Physics 127a: Class Notes

Lecture 4: Entropy

Second Law of Thermodynamics

If we prepare an isolated system in a macroscopic configuration that is not the equilibrium one, the subsequent evolution to equilibrium will lead to an increase of the entropy S. If the relaxation process passes through macroscopically defined configurations we can define an $S(t)$ that increases monotonically.

Note: Thermodynamics is only concerned with macroscopic states, i.e. ones that are essentially in equilibrium under some macroscopic constraints. A good example is two blocks of material at different temperatures. Thermodynamics tells you how to calculate the total entropy (e.g. integrate up the measured specific heat from zero temperature $S = \int C(T)/T \; dT$ for each system and add). If the two blocks are placed into contact, heat will flow between them until the temperature is equal, and you can again calculate the entropy. The second law says it must have increased! If the thermal contact is weak so that at any instant each body is effectively internally in equilibrium at some temperature, we can calculate $S(t)$ and this will increase monotonically.

Entropy in statistical mechanics

Consider an isolated macroscopic system of N particles in a volume V and with energy E. We define the entropy as

$$S(E, N, V) = k \; \ln \Omega(E, N, V) \tag{1}$$

where $\Omega(E, N, V)$ is the number of accessible states at the given values of E, N, V.

Since E, N, and V are all fixed there is nothing here that can evolve, so we need to generalize slightly. Suppose there is an internal macroscopic variable X (such as the partition of the total energy or number of particles between two halves of the system) that can be used to constrain the system away from equilibrium. The *entropy* of the system in the macroscopic configuration X is related to statistical quantities via

$$S(E, N, V, X) = k \; \ln \Omega(E, N, V, X) \tag{2}$$

where $\Omega(E, N, V, X)$ is the number of accessible states at the given values of E, N, V (which are fixed in an isolated system) *and with the constraint given by* X.

In these expressions k is a constant known as the Boltzmann constant. (Sometimes I will write it as k_B.) The increase of entropy in the second law of thermodynamics corresponds to the evolution from a *less* probable X (fewer accessible microstates, each equally likely) to a more probable X. Or to say it another way, most microstates sampled by the dynamics will correspond to the "more probable" X. As we saw in the coin-flip example, for macroscopic systems there are vastly more accessible states at the most probable value of X, so that the "likelihood" of evolving to a more probably X becomes a certainty.

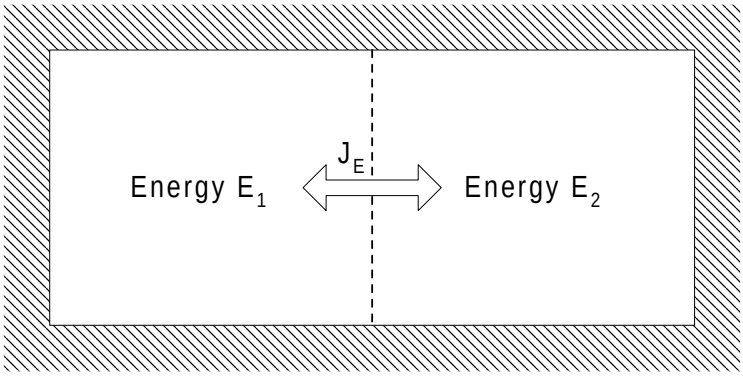
Any monotonic relationship between S and Ω would yield the increase of S. The ln function is used because we want *the entropy for independent systems to be additive*, as required for consistency with the thermodynamic entropy. (If Ω_1, Ω_2 are the number of accessible states for the two independent systems, then the total number of accessible states is $\Omega_1 \Omega_2$).

Notice we are defining the entropy of a *system* (as in thermodynamics) and it is only defined as a function of a *macroscopic configuration* (i.e. for systems effectively in equilibrium under a macroscopic constraint). This makes sense since the number of accessible states is only physically relevant if the system has time to explore them (or at least a representative subset of them) at essentially fixed X. This is appropriate to match to the thermodynamic notions of S. Later we will talk about possibly more general reformulations in terms of the entropy of an *ensemble*, and the entropy of *microscopically* defined configurations.

Equilibration

Investigating the approach to equilibrium under the transfer of energy allows us to relate the temperature, chemical potential, and pressure to S and so to the microscopic quantity Ω. Caluclating Ω from first principles allows us to calculate these physical quantities.

Equilibration under the transfer of energy



Consider an isolated system consisting of two subsystems that are in weak contact so that energy can flow between them, but the individual number of particles and volumes N_1, V_1 and N_2, V_2 are fixed. The energies of the subsytems are E_1, E_2 and $E_1 + E_2 = E$, a constant. We want to know what is the partition of energy in equilibrium, i.e. how much energy will be in subsytem 1 and how much in subsystem 2. For a particular energy partition we have the number of accessible states for the configuration with subsystem 1 having energy E_1 out of the total energy E is

$$\Omega(E_1, E) = \Omega_1(E_1)\Omega_2(E_2) \text{ with } E_2 = E - E_1, \tag{3}$$

or in terms of the entropy

$$S(E_1, E) = S_1(E_1) + S_2(E_2). \tag{4}$$

In terms of the general discussion, E_1 is playing the role of X. Note that $S_1(E_1)$, $S_2(E_2)$ are the expressions that would be obtained for the individual systems if they were each isolated.

Energy will flow in the direction that increases Ω, S, and the equilibrium partition will be the value of E_1 (and then $E_2 = E - E_1$) that maximizes Ω and S. This is given by differentiation

$$\frac{\partial S}{\partial E_1} = 0 \qquad \Rightarrow \qquad \frac{\partial S_1(E_1)}{\partial E_1} = \frac{\partial S_2(E_2)}{\partial E_2} \text{ with } E_2 = E - E_1. \tag{5}$$

Thus the equilibration is given by the equality of the quantity $\partial S/\partial E$ for each system. Thermodynamically we associate equilibrium under energy transfer with equality of temperature, so T should be related to $\partial S/\partial E$. Further considerations show the appropriate definition is

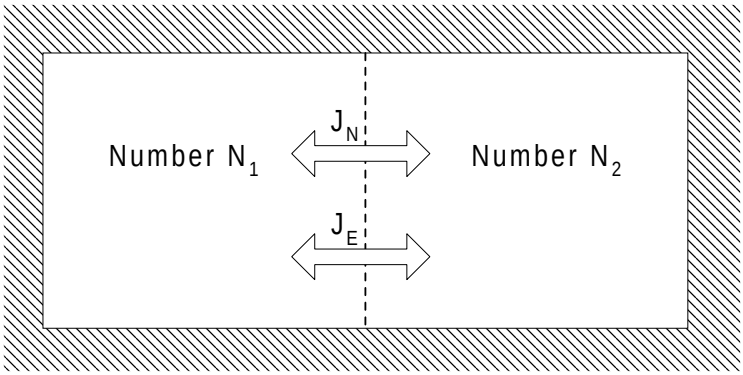
$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V}. \tag{6}$$

where the fact that N and V are constant in the differentiation is now noted. (Actually, see the homework, many things would have been simpler if the "temperature" had been defined so that it corresponds to $\partial S/\partial E$.

For example, who would be surprised that infinite beta-temperature, corresponding to our zero temperature, is unreachable?).

Is the final entropy the sum of the entropies of the two subsystems for the equilibrium energy partition? You might think the answer is *No*, since the accessible states also include those with fluctuations of E_1 away from the entropy-maximizing value. However there are so *vastly* many more states at the most probable value of E_1, that the extra states only change the size of the entropy by an amount less than $O(N)$, an amount not of concern in the thermodynamic context.

Equilibration under the change of particles and energy



Similar considerations show that

$$S(N, N_1) = S_1(N_1) + S_2(N - N_2) \tag{7}$$

should be maximized, so that

$$\left(\frac{\partial S_1}{\partial N_1}\right) = \left(\frac{\partial S_2}{\partial N_2}\right). \tag{8}$$

Thus in addition to $T_1 = T_2$ we get $\mu_1 = \mu_2$ where the chemical potential μ is defined as

$$\frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{E,V} \tag{9}$$

where the factor of T and the minus sign are to get agreement with the conventional usage.

Equilibration under the change of volume and energy If we allow a movable piston between the two subsystems, so that $V_1 + V_2 = V$ is fixed, but the individual volumes may change, similar arguments show that in addition to $T_1 = T_2$ in equilibrium we must have

$$\left(\frac{\partial S_1}{\partial V_1}\right) = \left(\frac{\partial S_2}{\partial V_2}\right). \tag{10}$$

We associate the equilibrium under mechanical motion with equality of pressure, $P_1 = P_2$, which is consistent with this result if we define

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N}. \tag{11}$$

You might ask what about equilibration under the change of volume but not energy. The same argument would seem to imply $P_1/T_1 = P_2/T_2$. However this sort of contact does not correspond to any common physical experiment, since if the volume changes the moving piston necessarily does work on the gas, and so the energy changes.

Entropy of the Classical Monatomic Ideal Gas

For N particles the energy is

$$E = \sum_{i=1}^{3N} \frac{p_i^2}{2m} \tag{12}$$

with p_i the $3N$ components of momentum. The energy of the ideal gas does not depend on the position coordinates. The entropy is determined by $\Omega(E)$ the number of states at energy E. First we will calculate $\Sigma(E)$ which is the number of states with energy *less* than E.

Clearly

$$\Sigma(E) = \frac{\int \ldots \int_{|p|<\sqrt{2mE}} d^{3N}p \int \ldots \int_{V^n} d^{3N}x}{\text{Volume of phase space per state}} \tag{13}$$

where $|p|$ is the length of the $3N$ dimensional momentum vector, $d^{3N}p$ denotes the integration over the $3N$ momentum coordinates etc. Let's look at each piece of this expression in turn.

- $\int \ldots \int_{|p|<\sqrt{2mE}} d^{3N}p$ is the volume of a $3N$ dimensional sphere of radius $\sqrt{2mE}$ which we write as $O_{3N}(\sqrt{2mE})$. This is just a geometrical calculation, which I will not go through (see, for example, Appendix C of Pathria). For a sphere of radius R in n dimensions $O_n(R) = C_n R^n$ with

  $$C_n = \frac{\pi^{n/2}}{\frac{n}{2}!} \tag{14}$$

  where the factorial of a half integral is defined in the usual iterative way $n! = n(n-1)!$ and with $\frac{1}{2}! = \sqrt{\pi}/2$. (This function can also be written in terms of the gamma function $\Gamma(n) = (n-1)!$)

- $\int \ldots \int_{V^n} d^{3N}x = V^N$

- The volume per state is arbitrary in a completely classical approach to the particle dynamics, which only deals with continuum variables. It is useful here [1] to make contact with quantum mechanics and we find

  $$\text{Volume of phase space per state} = h^{3N} N! \tag{15}$$

  The h^{3N} leads to an additive constant in the entropy per particle, and so is not too important. The $N!$ part is essential to find an entropy that is *extensive*, and was a rather mysterious ad hoc addition in the pre-quantum years this calculation was first done. The inclusion resolves the *Gibbs Paradox*.

  The factor of h for each x, p coordinate pair reflects the uncertainty principle

  $$\Delta x \Delta p_x \gtrsim h. \tag{16}$$

  More precisely, we imagine particles confined in a box of side L. In quantum mechanics boundary conditions are needed to define the wave function, yet in a macroscopic system we do not expect the precise nature of the boundaries to affect extensive quantities such as the entropy. We therefore choose the mathematically convenient *periodic boundary conditions* $\psi(x+L) = \psi(x)$ etc. (For a more detailed account of other choices see Pathria §1.4.) This leads to wave functions which are the products of exponentials

  $$\psi(x_1, x_2 \ldots) = e^{2\pi i n_1 x_1/L} \ldots \tag{17}$$

[1] We could proceed completely classically, and then the entropy would end up defined only up to an additive constant that depends on the choice of the volume of phase space per state. This might appear ugly, but since only *differences* of entropy have any thermodynamic consequence, it is not a real problem.

with $n_1, n_2 \ldots$ integers, so that $p_1 = n_1 2\pi\hbar/L = n_1 h/L$. The allowed momentum states form a "cubic" lattice in $3N$ dimensional momentum space with cube edge h/L and so the volume of phase space per state is $(h/L)^{3N} L^{3N} = h^{3N}$.

The factor of $N!$ arises because from quantum mechanics we recognize that *identical particles* are *indistinguishable*. In a two-particle, one-dimensional system, for example, this means that the phase space volumes with particle 1 at x, p and particle 2 at x', p' is the *same state* as the one with particle 1 at x', p', and particle 2 at x, p. So in this case 2 volumes of h^2 correspond to a *single* state. In the N particle system in 3 dimensions there are $N!$ configurations of the particles amongst different phase space volumes of h^{3N} that correspond to a single quantum state. This is the $N!$ factor that we must include in the volume of phase space per state.

Note that for a phase space point with two or more particles having the *same* coordinates and momenta, this correction factor is not correct. For example in the 2-particle one-dimension system there is a single phase space volume corresponding to both particles at x, p, and also a single quantum state, so no correction factor is needed. However the classical ideal gas is only a good description in the dilute, high temperature limit, where the probability of finding two or more particles within the same volume h^{3N} in phase space is negligible, and so these contributions with the "wrong" correction factor can be ignored. In fact this precisely defines the limit of a "classical gas" rather than a "quantum gas". In fact in the quantum limit, where these types of configurations become important, we truly need to worry about quantum issues: for example, for a Fermion gas the state with two particles in the same phase space volume is not allowed by the Pauli exclusion principle.

An aside: we are now in a position to fix the normalization of the phase space distribution $\rho(q, p)$. We choose a normalization so that $\rho(q, p)$ is the probability of finding the system in a quantum state (i.e. a volume of phase space $h^{3N} N!$) at q, p

$$\rho(q, p) \frac{d^{3N} q d^{3N} p}{N! h^{3N}} = \frac{dN_E}{N_E} \tag{18}$$

where dN_E is the number of members of the ensemble (of total number N_E) with phase space point in the volume $d^{3N} q d^{3N} p$ at q, p. Note the normalization is

$$\int \cdots \int \rho(q, p) \frac{d^{3N} q d^{3N} p}{N! h^{3N}} = 1 \tag{19}$$

For an isolated system in equilibrium where equal probabilities applies $\rho = 1/\Omega$.

We can now calculate $\Sigma(E)$

$$\Sigma(E) = \frac{C_{3N}}{N!} \left[\frac{V}{h^3} (2mE)^{3/2} \right]^N . \tag{20}$$

It should be recognized that $\Sigma(E)$ is a smoothed function, since we are counting the number of points on the hypercubic momentum lattice of side h/L inside a hypershpere, and this will jump discontinuously (see Pathria Fig. 1.2). However the jumps are *extremely* closely spaced (an energy of order e^{-N} for large N) and certainly of no concern in a macroscopic system.

Equally the number of states *at* an energy E is zero for most E, since the surface of the sphere will not typically hit one of the discrete momentum points. (Alternatively, $d\Sigma/dE$ is a set of delta-function spikes at the points where Σ jumps.) We need to define a smoothed $\Omega(E)$ by counting the number of states within some small energy band Δ. (Then our ensemble of isolated systems would be defined as having this spread of energies, etc.) Thus we define

$$\Omega = \frac{d\Sigma}{dE} \Delta . \tag{21}$$

Since $\Sigma \propto E^{3N/2}$, on taking logs we see

$$\ln \Omega = \ln \Sigma + \ln(\frac{3}{2}\frac{N}{E}\Delta). \tag{22}$$

The first term on the right hand side is $O(N)$, compared to which the second term is negligible for a *vast* range of choices of Δ, and can be ignored for macroscopic systems. (For example, we might choose Δ to be some tiny fraction of a typical energy per particle.) So the size of the choice of energy band Δ does not matter, and we can approximate the number of states near the surface of the hypersphere by the total number of states inside the sphere—such is the magic of high dimensions! Thus the entropy is $S \simeq k \ln \Sigma$.

Now it is algebra. Use Stirling's approximation

$$\ln C_{3N} \simeq \frac{3N}{2}\ln\pi - \frac{3N}{2}\ln\frac{3N}{2} + \frac{3N}{2} \tag{23}$$

$$\ln N! \simeq N \ln N - N \tag{24}$$

to find the *Sackur-Tetrode* expression for the entropy of the classical ideal gas

$$S = Nk\left\{\ln\left[\frac{V}{Nh^3}\left(\frac{4\pi m E}{3N}\right)^{3/2}\right] + \frac{5}{2}\right\}. \tag{25}$$

As promised, this is an *extensive* quantity.

From this expression it is easy to derive the basic thermodynamic results for the ideal classical monatomic gas. To take derivatives it is convenient to write

$$S = Nk\left[\ln V + \frac{3}{2}\ln E - \frac{5}{2}\ln N + \text{consts}\right] \tag{26}$$

- $E(T)$: Use

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V} \qquad \text{to find} \qquad E = \frac{3}{2}NkT \tag{27}$$

  and so the specific heat at constant volume

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{3}{2}Nk \tag{28}$$

- Ideal gas law: use

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} \qquad \text{to find} \qquad PV = NkT. \tag{29}$$

  Note that

$$P = \frac{2}{3}\frac{E}{V} \tag{30}$$

  a result that can be derived directly and generally using $P = -(\partial E/\partial V)_S$.

- Specific heat at constant pressure: we must include the work done against the pressure as the volume changes

$$C_P = \frac{d}{dT}(E + PV) = \frac{5}{2}Nk \tag{31}$$

  so that $\gamma = C_P/C_V = 5/3$. Check that if you write the entropy as a function of N, T, P i.e. $S = S(N, T, P)$ then you can calculate C_P as $T(\partial S/\partial T)_{N,P}$.

- Constant entropy: for changes of a gas volume at constant entropy (and N of course) we have

$$VE^{3/2} = \text{const}, \tag{32}$$

which leads to

$$VT^{3/2} = \text{const}, \tag{33a}$$

$$PV^{5/3} = \text{const}. \tag{33b}$$

- Chemical potential: because of the overall N factor the constants in the entropy expression are important when we calculate $\mu = -T(\partial S/\partial N)_{E,V}$

$$\mu = -kT \ln \left[\left(\frac{V}{Nh^3} \right) \left(\frac{4\pi m E}{3N} \right)^{3/2} \right]. \tag{34}$$