

Welcome aboard the Ph12c final review session!

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1 Ch2 — Entropy, temperature

The entropy is some measure of the number of states, and is defined

$$\sigma(N, U) = \log(g(N, U)) \quad (1)$$

If we then take our system to be in thermal contact with another system, then we can define some temperature

$$\frac{1}{\tau} = \left. \frac{\partial \sigma}{\partial U} \right|_N \quad (2)$$

to be some quantity that is constant between the two.

2 Ch3 — Thermal Equilibrium

If we then put our system in contact with a reservoir that is large, then if we Taylor expand the entropy about the energy of the small system and take the infinite reservoir limit then we obtain

$$P(\epsilon) = \frac{\exp(-\epsilon/\tau)}{Z} \quad (3)$$

$$Z = \sum \exp(-\epsilon/\tau) \quad (4)$$

Generally the expectation value of an observable $\langle f \rangle = \sum f(\epsilon_s) \frac{\exp(-\epsilon_s/\tau)}{Z}$, but we can often find easier ways to

do it, e.g. $U = \langle \epsilon_s \rangle = \tau^2 \frac{\partial \log Z}{\partial \tau}$

We can also define the heat capacity at constant volume

$$C_v = \left. \frac{\partial U}{\partial \tau} \right|_V \quad (5)$$

$$p = - \left. \frac{\partial U}{\partial V} \right|_\sigma \quad (6)$$

Note that p can fall out of a similar derivation as temperature; indeed we can note the similarity $\frac{1}{\tau} = \frac{\partial \sigma}{\partial U}, p = - \frac{\partial U}{\partial V}$.

3 Ch4 — Planck + Stefan-Boltzman stuff

3.1 Photon distribution

Note that the quantum harmonic oscillator (which is as we all know the most powerful system on earth, HOs) exhibits $\epsilon_s = s\hbar\omega$ for an occupancy s and a mode ω . Then we can compute

$$\langle s \rangle = \frac{1}{Z} \sum_s s \exp\left(-s \frac{\hbar\omega}{\tau}\right) \quad (7)$$

$$= \frac{1}{\exp\left(\frac{\hbar\omega}{\tau}\right) - 1} \quad (8)$$

which is the expected occupancy of each mode ω .

Then we want to sum over all ω that photons exhibit which is $\omega^2 = \frac{c^2 \pi^2}{L^2} (n_x^2 + n_y^2 + n_z^2)$ and so we want $U = \sum_n \langle \epsilon_n \rangle =$

$\frac{1}{8} \times 2 \times \int d^3n \langle \epsilon_n \rangle$ with the $1/8$ coming from only positive n and 2 comes from polarizations. Then we can compute this by going to spherical coordinates

$$U = \frac{1}{8} \times 2 \times 4\pi \int_0^\infty n^2 \left(\frac{1}{\exp(\frac{\hbar\omega}{\tau}) - 1} \right) dn \quad (9)$$

$$\frac{U}{V} = \frac{\pi^2}{15\hbar^3 c^3} \tau^4 \quad (10)$$

which is the *Boltzmann distribution*.

3.2 Blackbody radiation

For blackbody radiation, it's effectively like having a photon gas inside a box and puncturing a hole. We can compute this out and in the end we find that

$$J = \frac{\pi^2 \tau^4}{60\hbar^3 c^2} \equiv \sigma_B T^4 \quad (11)$$

with J the power per surface area of the blackbody per time.

3.3 Phonons

Phonons have N particles in a 3D lattice, so a total of $3N$ D.O.F. We note that this imposes an upper constraint on the number n of modes, compared to our photon example. So we enforce this constraint by requiring

$$3N = \frac{3}{8} \int_0^{N_D} 4\pi n^2 dn \quad (12)$$

with N_D the maximum radius of the configuration space n sphere such that we have $3N$ modes. Solving this out we find

$$n_D = \left(\frac{6N}{\pi} \right)^{1/3}. \text{ Then}$$

$$U = \sum_{n=1}^{N_D} \frac{\hbar\omega_n}{\exp(\frac{\hbar\omega_n}{\tau}) - 1} \quad (13)$$

and we can usually compute high and low temperature limits. Note that $\omega_n^2 = \frac{c^2 \pi^2}{L^2} (n_x^2 + n_y^2 + n_z^2)$ as usual, with c the speed of sound.

4 Ch5 — Diffusive equilibrium, chemical potential

We define the chemical potential of two systems to be equal when the two systems are in diffusive equilibrium. The strict

definition is given

$$\mu(\tau, V, N) = \left. \frac{\partial F}{\partial N} \right|_{\tau, V} \quad (14)$$

Note that we will have a fancy pants way of computing this in a second¹. Then the thermodynamic identity takes on its full form

$$dU = \tau d\sigma - p dV + \mu dN \quad (15)$$

This then takes us to the Gibbs distribution. If we do a similar sort of thing to our derivation of the Boltzmann factor and expand the entropy against a large reservoir then we find the Gibbs factor

$$P(N, \epsilon) = \frac{\exp[(N\mu - \epsilon)/\tau]}{\mathcal{Z}} \quad (16)$$

with \mathcal{Z} the *grand partition function*

$$\mathcal{Z} = \sum_{n=0}^{\infty} \sum_{s(N)} \exp[(N\mu - \epsilon_s)/\tau] \quad (17)$$

The best way to write down the grand sums is to write down a table to keep track of all available states. We won't be required to do anything too hard with grand partition functions.

5 Ch6/7 — Bosons/Fermions

Bosons have symmetric wavefunctions, fermions have anti-symmetric. Note that exclusion principle is because if we try to put two fermions in the same state the total wavefunction vanishes.

5.1 Fermi-Dirac distribution

If we consider a reservoir that can dump up to one fermion into a particular orbital of energy ϵ , then we can construct the grand sum and take the appropriate derivative to find the expected occupancy

$$\langle N(\epsilon) \rangle = f(\epsilon) = \frac{1}{\exp[(\epsilon - \mu)/\tau] + 1} \quad (18)$$

the *Fermi-Dirac distribution*.

5.2 Bose-Einstein distribution

If we consider now a reservoir that can dump any number of bosons into a particular orbital of energy ϵ (no longer limited by exclusion principle) then we can construct the grand sum

¹We can already see from above that μ will be part of a Legendre transform out of F into another potential (the Gibbs) because it is computing the conjugate variable to N under potential F

again (going to be an infinite sum, geometric series) and take derivatives to find occupancy

$$\langle N(\epsilon) \rangle = f(\epsilon) = \frac{1}{\exp[(\epsilon - \mu)/\tau] - 1} \quad (19)$$

the *Bose-Einstein distribution*. Of course both the FD and the BE reduce to ideal gas in the $\tau \gg \epsilon$ limit.

6 Ch 8 — Thermo examples

6.1 Example: Carnot engine with rocks

Two solid bodies have $U = NCT$ at initial temperatures T_1, T_2 . We stick them into a Carnot (reversible) engine such that we extract work in bringing both bodies to T_f . Find T_f and the work done.

We note that $dU = dQ$ because $pdV = 0$ ($dV = 0$ because solid bodies). We can rewrite $dQ = \frac{\partial U}{\partial T} dT$. Note then that $dQ_1 = NCdT_1, dQ_2 = NCdT_2$, and since we operate reversibly $d\sigma = 0 = \frac{dQ_1}{T_1} + \frac{dQ_2}{T_2}$. This then gives us that

$$\frac{dT_1}{T_1} = -\frac{dT_2}{T_2} \quad (20)$$

$$\int_{T_1}^{T_f} \frac{dT_1}{T_1} = \int_{T_2}^{T_f} -\frac{dT_2}{T_2} \quad (21)$$

$$\ln \frac{T_f}{T_1} = \ln \frac{T_2}{T_f} \quad (22)$$

$$T_f = \sqrt{T_1 T_2} \quad (23)$$

We can then compute the work that we can get out. Body 1 cools from $T_1 \rightarrow T_f$ so its change in internal energy is $NC(T_1 - T_f)$ and similarly for body 2 $NC(T_2 - T_f)$ so the total work that we can get out is $NC(T_1 + T_2 - 2T_f)$.

6.2 Reversible isobaric cycle

This cycle looks like Figure 1 for some ideal gas. Find the

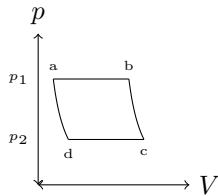


Figure 1: Let the slanted ones be adiabats.

efficiency $\eta = \frac{Q_h - Q_l}{Q_h} = 1 - \frac{Q_l}{Q_h}$ in terms of p_1, p_2 given $C_p = \frac{5}{2}N$.

During the isobars we recall $dH = dQ$ so $\Delta Q = \Delta U + p\Delta V$. Computing at p_1 we find

$$\Delta Q_h = \Delta U + p\Delta V \quad (24)$$

$$= \frac{3}{2}N(T_b - T_a) + p_1(V_b - V_a) \quad (25)$$

$$= C_p(T_b - T_a) \quad (26)$$

where we note that because of reversibility $p_1 V = NT$. We note that over the other leg we find $\Delta Q_l = C_p(T_c - T_d)$ and so

$$\eta = 1 - \frac{T_c - T_d}{T_b - T_a} \quad (27)$$

$$= 1 - \frac{p_2 V_c - p_2 V_d}{p_1 V_b - p_1 V_a} \quad (28)$$

and then since we know that in adiabatic stuff $p_2 V_d^\gamma = p_1 V_a^\gamma$ because they're connected adiabatically, with $\gamma = \frac{C_p}{C_v} = \frac{5}{3}$. This kills the volumes and we find

$$\eta = 1 - \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}} \quad (29)$$

7 Miscellaneous Stuff

7.1 Thermodynamics Potentials

We're familiar with quite a few potentials, and these can yield some equations. For example

- $U(\sigma, V)$ which has $dU = \tau d\sigma - pdV$, which we can see as the sum of the random internal energy and the mechanical energy.
- $F(\tau, V)$ *Helmholtz Free Energy* which is useful in constant τ process because it tells us the work done. We can then examine

$$F = U - \tau\sigma \quad (30)$$

$$dF = dU - \tau d\sigma - \sigma d\tau \quad (31)$$

$$= -pdV \quad (32)$$

so F changes by the amount of work done if $d\tau = 0$.

- $H(\sigma, p)$ *Enthalpy* for constant p processes. We can see its utility by differentials and plugging in dU from before

$$H = U + pV \quad (33)$$

$$dH = \tau d\sigma - pdV + pdV = dQ \quad (34)$$

which shows that at constant pressure.

7.2 Classical Statmech approach to ideal gas

Recall that the partition function for an ideal gas goes something like

$$Z \propto \sum_{n_{\{x,y,z\}}} \exp(-\alpha^2(n_x^2 + n_y^2 + n_z^2)) \quad (35)$$

$$\propto \left[\int_0^\infty dn e^{-\alpha^2 n^2} \right]^3 \quad (36)$$

where classically states are labelled by a continuum rather than a discretum like in QM.

We can also construct the partition function up from an integral over classical phase space, which looks like

$$Z = \int dp \int dx \exp\left[-\frac{1}{\tau} \epsilon(p, x)\right] \quad (37)$$

with $\epsilon(p, x) = \frac{p^2}{2m} + V(x)$.

7.3 Harmonic Oscillator, classical/quantum

Let's do a example problem of a classical and quantum harmonic oscillator. Exhibit n non-interacting particles in 3D that each obey Hamiltonian $H_i = \frac{p_i^2}{2m} + \frac{1}{2} k x_i^2$. Find C_v .

We do this classically, with (37). Then we note that the full partition function is given $Z = Z_1^N$ with

$$Z_1 = \int_{-\infty}^{\infty} d^3x d^3p \exp\left(-\frac{1}{\tau} \left[\frac{p^2}{2m} + \frac{kx^2}{2}\right]\right) \quad (38)$$

the individual partition functions. Thankfully the integrand factors, so it actually looks like

$$Z_1 = \left[\int_{-\infty}^{\infty} d^3p \exp\left(-\frac{p^2}{2m\tau}\right) \right]^3 \left[\int_{-\infty}^{\infty} d^3x \exp\left(-\frac{kx^2}{2\tau}\right) \right]^3 \quad (39)$$

$$Z = \left[8 \left(\frac{\pi^2 m \tau^2}{k} \right)^{3/2} \right]^N \quad (40)$$

This alone doesn't yield well to intuition, but if we compute $U = \tau^2 \frac{\partial \ln Z}{\partial \tau}$ then we get

$$U = \tau^2 \frac{\partial \ln Z}{\partial \tau} = 3N\tau \quad (41)$$

$$C_v = 3N \quad (42)$$

This is an example of the *equipartition theorem*, which is that we get $\frac{N}{2}$ to C_v for every D.O.F that appears quadratically in the Hamiltonian. Since we have $3p + 3x = 6$ degrees of freedom we do indeed get $C_v = 3N$.

Let's now do this quantum mechanically. We know that quantum mechanically we have $E = \hbar\omega(n_x + n_y + n_z)$ up to a zero point energy. Then our partition function looks like

$$Z_1 = \sum_{n_{\{x,y,z\}}} \exp\left[-\frac{\hbar\omega}{\tau}(n_x + n_y + n_z)\right] \quad (43)$$

$$Z = Z_1^N = \left[\frac{1}{1 - \exp\left(-\frac{\hbar\omega}{\tau}\right)} \right]^{3N} \quad (44)$$

where we go to the integral and evaluate the integral using the same technique as in the Planck distribution. We then obtain

$$U = \frac{3N\hbar\omega}{e^{\hbar\omega/\tau} - 1} \quad (45)$$

$$C_v = 3N \frac{\hbar^2 \omega^2}{4\tau^2} \text{csch}^2 \frac{\hbar\omega}{2\tau} \quad (46)$$

and when we take $\hbar \rightarrow 0$ we have $C_v = 3N - O(\hbar^2)$.