5.60 Thermodynamics & Kinetics
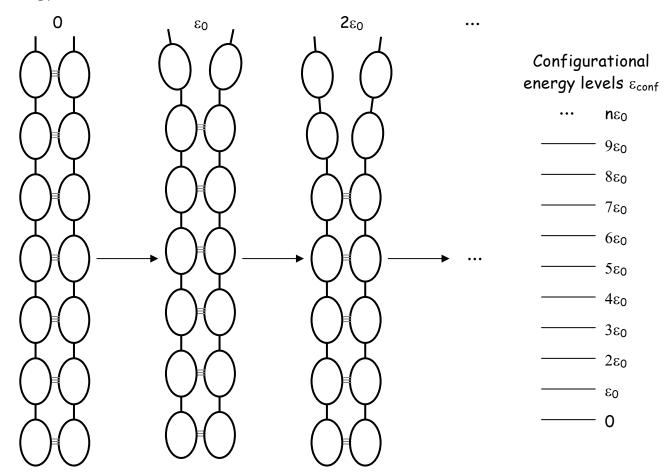Spring 2008

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 $-\varepsilon_0$.
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: $\varepsilon = n\varepsilon_0$ (n = 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).

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

$$= 1 + e^{-\varepsilon_0/kT} + \left(e^{-\varepsilon_0/kT}\right)^2 + \left(e^{-\varepsilon_0/kT}\right)^3 + \cdots \equiv 1 + x + x^2 + x^3 + \cdots = \frac{1}{1-x} \quad \text{where } x \equiv e^{-\varepsilon_0/kT}$$

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

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

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

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

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

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

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

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

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

Low-T limit: $U_{conf} = 0$, $C_{Vconf} = 0$. 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: $\displaystyle\lim_{T\to\infty} U_{conf} = N\varepsilon_0\frac{1}{\left(1 + \varepsilon_0/kT - 1\right)} = NkT$, $\displaystyle\lim_{T\to\infty} C_{V\,conf} = Nk$

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: $U_{conf} \propto T$, C_{Vconf} is T-independent in the high-T limit.

Entropy & probability distributions

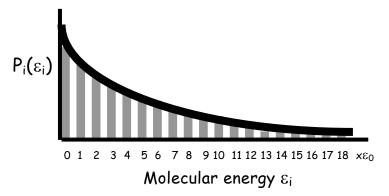Low-T limit: $S_{conf} = 0 = k\ln\Omega_{conf}$ since only the ground state is occupied.
High-T limit:

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

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

Note high-T limits for q and Q:

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

q is a measure of how many states the molecule has thermal access to.
For $kT \gg \varepsilon_0$, it's just the ratio kT/ε_0
If $kT = 10\varepsilon_0$ then molecules have thermal access to ~ 10 states.
Boltzmann distribution $P_i(\varepsilon_i)$ gives probabilities for each state:

Molecular energy ε_i

Most likely molecular energy ε is 0 (for nondegenerate levels)
Wide range of molecular levels may be occupied
Average molecular energy $\langle\varepsilon\rangle \gg 0$

System energy $U = N\langle\varepsilon\rangle \gg 0$
Individual molecular energies vary widely, but system energy does not

How come?
Recall $Q = \displaystyle\sum_{\substack{system \\ states\ i}} e^{-E_i/kT} = \sum_{\substack{system \\ energies\ E_i}} \Omega_{E_i} e^{-E_i/kT}$

Also recall $P_i = \dfrac{e^{-E_i/kT}}{\sum_i e^{-E_i/kT}} \Rightarrow P_{E_i} = \dfrac{\Omega_{E_i} e^{-E_i/kT}}{\sum_i e^{-E_i/kT}} = \dfrac{\Omega_{E_i} e^{-E_i/kT}}{Q}$

Measurement of macroscopic system energy always yields the same result
$\Rightarrow P(E) \approx 1$ for that system energy!

System degeneracy $\Omega(E_i)$ increases sharply as system energy E_i increases.
e.g. $\Omega(0) = 1$; $\Omega(\varepsilon_0) = N$; $\Omega(2\varepsilon_0) = N(N - 1)/2 + N \approx N^2/2$; etc.
This weights probability in favor of higher system energy.
Boltzmann factor decreases as system energy increases.
This weights probability in favor of lower system energy.
Average is a balance between these factors. Probability is very sharply peaked!

How much does the system energy fluctuate?
Molecular average energy = ‹ε›, molecular standard deviation $\sigma \approx$ ‹ε›
System energy = N x molecular average energy = N‹ε›
System standard deviation = $\sqrt{N}\,\sigma \approx \sqrt{N}$ ‹ε›

Relative system energy variation = $\dfrac{\sqrt{N}\langle\varepsilon\rangle}{N\langle\varepsilon\rangle} = \dfrac{\sqrt{N}}{N} \approx \dfrac{10^{12}}{10^{24}} = 10^{-12}$

Fluctuations are immeasurably small for a macroscopic system!

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: $E = \frac{1}{2}mv^2 + \frac{1}{2}kx^2$ = K.E. + 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 $\nu_0 = \dfrac{1}{2\pi}\sqrt{\dfrac{k}{m}}$

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

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

$$\varepsilon_0 = h\nu_0 = h\frac{1}{2\pi}\sqrt{\frac{k}{m}} \qquad h \equiv \text{Planck's constant}$$

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

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

$$= 1 + e^{-\varepsilon_0/kT} + \left(e^{-\varepsilon_0/kT}\right)^2 + \left(e^{-\varepsilon_0/kT}\right)^3 + \cdots \equiv 1 + x + x^2 + x^3 + \cdots = \frac{1}{1-x} \quad \text{where } x \equiv e^{-\varepsilon_0/kT}$$

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

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

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

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

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

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

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

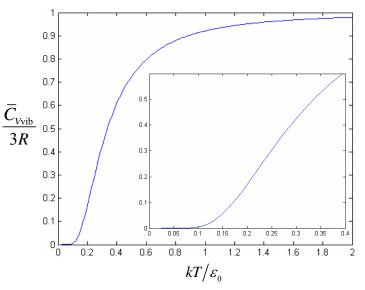Results are important for molecular & material vibrations.

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_{Vvib} = 0.

High-T limit: $\displaystyle\lim_{T\to\infty} U_{vib} = NkT$, $\displaystyle\lim_{T\to\infty} C_{V_{vib}} = Nk$

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

Crystal lattice acoustic vibrational frequencies ~ 30 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 $C_V \to 0$ 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 ‹ε› = $\frac{1}{2}$kT & for heat capacity is Cv = $\frac{1}{2}$k.

　　　‹ε_{trans}› = $\frac{1}{2}$kT x 3 = 3/2 kT
　　　‹ε_{rot}› = $\frac{1}{2}$kT x 2 = kT (linear) or $\frac{1}{2}$kT x 3 = 3/2 kT (nonlinear)
　　　‹ε_{vib}› = kT 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

$$\langle\varepsilon\rangle = \langle\varepsilon\rangle = \sum_i^\infty \varepsilon_i e^{-\varepsilon_i/kT} \Big/ \sum_i^\infty e^{-\varepsilon_i/kT}$$

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

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

Integrate numerator by parts

$$\int_{-\infty}^\infty x^2 e^{-x^2}dx = \int_{-\infty}^\infty x\left(xe^{-x^2}\right)dx \qquad [x \equiv u,\ xe^{-x^2} \equiv dv,\ v = \left(-1/2\right)e^{-x^2}]_{\triangle ABC}$$

$$= -\frac{1}{2}xe^{-x^2}\Big|_{-\infty}^\infty + \frac{1}{2}\int_{-\infty}^\infty e^{-x^2}dx = \frac{1}{2}\int_{-\infty}^\infty e^{-x^2}dx$$

$$\Rightarrow \qquad \boxed{\langle\varepsilon\rangle = \tfrac{1}{2}kT}$$

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