(2.1) **Entropy of Glasses.**


Glasses aren’t really in equilibrium. In particular they do not obey the third law of thermodynamics, that the entropy \( S \) goes to zero at zero temperature. Experimentalists measure a “residual entropy” by subtracting the entropy change from the known liquid entropy at the crystalline melting temperature \( T_c \):

\[
S_{\text{residual}} = S_{\text{liquid}} (T_c) - \int_0^{T_c} \frac{1}{T} \frac{dQ}{dT} dT.
\]

If you put a glass in an insulated box, it will warm up (very slowly) because of microscopic atomic rearrangements which lower the potential energy. So, glasses don’t have a well-defined temperature or specific heat. In particular, the heat flow upon cooling and on heating \( \frac{dQ}{dT} (T) \) won’t precisely match (although their integrals will agree by conservation of energy).

(a) By using the second law (entropy can only increase), show that the residual entropy measured on cooling is always less than the residual entropy measured on heating.

The residual entropy of a glass is about \( k_B \) per molecular unit. It’s a measure of how many different glassy configurations of atoms the material can freeze into (section I.46-4).

(b) In a molecular dynamics simulation with one hundred atoms, and assuming that the residual entropy is \( k_B \log 2 \) per atom, what is the probability that two coolings to zero energy will arrive at equivalent* atomic configurations? In a system with \( 10^{23} \) molecular units, with residual entropy \( k_B \log 2 \) per unit, how many coolings would be needed to arrive at the original configuration again, with probability 1/2?

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* Up to, *e.g.*, translations and rotations.
(2.2) **Shannon entropy.**


Entropy can be viewed as a measure of the lack of information you have about a system. Claude Shannon realized, back in the 1940’s, that communication over telephone wires amounts to reducing the listener’s uncertainty about the sender’s message, and introduced a definition of an information entropy.

Most natural languages (voice, written English) are highly redundant; the number of intelligible fifty-letter sentences is many fewer than $26^{50}$, and the number of ten-second phone conversations is far smaller than the number of sound signals that could be generated with frequencies between 60 and 20,000 Hz. Shannon, knowing statistical mechanics, defined the entropy of an ensemble of messages: if there are $N$ possible messages that can be sent in one package, and message $m$ is being transmitted with probability $p_m$, then Shannon’s entropy is

$$S = -k \sum_{1}^{N} p_m \log p_m$$

where instead of Boltzmann’s constant, Shannon picked $k = 1/\log 2$.

(a) Suppose that all possible sequences are equally likely, and that $N$ is a power of two. Show that Shannon’s entropy is the number of bits that would be needed to transmit a message.

This immediately suggests a theory for signal compression. If you can recode the alphabet so that common letters and common sequences of letters are abbreviated, while infrequent combinations are spelled out in lengthly fashion, you can dramatically reduce the channel capacity needed to send the data. (This is lossless compression, like zip and gz and gif).

(b) Argue that, if the Shannon entropy per unit time of a signal is larger than the number of bits per second possible for the communication channel, that no conceivable amount of compression can reliably transmit messages. (Hint: compute the Shannon entropy of the encoded messages in terms of the Shannon entropy of the unencoded messages. What ensemble of transmitted signals has the maximum entropy?)

Shannon, by outlining some primitive compression schemes, showed conversely the information entropy of the messages transmitted through the channel could be made arbitrarily close to that of the number of bits per second for the channel.

(c) Presuming that aliens understand Shannon’s ideas, suggest how this could make it difficult for SETI to recognize radio signals from advanced civilizations.

Shannon also developed a measure of the channel capacity of a noisy wire, and discussed error correction codes...
(2.3) **Dyson’s Time without End: Life and the Heat Death of the Universe.**
Freeman Dyson discusses how living things might evolve to cope with the cooling and dimming we expect during the heat death of the universe.
Dyson models an intelligent being as a heat engine that consumes a fixed entropy $\Delta S$ per thought.

(a) **Energy needed per thought.** Assume that the being draws heat $Q$ from a hot reservoir at $T_1$ and radiates it away to a cold reservoir at $T_2$. What is the minimum energy $Q$ needed per thought, in terms of $\Delta S$ and $T_2$? (You may take $T_1$ very large.)

(b) Write an expression for the maximum rate of thoughts per unit time $dH/dt$ (the inverse of the time $\Delta t$ per thought), in terms of $\Delta S$, $C$, and $T_2$.

**Time needed per thought to radiate energy.** Dyson shows, using theory not important here, that the power radiated by our intelligent–being–as–heat–engine is no larger than $CT_2^3$, a constant times the cube of the cold temperature. (The constant scales with the number of electrons in the being, so we can think of our answer $\Delta t$ as the time per thought per mole of electrons.)

(c) How many thoughts $H$ can an ecologically efficient being, radiating at a fixed multiple of $\Theta(t)$, have between now and time infinity, in terms of $\Delta S$, $C$, $A$, and the current time $t_0$?

**Time without end: Greedy beings.** Dyson would like his beings to be able to think an infinite number of thoughts before the universe ends, but consume a finite amount of energy. He proposes that his beings need to be profligate in order to get their thoughts in before the world ends: he proposes that they radiate at a temperature $T_2(t) \sim t^{-3/8}$ which falls with time, but not as fast as $\Theta(t) \sim t^{-1}$.

(d) Show that with Dyson’s radiation schedule, the total number of thoughts $H$ is infinite, but the total energy consumed $U$ is finite.
(2.4) Thermodynamics Review II: Gibbs-Duhem relation and the Clausius-Clapeyron equation.

(a) Using the fact that the entropy $S(N, V, E)$ is extensive, show that

$$N \frac{\partial S}{\partial N} \bigg|_{V,E} + V \frac{\partial S}{\partial V} \bigg|_{N,E} + E \frac{\partial S}{\partial E} \bigg|_{N,V} = S.$$ 

Show from this that in general

$$S = \frac{(E + pV - \mu N)}{T}$$

and hence $E = TS - pV + \mu N$. This is Euler’s equation.

(b) Thermodynamics is invariant under an overall shift $s_0$ of the entropy per particle; non-relativistic quantum mechanics is invariant under shifts of the total energy (say, by $mc^2$ per particle). How are these shifts consistent with Euler’s relation? What else must shift?

As a state function, $S$ is supposed to depend only on $E$, $V$, and $N$. But equation (2.4.1) seems to show explicit dependence on $T$, $p$, and $\mu$ as well: how can this be?

(c) One answer is to write the latter three as functions of $E$, $V$, and $N$. Do this explicitly for the ideal gas, using last week’s equation (1.4.2)

$$S(N, V, E) = \frac{5}{2} N k_B + N k_B \log \left[ \frac{V}{N h^3} \left( \frac{4\pi m E}{3N} \right)^{3/2} \right],$$

and your (or the grader’s) results for problem 1.4(c), and verify equation (2.4.1) in that case.

Another answer is to consider a small shift of all six variables. We know that $dE = TdS - pdV + \mu dN$, but if we shift all six variables in Euler’s equation we get $dE = TdS - pdV + \mu dN + SdT - Vdp + Nd\mu$. This implies the Gibbs-Duhem relation

$$0 = SdT - Vdp + Nd\mu.$$ 

It means that the intensive variables $T$, $p$, and $\mu$ are not all independent.

![Generic phase diagram](http://server.chem.ufl.edu/itl/2045_s99/lectures/lec_f.html)
**Clausius-Clapeyron equation.** Consider the phase diagram above. Along an equilibrium phase boundary, the temperatures, pressures, and chemical potentials of the two phases must agree: otherwise a flat interface between the two phases would transmit heat, shift sideways, or leak particles, respectively (violating the assumption of equilibrium).

(d) Apply the Gibbs-Duham relation to both phases, for a small shift by $\Delta T$ across the phase boundary. Let $s_1, v_1, s_2,$ and $v_2$ be the molecular entropies and volumes for the two phases; derive the Clausius-Clapeyron equation for the slope of the coexistence line on the phase diagram

$$dP/dT = (s_1 - s_2)/(v_1 - v_2).$$  \hspace{1cm} (2.4.3)

(e) **Latent Heat.** It’s hard to experimentally measure the entropies per particle: we don’t have an entropy thermometer. But, as you will remember, the entropy difference upon a phase transformation $\Delta S = Q/T$ is related to the heat flow $Q$ needed to induce the phase change. Let the latent heat $L$ be the heat flow per molecule: write a formula for $dP/dT$ not involving the entropy.
(2.5) **Excited Atoms, Negative Temperature, and Micro→Canonical.**

A system of $N$ atoms can be in the ground state or in an excited state. For convenience, we set the zero of energy exactly in between, so the energies of the two states of an atom are $\pm \epsilon/2$. The atoms are isolated from the outside world. There are only weak couplings between the atoms, sufficient to bring them into internal equilibrium but without other effects.

(a) **Microcanonical Entropy.** If the net energy is $E$ (corresponding to a number of excited atoms $m = E/\epsilon + N/2$), what is the entropy $S(E)$ of our system? Simplify your expression using Stirling’s formula.

(b) **Negative Temperature.** Find the temperature. What happens to the temperature when $E > 0$?

This is called a population inversion. Population inversion is the driving mechanism for lasers. We’ll see later that microcanonical simulations can lead also to states with negative specific heats.

For many quantities, the thermodynamic derivatives have natural interpretations when viewed as sums over states. It’s easiest to see this in small systems.

(c) **Canonical Ensemble for Single Atom.** We now take one of our atoms and couple it to a heat bath of temperature $T = 1/\beta$. Write explicit formulas for $Z$, $E$, and $S$ as a trace (or sum) over the states of the atom. Calculate the Helmholtz free energy $A$, $E$ from derivatives of $A$, and $S$ from $A = E - TS$; the latter two formulas should agree with the averages from the tracing over states. (What happens to $E$ as $T \to \infty$? How does this relate to part (b)?)

(d) **Canonical-Microcanonical Correspondence.** Find the entropy in the canonical distribution for $N$ atoms coupled to the outside world, from your answer to part (c). How can you understand the value of $S(T = \infty) - S(T = 0)$ simply? Show that the canonical and microcanonical definitions agree, for large $N$ and for net number of excitations not too near to zero or $N$, (the region where Stirling’s formula is applicable). You’ll need to know the rather useful formula $\text{arctanh}(x) = (1/2) \log ((1 + x)/(1 - x))$.

(e) **Fluctuations.** Show that the root-mean-squared fluctuations in the energy in the canonical distribution are related to the specific heat. Calculate them. How much does the entropy change in this range of energies? Note that the canonical entropy is an average of the microcanonical entropies over the different energies, weighted by the probability for each energy. Does this explain why the two entropies stay nearly the same?
Specific Heat of Insulators.

(a) **Phonons in One Dimension.** A nano-string of length $L$ with mass per unit length $\mu$ under tension $\tau$ has a vertical, transverse displacement $u(x, t)$. The kinetic energy density is $(\mu/2)(\partial u/\partial t)^2$ and the potential energy density is $(\tau/2)(\partial u/\partial x)^2$. Change variables from $u(x, t)$ to normal modes $q_k(t)$ with $u(x, t) = \sum_n q_n(t) \sin(k_n x)$, $k_n = n\pi/L$, and show that the system is a sum of harmonic oscillators. Calculate the density of states per unit frequency $g(\omega) = \sum_n \delta(\omega - \omega_{k_n})$ and the specific heat of the string $c(T)$ per unit length in the limit $L \to \infty$, treating the oscillators quantum mechanically. What is the specific heat of the classical string?

(b) **Phonons in the Debye Approximation.** In three dimensions, the density of states for bulk phonons $g(\omega) \propto \omega^2$ at low frequencies. (At frequencies where the wavelength of the phonons becomes comparable to the lattice constant, more complicated structure occurs in the density of states.) With what power will the specific heat vanish for an insulating crystal?

The reason the specific heat of crystals gets small at low temperatures is that in a harmonic system many atoms must move cooperatively to get low frequencies. If we allow for strong anharmonicity, though, one can get quantum tunneling centers which give very low frequencies indeed.

An atom or a group of atoms with a double-well potential has an energy splitting between the ground state and the first excited state of $E = \sqrt{\epsilon^2 + \Delta^2}$, where $\epsilon$ is the asymmetry and $\Delta \propto \exp(-\sqrt{2MV_0Q_0/\hbar})$ is the quantum tunneling matrix element (related to the overlap of the “ground states in each well”). If the barrier is high $\Delta$ can become very small indeed, so for symmetric double wells you get excitations at low energies. However, the time to tunnel between two asymmetric wells scales as $\Delta^2$, so if the barrier gets too high the atom can’t tunnel during the experiment.
Tunneling Center: Li$^+$ in KCl.


A lithium substitutional impurity in potassium chloride will sit off-center (pointing towards one of the eight corners of the cube), with a small tunneling barrier leading to a tunneling amplitude $\Delta = 0.82\text{cm}^{-1} = 1.134K$ for hopping to the neighboring wells. One can show that this eight-level system is equivalent to three two-level systems with energy splitting $E = \Delta$, similar to those you studied in problem (2.5).

(c) Does the curve for pure KCl on the left agree with what you expect for phonons from part (b)? Plot the specific heat you expect for the dilute lithium impurities, and compare qualitatively to the specific heat with phonons subtracted off on the right. Tunneling defects at rather low concentration can produce huge effects in insulators at low temperatures, because there is no competition in that energy range.
Two-Level Systems and Low Temperature Glasses. Around 1970 in LASSP, Bobby Pohl and his graduate student Zeller (who got a master’s degree for this famous work) discovered that all glasses have similar low temperature properties. Above left is the specific heat of glassy and crystalline silica: notice that the glass has an extra specific heat at low temperatures. It was quickly realized that many of these properties could be explained rather nicely in terms of double wells. Presumably the atoms in the glass didn’t all have assigned positions the way they do in the crystal, and a few can tunnel at low temperatures (a few per million are active below 1 K). The tunneling centers important to the specific heat have tunneling matrix elements $\Delta$ much smaller than their asymmetries $\epsilon$.

(d) **Specific Heat of Glasses.** If the density of tunneling centers per unit energy with asymmetries near $\epsilon$ is nearly constant over a range of asymmetries that is large compared to the temperature, and if the tunneling matrix elements are small compared to the temperature, calculate the power law for the contribution of the tunneling centers to the specific heat.

(e) **Lack of Ergodicity and the Time-Dependent Specific Heat.** Some of the possible atomic rearrangements in glasses have very high barriers. The figure above right shows the change in the measured specific heat as the time-scale of the experiment is changed. Explain why a time-dependence is expected. Is this glass in equilibrium? Does it leak heat over time?
(2.7) Does Entropy Increase?

The second law of thermodynamics says that entropy always increases. Perversely, it’s easy to show that in an isolated system, no matter what non-equilibrium condition it starts in, entropy as precisely defined stays constant in time.

Entropy is Constant: Classical. Liouville’s theorem tells us that the total derivative of the probability density is zero: following the trajectory of a system, the local probability density never changes. The equilibrium states have probability densities that only depend on energy and number. Clearly something is wrong: if the density starts non-uniform, how can it become uniform?

(a) Let \( \rho(P,Q) \) is the probability density in phase space (where \( P = (p_1, \ldots, p_{3N}) \) are momenta and \( Q = (q_1, \ldots, q_{3N}) \) are the momenta). Show, for any function \( f(\rho) \), that\[ \frac{\partial f(\rho)}{\partial t} = \nabla \cdot \left[ f(\rho) \left( \dot{P}, \dot{Q} \right) \right] = \sum_\alpha \frac{\partial}{\partial p_\alpha} (f(\rho) \dot{p}_\alpha) + \frac{\partial}{\partial q_\alpha} (f(\rho) \dot{q}_\alpha). \] Hence, (by Gauss’s theorem in \( 6N \) dimensions), show \( \int \frac{\partial f(\rho)}{\partial t} dP dQ = 0 \), assuming that the probability density vanishes at infinite momenta and positions. Show, thus, that the entropy \( S = -k_B \int \rho \log \rho \) is constant in time.

(b) Entropy is Constant: Quantum. Prove that \( S = \text{Tr} \hat{\rho} \log \hat{\rho} \) is time-independent, where \( \hat{\rho} \) is any density matrix.

The Arnol’d Cat. Why do we think entropy increases? First, points in phase space don’t just swirl in circles: they get stretched and twisted and folded back in complicated patterns – especially in systems where statistical mechanics seems to hold! Arnol’d, in a takeoff on Schrödinger’s cat, suggested the following analogy. Instead of a continuous transformation of phase space onto itself preserving \( 6N \)-dimensional volume, let’s think of an area-preserving mapping of the plane into itself. (You might think of the mapping as a Poincaré section, remembering last problem set.) Consider the mapping \[ \Gamma \left( \begin{array}{c} x \\ y \end{array} \right) = \left( \begin{array}{c} x + y \\ x + 2y \end{array} \right) \mod n. \]

See the map illustrated below.

(c) Check that \( \Gamma \) preserves area (what is the determinant?). Show that it takes a square \( n \times n \) (or a picture of \( n \times n \) pixels) and maps it into itself with periodic boundary conditions. (With less cutting and pasting, you can view it as a map from the torus into itself.) As a linear map, find the eigenvalues and eigenvectors. Argue that a small neighborhood (say a circle in the center of the picture) will initially be stretched along an irrational direction, and then folded back into a thin line covering the square uniformly.

While there are always exactly the same number of pixels that are black, white, and each shade of gray, they rapidly get so kneaded together that everything looks a uniform color. So, by putting a limit to the resolution of our measurement (rounding errors on the computer, for example), or by introducing any tiny coupling to the external world, the final state can be seen to rapidly approach equilibrium, proofs to the contrary notwithstanding!
(2.8) **Maximizing Entropy.**

Pathria, problem 3.6, page 84.

(2.9) **Laplace (1749-1827), Lagrange (1736-1813) and Legendre (1752-1833).**

(a) **Laplace Transform.** Show (or note) that the canonical partition function can be written as the Laplace transform of the microcanonical partition function. I’ve never noticed that this was useful.

(b) **Lagrange Multipliers.** Show (or note) that in statistical mechanics one can go from the microcanonical distribution to the canonical distribution by adding a Lagrange multiplier, exchanging the constraint on the energy for a temperature. Similarly, show one goes from the canonical to the grand canonical distribution by adding the chemical potential as a Lagrange multiplier.

(c) **Legendre Transforms.** What thermodynamics potentials correspond to the microcanonical, canonical, and grand canonical ensembles? Give the Legendre transformations which lead one from one to the other.