

MODEL SYSTEMS

Starting with QM energy levels for molecular translation, rotation, & vibration, solve for q and Q , & all the thermodynamics, for these degrees of freedom. The results are the fundamentals of molecular statistical mechanics.

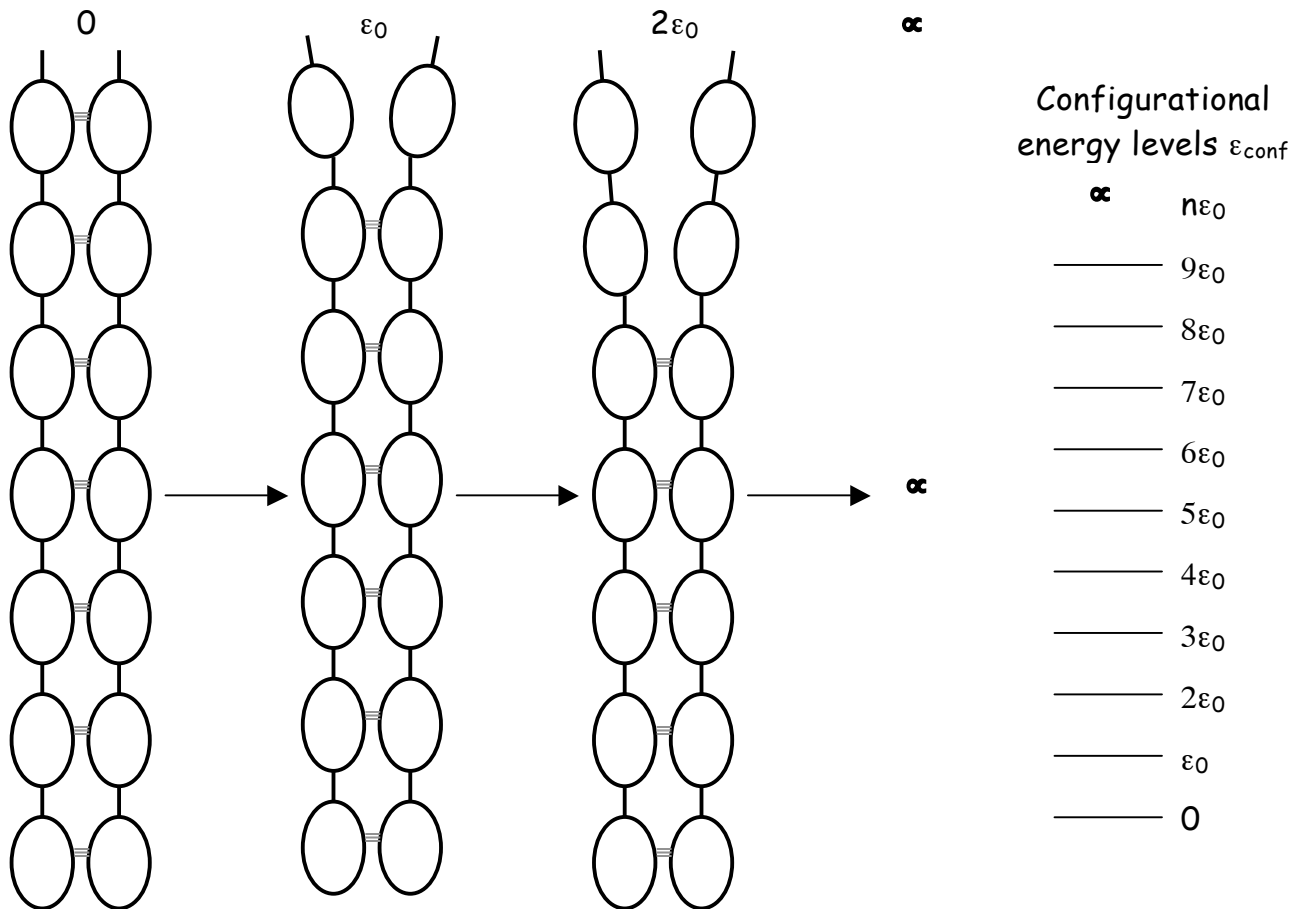
We'll derive the results for a classical model that maps onto QM vibrations. Then we'll compare to results (given, not derived) for translation and rotation.

Double-stranded polymer model

Each monomer in one strand interacts with a monomer in the other strand.

Interaction energy for each monomer pair is $-\epsilon_0$.

The strands can "unzip" from one end, rupturing the interactions of the end monomers, then the next ones, then the next, and so on. Each ruptured interaction raises the energy by ϵ_0 . The three lowest-energy states and the energy levels are illustrated below.



Nondegenerate evenly spaced levels, separated by energy ϵ_0 : $\epsilon = n\epsilon_0$ ($n = \text{integer}$)

For a very long polymer, there is a large number of levels. Then we can extend the sum over states in q_{conf} to infinity because the highest energies are much bigger than kT anyway (so the corresponding terms in the sum are negligible).

$$\begin{aligned}
 q_{\text{conf}} &= \sum_n e^{-\varepsilon_n/kT} \approx \sum_n e^{-n\varepsilon_0/kT} = 1 + e^{-\varepsilon_0/kT} + e^{-2\varepsilon_0/kT} + e^{-3\varepsilon_0/kT} + \dots \\
 &= 1 + e^{-\varepsilon_0/kT} + (e^{-\varepsilon_0/kT})^2 + (e^{-\varepsilon_0/kT})^3 + \dots \equiv 1 + x + x^2 + x^3 + \dots = \frac{1}{1-x} \\
 q_{\text{conf}} &= \frac{1}{1 - e^{-\varepsilon_0/kT}}
 \end{aligned}$$

So q_{conf} takes a very simple closed form. Everything else follows.

$$\begin{aligned}
 Q_{\text{conf}} &= (q_{\text{conf}})^N = \left(\frac{1}{1 - e^{-\varepsilon_0/kT}} \right)^N \\
 A_{\text{conf}} &= -NkT \ln q_{\text{conf}} = -NkT \ln \left(\frac{1}{1 - e^{-\varepsilon_0/kT}} \right) = NkT \ln(1 - e^{-\varepsilon_0/kT}) \\
 \mu_{\text{conf}} &= \left(\frac{\partial A_{\text{conf}}}{\partial N} \right)_{T,V} = kT \ln(1 - e^{-\varepsilon_0/kT}) \quad A_{\text{conf}} \text{ scales with } N, \mu_{\text{conf}} = A_{\text{conf}}/N \\
 U_{\text{conf}} &= NkT^2 \frac{d \ln q_{\text{conf}}}{dT} = -NkT^2 \frac{1}{(1 - e^{-\varepsilon_0/kT})} (-e^{-\varepsilon_0/kT}) \left(\frac{\varepsilon_0}{kT^2} \right) = N\varepsilon_0 \frac{e^{-\varepsilon_0/kT}}{(1 - e^{-\varepsilon_0/kT})} = N\varepsilon_0 \frac{1}{(e^{\varepsilon_0/kT} - 1)} \\
 C_{V \text{ conf}} &= \frac{dU_{\text{conf}}}{dT} = N\varepsilon_0 \frac{-e^{\varepsilon_0/kT} (-\varepsilon_0/kT^2)}{(e^{\varepsilon_0/kT} - 1)^2} = Nk \left(\frac{\varepsilon_0}{kT} \right)^2 \frac{e^{\varepsilon_0/kT}}{(e^{\varepsilon_0/kT} - 1)^2} \\
 S_{\text{conf}} &= -\frac{A_{\text{conf}}}{T} + \frac{U_{\text{conf}}}{T} = Nk \left[-\ln(1 - e^{-\varepsilon_0/kT}) + \frac{\varepsilon_0/kT}{e^{\varepsilon_0/kT} - 1} \right]
 \end{aligned}$$

Particularly important are U_{conf} and $C_{V \text{ conf}}$ and their high-T and low-T limits. Both quantities scale with N , so we have them per molecule too.

Low-T limit: $U_{\text{conf}} = 0$, $C_{V \text{ conf}} = 0$. As we've seen before, at low T all the molecules are in the ground state, and a slight increase in T leaves them there, so the system energy does not increase.

High-T limit: $\lim_{T \rightarrow \infty} U_{\text{conf}} = N\varepsilon_0 \frac{1}{(1 + \varepsilon_0/kT - 1)} = NkT$, $\lim_{T \rightarrow \infty} C_{V \text{ conf}} = Nk$

Once kT exceeds the energy spacing, then further increase in T increases the occupation of higher levels, but the amount of energy increase with T doesn't change any further: $U_{\text{conf}} \propto T$, $C_{V\text{conf}}$ is T -independent in the high- T limit.

Entropy & populations

Low- T limit: $S_{\text{conf}} = 0 = k \ln \Omega_{\text{conf}}$ since only the ground state is occupied.

High- T limit:

$$\lim_{T \rightarrow \infty} S_{\text{conf}} = Nk \left[-\ln(1 - (1 - \varepsilon_0/kT)) + \frac{\varepsilon_0/kT}{1 + \varepsilon_0/kT - 1} \right] = Nk \left[-\ln(\varepsilon_0/kT + 1) \right]$$

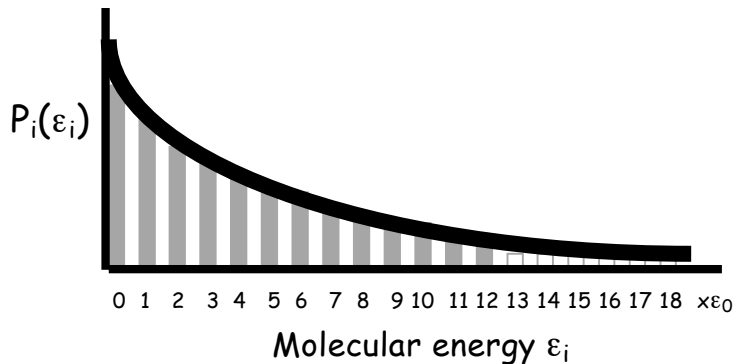
$$= Nk \ln(kT/\varepsilon_0) = k \ln(kT/\varepsilon_0)^N$$

Note high- T limits for q and Q :

$$\lim_{T \rightarrow 0} q_{\text{conf}} = 1 = \lim_{T \rightarrow 0} Q_{\text{conf}} \quad \lim_{T \rightarrow \infty} q_{\text{conf}} = \frac{kT}{\varepsilon_0}, \quad \lim_{T \rightarrow \infty} Q_{\text{conf}} = \left(\frac{kT}{\varepsilon_0} \right)^N$$

q is a measure of how many states the molecule has thermal access to.

For $kT \gg \varepsilon_0$, it's the ratio kT/ε_0 , e.g. if $kT = 50$ then molecules have thermal access to ~ 50 states. Probability for a molecule to be in a state declines exponentially with energy of the state - no sharp cutoff of probabilities.



Most likely molecular energy is 0 (for nondegenerate levels)

Wide range of molecular levels may be occupied

Most likely system energy $\gg 0$ since system microstate degeneracies increase sharply with system energy E . For 10^{24} molecules, there are 10^{24} microstates of the system with all the molecules in the ground state and one in the first excited state ($n = 1$). There are $(10^{24})^2$ microstates of the system with two molecules in $n = 1$ plus 10^{24} microstates with one molecule in the $n = 2$ level, so there are $(10^{24})^2 + 10^{24}$ total microstates with total energy $2\varepsilon_0$. And so on - the

system degeneracy $\Omega(E)$ increases sharply with E . But eventually the Boltzmann factor wins, so the probability of very high system E is low.

How much does the system energy fluctuate? Very little!

System energy $\propto N \times$ molecular average energy

Fluctuation or standard deviation in system energy $\propto \sqrt{N}$ \times molecular average energy. So variation $\sim \frac{\text{average}}{\sqrt{N}}$, e.g. for 10^{24} molecules, std deviation $\sim 10^{-12}$

times the average value - way too small to measure.

Back to system entropy, $S = -k \sum_i p_i \ln p_i$ for system at constant T .

But we can approximate $S = k \ln \Omega$ where $\Omega(E)$ is the degeneracy for the most probable level. This is OK because the range of system energies is very small.

Vibrational partition function & thermodynamics

The double-stranded polymer model used here gives the same energies as quantum mechanical vibrational modes of molecules and materials.

Classical vibration: $E = \frac{1}{2}mv^2 + \frac{1}{2}kx^2 = \text{K.E.} + \text{P.E.}$, where m is mass, v is velocity, k is force constant (for this section only, normally it's the Boltzmann constant), and x is displacement.

Natural resonance frequency $\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$

Vibrational amplitude & energy can take on any value, continuously.

QM vibrational states: nondegenerate, spaced by equal amounts. Spacing is

$$\epsilon_0 = h\nu_0 = h \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad h \equiv \text{Planck's constant}$$

We've already done this problem! We can define the zero of vibrational energy as the lowest vibrational level, and we get identical results.

$$q_{vib} = \sum_n e^{-\varepsilon_n/kT} \approx \sum_n e^{-n\varepsilon_0/kT} = 1 + e^{-\varepsilon_0/kT} + e^{-2\varepsilon_0/kT} + e^{-3\varepsilon_0/kT} + \dots$$

$$= 1 + e^{-\varepsilon_0/kT} + (e^{-\varepsilon_0/kT})^2 + (e^{-\varepsilon_0/kT})^3 + \dots \equiv 1 + x + x^2 + x^3 + \dots = \frac{1}{1-x}$$

$$q_{vib} = \frac{1}{1 - e^{-\varepsilon_0/kT}}$$

$$Q_{vib} = (q_{vib})^N = \left(\frac{1}{1 - e^{-\varepsilon_0/kT}} \right)^N$$

$$A_{vib} = -NkT \ln q_{vib} = -NkT \ln \left(\frac{1}{1 - e^{-\varepsilon_0/kT}} \right) = NkT \ln(1 - e^{-\varepsilon_0/kT})$$

$$\mu_{vib} = \left(\frac{\partial A_{vib}}{\partial N} \right)_{T,V} = kT \ln(1 - e^{-\varepsilon_0/kT}) \quad A_{vib} \text{ scales with } N, \mu_{vib} = A_{vib}/N$$

$$U_{vib} = NkT^2 \frac{d \ln q_{vib}}{dT} = -NkT^2 \frac{1}{(1 - e^{-\varepsilon_0/kT})} (-e^{-\varepsilon_0/kT}) \left(\frac{\varepsilon_0}{kT^2} \right) = N\varepsilon_0 \frac{e^{-\varepsilon_0/kT}}{(1 - e^{-\varepsilon_0/kT})} = N\varepsilon_0 \frac{1}{(e^{\varepsilon_0/kT} - 1)}$$

$$C_{V,vib} = \frac{dU_{vib}}{dT} = N\varepsilon_0 \frac{-e^{\varepsilon_0/kT} (-\varepsilon_0/kT^2)}{(e^{\varepsilon_0/kT} - 1)^2} = Nk \left(\frac{\varepsilon_0}{kT} \right)^2 \frac{e^{\varepsilon_0/kT}}{(e^{\varepsilon_0/kT} - 1)^2}$$

$$S_{vib} = -\frac{A_{vib}}{T} + \frac{U_{vib}}{T} = Nk \left[-\ln(1 - e^{-\varepsilon_0/kT}) + \frac{\varepsilon_0/kT}{e^{\varepsilon_0/kT} - 1} \right]$$

Results are important for molecular & material vibrations.

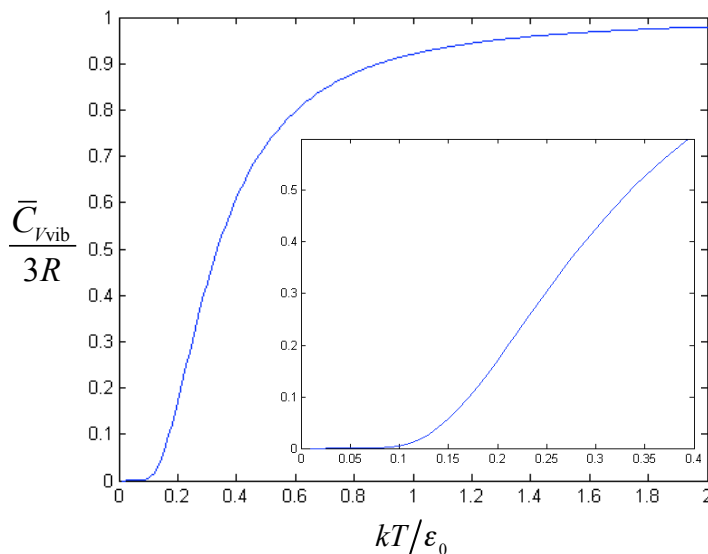
Vibrational energy & heat capacity results & limiting values:

Low-T limit: $U_{vib} = 0$ ($= N(\frac{1}{2}\varepsilon_0)$ with the zero as usually defined), $C_{V,vib} = 0$.

High-T limit: $\lim_{T \rightarrow \infty} U_{vib} = NkT$, $\lim_{T \rightarrow \infty} C_{V,vib} = Nk$

Molecular vibrational frequencies $\sim 1000\text{-}3000 \text{ cm}^{-1}$. kT at 300 K $\sim 200 \text{ cm}^{-1}$.
 \Rightarrow most molecules in ground vibrational states at room T (low-T limit).

Crystal lattice acoustic vibrational frequencies $\sim 30 \text{ cm}^{-1} \Rightarrow$ most crystals are in the high-T limit. For N atoms in



an atomic crystal, there are $3N$ vibrational modes, so at room T , $C_V = 3Nk = 3nR$. This was used to determine molecular weights!

No one could explain why $C_V \rightarrow 0$ at low T until Einstein suggested in 1905 that if energy was quantized, not continuous, then kT can be much lower than the first excited state energy. (Not possible if energy is continuous.)

Molecular translation & rotation, classical equipartition of energy

Results are derived in statistical mechanics course 5.62 (and in your text). One key result: for each degree of freedom (3 translational, 2 or 3 rotational), high- T limit for energy is $\langle \epsilon \rangle = \frac{1}{2}kT$ & for heat capacity is $C_V = \frac{1}{2}k$.

$$\langle \epsilon_{\text{trans}} \rangle = \frac{1}{2}kT \times 3 = 3/2 kT$$

$$\langle \epsilon_{\text{rot}} \rangle = \frac{1}{2}kT \times 2 = kT \text{ (linear) or } \frac{1}{2}kT \times 3 = 3/2 kT \text{ (nonlinear)}$$

$$\langle \epsilon_{\text{vib}} \rangle = kT \text{ per vibrational mode}$$

This is the *classical equipartition of energy*. Why does it come about?

Each degree of freedom has kinetic energy given classically by $\frac{1}{2}mv^2$. ($\frac{1}{2}I\omega^2$ for rotation where I = moment of inertia and ω = angular velocity.)

Vibrational degrees of freedom: kinetic energy $\frac{1}{2}mv^2$ & potential energy $\frac{1}{2}kx^2$.

All these "squared" energy terms can be written in the form ay^2 .

The average molecular energy for any of these degrees of freedom is given by

$$\langle \epsilon \rangle = \langle \epsilon \rangle = \frac{\sum_i \epsilon_i e^{-\epsilon_i/kT}}{\sum_i e^{-\epsilon_i/kT}}$$

But if the levels are spaced close together relative to kT , then we can convert the sums into integrals. If we treat the energy classically then it's just

$$\langle \epsilon \rangle = \frac{\int_{-\infty}^{\infty} ay^2 e^{-ay^2/kT} dy}{\int_{-\infty}^{\infty} e^{-ay^2/kT} dy} = \frac{kT \int_{-\infty}^{\infty} x^2 e^{-x^2} dx}{\int_{-\infty}^{\infty} e^{-x^2} dx} \quad \text{where } x^2 = ay^2/kT$$

Integrate numerator by parts

$$\begin{aligned} \int_{-\infty}^{\infty} x^2 e^{-x^2} dx &= \int_{-\infty}^{\infty} x (x e^{-x^2}) dx \quad [x \equiv u, x e^{-x^2} \equiv dv, v = (-1/2)e^{-x^2}] \\ &= -\frac{1}{2} x e^{-x^2} \Big|_{-\infty}^{\infty} + \frac{1}{2} \int_{-\infty}^{\infty} e^{-x^2} dx = \frac{1}{2} \int_{-\infty}^{\infty} e^{-x^2} dx \end{aligned}$$

$$\Rightarrow \boxed{\langle \epsilon \rangle = \frac{1}{2} kT}$$

$\frac{1}{2}kT$ energy per kinetic and potential energy degree of freedom in high-T limit