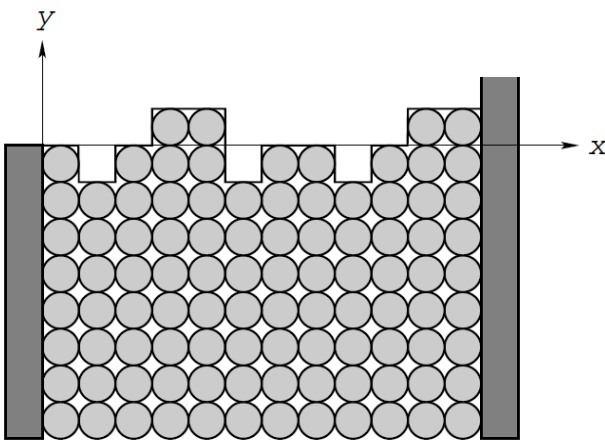


Figure 3: Depiction of the crystal structure used in Problem #1 (Garrod Fig. 4.11).

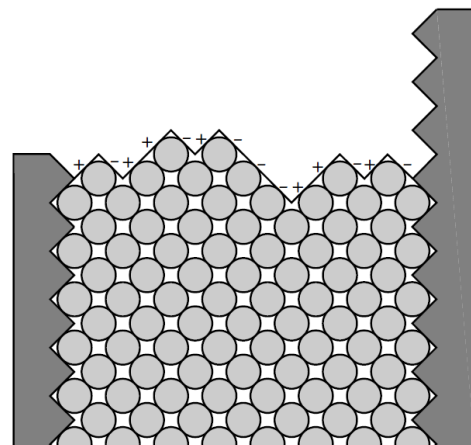


Figure 4: Depiction of the crystal structure used in Problem #2 (Garrod Fig. 4.12).

4 Garrod 4.19: Rotational Partition Function of Diatomic Molecules.

The rotational partition function of a diatomic molecule calculated by classical mechanics is $z(\text{rot}) = 2I/\beta\hbar^2$. Calculated quantum mechanically, $z(\text{rot})$ is given by the following sum over rotational states

$$z(\text{rot}) = \sum_{\ell} g_{\ell} \exp(-\beta\epsilon_{\ell}) , \quad (47)$$

where $g_{\ell} = (2\ell + 1)$ is the degeneracy of the rotational state of angular momentum $\sqrt{\ell(\ell + 1)}/\hbar$ and $\epsilon_{\ell} = \ell(\ell + 1)\hbar^2/2I$.

4.1 Integral Representation.

Show that, if the quantum mechanical sum is approximated by an integral over a continuous ℓ variable, the classical value is obtained. This procedure would be valid for small values of $\beta\hbar^2/2I$ ($kT \gg \hbar^2/2I$).

In the classical limit, the separations in ℓ are infinitesimal, so we may take ℓ to be continuous and replace the sum with an integral

$$z(\text{rot}) = \int_0^{\infty} (2\ell + 1) \exp[-\beta\ell(\ell + 1)\hbar^2/2I] d\ell , \quad (48)$$

which if we define $L = 2I/\beta\hbar^2$, we see the integral is just

$$z(\text{rot}) = \int_0^{\infty} (2\ell + 1) e^{-\ell(\ell+1)/L} d\ell = L , \quad (49)$$

by noting that $\frac{d}{d\ell}[\ell^2 + \ell] = 2\ell + 1$. We see from the definition of L , that the integral results in the classical value, as expected.

4.2 Numerical Evaluation of Sum.

Evaluate the sum numerically for $\beta\hbar^2/2I = 1, 0.5,$ and 0.1 and compare your result with the classical approximation.

Using the same definition of L , the sum can be written explicitly as

$$z(\text{rot}) = \sum_{\ell=0}^{\infty} (2\ell + 1) e^{-L\ell(\ell+1)} , \quad (50)$$

which we can evaluate in MATHEMATICA for values of L , to find

$$L = 1.0 : z(\text{rot}) = 1.41844 \quad z_{cl} = 1/L = 1 \quad (51)$$

$$L = 0.5 : z(\text{rot}) = 2.37034 \quad z_{cl} = 2 \quad (52)$$

$$L = 0.1 : z(\text{rot}) = 10.3401 \quad z_{cl} = 10 , \quad (53)$$

where z_{cl} is the classical partition function. The partition function increases as temperature increases, as expected. Additionally, the classical value approaches the actual value as the temperature increases (and the other parameters - I - remain constant).

5 Garrod 4.25: Polymer of Two-State Monomers.

A long polymer under tension τ is made up of N monomers that can each be in a compact or an elongated state. Thus the polymer has $2N$ possible states. Assume that the length of the polymer is $L = N_c \ell_c + N_e \ell_e$, where $\ell_e > \ell_c$ and N_c and N_e are the numbers of compact and elongated monomers, respectively.

5.1 Average Length.

Take the energy as $E = \tau(N\ell_e - L)$ and calculate the average length as a function of T and τ .

Using the definition of L we find the energy to be

$$E = \tau(N\ell_e - L) = \tau([N_e + N_c]\ell_e - N_c\ell_c - N_e\ell_e) = \tau(N_c\ell_e - N_c\ell_c) = \tau N_c \Delta\ell, \quad (54)$$

where $\Delta\ell = \ell_e - \ell_c$, which is a positive number if the elongated length is longer than the contracted length of the monomer. The number of microstates is easily defined

$$\sum e^{-\beta\tau\Delta\ell N_c}, \quad (55)$$

but this does not include the degeneracy of the microstates that lead to the same macrostate. The degeneracy factor is

$$\frac{N!}{N_c!(N - N_c)!} = \frac{N!}{N_e!N_c!} = \binom{N}{N_e} = \binom{N}{N_c}, \quad (56)$$

so the partition function is

$$Z = \sum_{N_c=0}^N \binom{N}{N_c} e^{-\beta\tau\Delta\ell N_c}. \quad (57)$$

Alternatively, we could view this system similarly to problems 1 and 2, where each independent variable (monomer state) can take one of two values, ℓ_e or ℓ_c . We can define a new independent variable η_i , which can take the value one or zero, corresponding to

$$\eta_i = \begin{cases} 0 & \text{extended} \\ 1 & \text{contracted} \end{cases}, \quad (58)$$

so we can now write a partition function

$$Z = \sum_{\eta_0=0}^1 \sum_{\eta_1=0}^1 \dots \sum_{\eta_N=0}^1 e^{-\beta\tau\Delta\ell \sum_{i=1}^N \eta_i} = \left[\sum_{\eta=0}^1 e^{-\beta\tau\Delta\ell \eta} \right]^N = [1 + e^{-\beta\tau\Delta\ell}]^N. \quad (59)$$

From Equation 54, we find that $\langle E \rangle = \tau\Delta\ell \langle N_c \rangle$, so

$$\langle E \rangle = -\frac{\partial \log Z}{\partial \beta} = - \left[-N\tau\Delta\ell \frac{e^{-\beta\tau\Delta\ell}}{1 + e^{-\beta\tau\Delta\ell}} \right] = N\tau\Delta\ell (1 + e^{-\beta\tau\Delta\ell})^{-1}, \quad (60)$$

thus the expected number of contracted monomers is

$$\langle N_c \rangle = \frac{N}{1 + e^{-\beta\tau\Delta\ell}}. \quad (61)$$

Therefore, using the definition of L in terms of the number of each state, we see

$$\langle L \rangle = \langle N_c \rangle \ell_c + (N - \langle N_c \rangle) \ell_e = \Delta\ell \langle N_c \rangle + N\ell_e = \frac{N\Delta\ell}{1 + e^{-\beta\tau\Delta\ell}} + N\ell_e. \quad (62)$$

5.2 Response to Temperature Change.

Consider the polymer chain under nonzero tension τ . Does its length increase or decrease when the temperature is increased? (Justify mathematically, and explain physically.)

When we examine Equation 62, we see the exponential of $-1/T$ is in the denominator, so at low temperature, the exponential becomes negligible compared to one, so the denominator is just one, which maximizes this function. At high temperature, the exponential approaches one, so the denominator is about 2, which minimizes the function, as seen in Figure 5 (note that the x -axis is in terms of $1/T$). The physical meaning of this is that at high temperatures (low β), the energy due to heat goes into putting each monomer into it's contracted state. This is to say the contracted states have higher internal energy. We can consider a polymer chain that at some temperature has the majority of the monomers in the elongated state, where the polymer can cross over itself in arbitrary ways, which has high entropy. As we remove energy (lower the temperature), the size of each monomer reduces and the chain "straightens" out. which is a state with much higher order, or lower entropy. This can be seen in two examples. If you hold a rubber band to your lips while it is untensioned, and stretch it out, you will feel its temperature drop. Additionally, if you point a hair dryer at plastic wrap, it shrinks and shrivels up (i.e. Shrinky DinksTM).

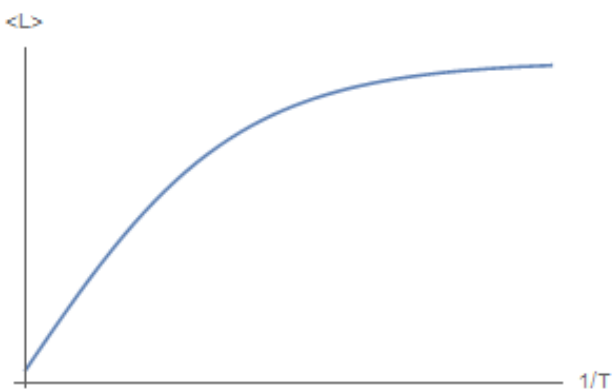


Figure 5: The expected length (Equation 62) of a polymer change depending on its temperature. The x -axis is expressed as $1/T$, high values are low temperatures. Note we have set $\tau = \Delta\ell = 1$, and $N = 100,000$, but the axes values are not displayed because only the functional form matters.