

PHYS 427 - Thermal and Statistical Physics - Discussion 05 - Solutions

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0. **Helmholtz free energy:** In our previous studies of closed systems, the entropy was naturally expressed as a function of the energy, volume, particle number, etc.:

$$S = S(U, V, N, \dots). \quad (1)$$

We defined temperature T , pressure p and chemical potential μ as derivatives of the entropy:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{V,N} \quad p = T \left(\frac{\partial S}{\partial V} \right)_{U,N} \quad \mu = -T \left(\frac{\partial S}{\partial N} \right)_{U,V}. \quad (2)$$

When U , V and N change by small amounts dU , dV and dN , the corresponding change in $S(U, V, N)$ is, by the chain rule,

$$dS = \left(\frac{\partial S}{\partial U} \right)_{V,N} dU + \left(\frac{\partial S}{\partial V} \right)_{U,N} dV + \left(\frac{\partial S}{\partial N} \right)_{U,V} dN \quad (3)$$

$$= \frac{1}{T} dU + \frac{p}{T} dV - \frac{\mu}{T} dN. \quad (4)$$

This is called the **fundamental thermodynamic relation** (FTR) and it's commonly rearranged as

$$\boxed{dU = TdS - pdV + \mu dN.} \quad (5)$$

- (a) Using the FTR, derive an expression for dF . Conclude that the Helmholtz free energy is naturally expressed as a function of T , V and N

- (b) Express S , p and μ as derivatives of the Helmholtz free energy.

- (a) The notation " dF " means "a tiny change in F ". Using the expression $F = U - TS$, we get

$$dF = dU - d(TS) \quad (6)$$

$$= dU - TdS - SdT. \quad (7)$$

Here I used the product rule of differential calculus. If it's not clear why we can do that, imagine that everything (F , U , T and S) varies as a function of a parameter λ and then write $dF = \frac{dF}{d\lambda} d\lambda$ for the change in F that occurs when λ changes by an amount $d\lambda$. Then you can insert $F = U - TS$ and use the product rule in the more familiar form $\frac{d}{d\lambda}(TS) = T \frac{dS}{d\lambda} + S \frac{dT}{d\lambda}$. Also, another way to think about this is to think about changing $U \rightarrow U + dU$ and similarly for T and S . Then

$$dF = [F + dF] - [F] \quad (8)$$

$$= [(U + dU) - (T + dT)(S + dS)] - [U - TS] \quad (9)$$

$$= dU - TdS - SdT - dTdS, \quad (10)$$

where I discarded the really small term $dT dS$.

Finally, use the FTR to eliminate dU from the above expression, giving

$$dF = -SdT - pdV + \mu dN. \quad (11)$$

Notice what this is telling us. It's telling us exactly how F changes when we change T by an amount dT , V by an amount dV , and N by an amount dN . In other words, the value of F can be thought of as depending on the independent variables T , V and N . So we write $F = F(T, V, N)$.

(b) If we consider a process in which V and N are held constant, then the last two terms vanish and we have

$$dF|_{V,N} = -SdT|_{V,N}, \quad (12)$$

where the subscript denotes the variables are being held constant. We rearrange to obtain

$$S = - \left(\frac{\partial F}{\partial T} \right)_{V,N}. \quad (13)$$

Similarly you can show

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

Alternatively, we could have written out the chain rule for $F(T, V, N)$, namely

$$dF = \left(\frac{\partial F}{\partial T} \right)_{V,N} dT + \left(\frac{\partial F}{\partial V} \right)_{T,V} dV + \left(\frac{\partial F}{\partial N} \right)_{T,V} dN \quad (15)$$

and compared to (11).

1. **Two-state systems:** The simplest non-trivial quantum systems have only two states. Examples include a particle with a spin-1/2 degree of freedom, a photon with two polarization states, a neutrino oscillating between two of its flavours, certain superconducting circuits, and many more. Two-state quantum systems like these can be used as qubits in a quantum computer. Here we'll consider something less sophisticated, but also interesting: a bunch of two-state systems in a bath.

Consider lattice with N sites. On each site lives a two-state system whose two microstates $|0\rangle$ and $|1\rangle$ have energies 0 and Δ , respectively. The two-state systems do not interact with each other. The collection of all N two-state systems will be called \mathcal{S} . Assume \mathcal{S} is in thermal equilibrium with a heat bath (thermal reservoir) at temperature T .

- (a) Compute the partition function $Z(T, N)$ of \mathcal{S} .
- (b) Compute its Helmholtz free energy $F(T, N)$.
- (c) Compute its entropy $S(T, N)$.
- (d) Compute its chemical potential $\mu(T, N)$.
- (e) Compute its energy...

- i. ...using the "math trick" $U = -\frac{\partial}{\partial \beta} \ln Z$.

ii. ...from the definition of the Helmholtz free energy, $F = U - TS$.

Your two answers should agree! (Do you see why these two approaches are equivalent?)

(a) We have a system of N non-interacting, distinguishable identical systems. They're distinguishable because they're assumed to live immovably on the lattice sites. Therefore (see lecture notes), the partition function of \mathcal{S} is

$$Z = Z_1^N, \quad (16)$$

where Z_1 is the partition function of a single two-state system considered alone. That is, $S_1 = 1 + e^{-\beta\Delta}$, so

$$Z = (1 + e^{-\beta\Delta})^N. \quad (17)$$

That's it, but we can also take the opportunity to prove this more directly. Suppose $N = 2$. Then there are 4 microstates of \mathcal{S} . There's the one where both sites have 0 energy (total energy $\varepsilon = 0$). There's the one where the first site has 0 and the second site has Δ (total $\varepsilon = \Delta$). There's the one where the first site has Δ and the second site has 0 (total $\varepsilon = \Delta$). Finally, there's the one where both sites have Δ (total $\varepsilon = 2\Delta$).

The partition function of \mathcal{S} is

$$Z = \sum_{\text{states of } \mathcal{S}} e^{-\beta\varepsilon} \quad (18)$$

$$= 1 + e^{-\beta\Delta} + e^{-\beta\Delta} + e^{-\beta 2\Delta} \quad (19)$$

$$= (1 + e^{-\beta\Delta})^2. \quad (20)$$

In the last line, I just noticed that the sum factorizes nicely. If we repeated this with $N = 3$, we'd find $Z = (1 + e^{-\beta\Delta})^3$, and so on. This is just the result (16). The essential features of this problem that make this factorization work are that the systems living on the sites are identical, they are distinguishable, and most importantly they are non-interacting (so that the total energy is the sum of the individual energies of the sites).

(b) The Helmholtz free energy is then

$$F(T, N) = -kT \ln Z = -Nk_B T \ln(1 + e^{-\beta\Delta}) \quad (21)$$

(c) As found in the previous problem, the entropy is found by taking a derivative of F :

$$S(T, N) = - \left(\frac{\partial F}{\partial T} \right)_N \quad (22)$$

$$= Nk_B \left[\ln(1 + e^{-\beta\Delta}) + T \frac{1}{1 + e^{-\beta\Delta}} \frac{\Delta e^{-\beta\Delta}}{k_B T^2} \right] \quad (23)$$

$$= Nk_B \left[\ln(1 + e^{-\beta\Delta}) + \beta\Delta \frac{1}{e^{\beta\Delta} + 1} \right] \quad (24)$$

(d) The chemical potential is found by taking a derivative of F :

$$\mu(T, N) = \left(\frac{\partial F}{\partial N} \right)_T \quad (25)$$

$$= -k_B T \ln(1 + e^{-\beta\Delta}) \quad (26)$$

(e) (i) Taking the derivative of $\ln Z$:

$$U(T, N) = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \quad (27)$$

$$= -\frac{1}{(1 + e^{-\beta\Delta})^N} N(1 + e^{-\beta\Delta})^{N-1} (0 - \Delta e^{-\beta\Delta}) \quad (28)$$

$$= N\Delta \frac{e^{-\beta\Delta}}{1 + e^{-\beta\Delta}} \quad (29)$$

$$= N\Delta \frac{1}{e^{\beta\Delta} + 1}. \quad (30)$$

Note that this result is actually something familiar in disguise. We are free to shift the zero-point of the energy of each site down by an amount $-\Delta/2$, so that the energies of the two-state system are $-\Delta/2$ and $\Delta/2$ (instead of 0 and Δ). Then, without doing any additional calculation, we know that the result for U will be the same as above, except shifted down by an amount $-\Delta/2$ for each of the N sites, i.e.

$$U = N\Delta \frac{1}{e^{\beta\Delta} + 1} - N\frac{\Delta}{2} \quad (31)$$

$$= \frac{N\Delta}{2} \left[\frac{2}{1 + e^{\beta\Delta}} - 1 \right] \quad (32)$$

$$= \frac{N\Delta}{2} \left[\frac{1 - e^{\beta\Delta}}{1 + e^{\beta\Delta}} \right] \quad (33)$$

$$= \frac{N\Delta}{2} \left[\frac{e^{-\beta\Delta/2} - e^{\beta\Delta/2}}{e^{-\beta\Delta/2} + e^{\beta\Delta/2}} \right] \quad (34)$$

$$= \frac{N\Delta}{2} \tanh \left(\frac{\beta\Delta}{2} \right) \quad (35)$$

If the system under consideration is a paramagnet, then the energy spacing between spin-up and spin-down is $2\mu B$, as we've seen earlier in the course. Inserting this gives the familiar result

$$U = N\mu B \tanh \left(\frac{\mu B}{k_B T} \right). \quad (36)$$

We derived this earlier in the course for a closed system using the microcanonical ensemble, but the result is the same for a system thermally coupled to a reservoir.

(e) (ii) From the definition of the Helmholtz free energy and our previous results for F and S , we have

$$U = F + TS \quad (37)$$

$$= \cancel{-Nk_B T \ln(1 + e^{-\beta\Delta})} + Nk_B T \left[\cancel{\ln(1 + e^{-\beta\Delta})} + \beta\Delta \frac{1}{e^{\beta\Delta} + 1} \right] \quad (38)$$

$$= N\Delta \frac{1}{e^{\beta\Delta} + 1}. \quad (39)$$

These two approaches are of course equivalent, and in fact it's straightforward to go from

one to the other. It's a good exercise:

$$U = -\frac{\partial}{\partial\beta} \ln Z \quad (40)$$

$$= \frac{\partial}{\partial\beta} \left(\frac{F}{k_B T} \right) \quad (41)$$

$$= \frac{\partial T}{\partial\beta} \frac{1}{k_B} \frac{\partial}{\partial T} \left(\frac{F}{T} \right) \quad (42)$$

$$= -T^2 \frac{\partial}{\partial T} \left(\frac{F}{T} \right) \quad (43)$$

$$= -T^2 \left[\frac{1}{T} \left(\frac{\partial F}{\partial T} \right) - \frac{F}{T^2} \right] \quad (44)$$

$$= -T^2 \left[\frac{1}{T} (-S) - \frac{F}{T^2} \right] \quad (45)$$

$$= F + TS. \quad (46)$$

2. **3D classical harmonic oscillator:** Consider a classical three-dimensional oscillator in thermal equilibrium with a reservoir at temperature T . The oscillator's Hamiltonian is $H(\vec{q}, \vec{p}) = \frac{1}{2m} \vec{p}^2 + \frac{1}{2} m \omega^2 \vec{q}^2$.

(a) Show that the partition function of the oscillator is

$$Z = \left(\frac{k_B T}{\hbar \omega} \right)^3. \quad (47)$$

- (b) Compute the energy of the oscillator and check that your answer agrees with the equipartition theorem.
- (c) The probability that the oscillator will occupy a small region in phase space about the point (\vec{q}, \vec{p}) is

$$\frac{e^{-\beta H(\vec{q}, \vec{p})}}{Z} \frac{d^3 q d^3 p}{(2\pi \hbar)^3}. \quad (48)$$

Integrate over all possible position values and momentum orientations of the oscillator. Hence show that the probability of the magnitude of the oscillator's momentum being between p and $p + dp$ is given by

$$4\pi \left(\frac{1}{2\pi m k_B T} \right)^{3/2} p^2 \exp\left(-\frac{p^2}{2m k_B T} \right) dp. \quad (49)$$

First, let me say a little more about why

$$Z = \int \frac{d^D q d^D p}{(2\pi\hbar)^3} e^{-\beta H(\vec{q}, \vec{p})} \quad (50)$$

makes sense given our rule for counting states. The rule is that, very generally, a classical phase space volume of $(2\pi\hbar)^D$ is equivalent to one quantum state. So in a given tiny classical phase space volume $d^D q d^D p$, the rule tells us to imagine there are $d^D q d^D p / (2\pi\hbar)^D$ discrete states. Each state in the volume centered at \vec{q}, \vec{p} contributes a term $e^{-\beta\varepsilon}$ to the partition function, where ε is the energy of a system with coordinates \vec{q} and \vec{p} , in other words $\varepsilon = H(\vec{q}, \vec{p})$. So each phase-space volume $d^D q d^D p$ contributes a term $\frac{d^D q d^D p}{(2\pi\hbar)^D} e^{-\beta H(\vec{q}, \vec{p})}$ to Z . Then we have to add up all the terms arising from all possible states of the system, i.e. we have to integrate over q and p . That gives (50). This doesn't explain *why* the state-counting rule works, but *how*.

If you're up for a challenge, you might like to see *why* the state-counting rule in (50) works for a specific system, an ideal monatomic gas with only a single gas particle. Start with the quantum expressions $Z = \sum_i e^{-\beta\varepsilon_i}$ and $\varepsilon_i = \frac{\hbar^2}{2m} 2\pi^2 L^2 (n_{xi}^2 + n_{yi}^2 + n_{zi}^2)$, where $n_{xi} = 1, 2, \dots$ and similarly for n_{yi} and n_{zi} . Then approximate the sum by an integral in the classical limit where \hbar is very small. Finally, change variables in the integral to $p_x = \hbar\pi n_x / L$, and similarly for p_y and p_z . Also, write $L^3 = \int d^3 q$ (an integral over all space). Then you'll end up with an expression which looks like (50) with $D = 3$ and $H(\vec{q}, \vec{p}) = \vec{p}^2 / 2m$. By doing this exercise, you'll see how the $(2\pi\hbar)^D$ arises, at least for the ideal gas. In practice when dealing with a classical system, we just start with (50).

(a) Here I'm using the abstract notation $\vec{q} = (q_1, q_2, q_3)$ for the generalized coordinates, even though in the case of a 3D oscillator the generalized coordinates are just the cartesian coordinates of the mass's position, more commonly called (x, y, z) .

$$Z = \int \frac{d^3 q d^3 p}{(2\pi\hbar)^3} \exp \left[-\beta \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) - \beta \frac{1}{2} m \omega^2 (q_x^2 + q_y^2 + q_z^2) \right] \quad (51)$$

$$= \frac{1}{(2\pi\hbar)^3} \left(\int_{-\infty}^{\infty} dp e^{-\frac{\beta}{2m} p^2} \right)^3 \left(\int_{-\infty}^{\infty} dq e^{-\frac{\beta m \omega^2}{2} q^2} \right)^3 \quad (52)$$

$$= \frac{1}{(2\pi\hbar)^3} \left(\frac{\pi}{\beta/2m} \right)^{3/2} \left(\frac{\pi}{\beta m \omega^2 / 2} \right)^{3/2} \quad (53)$$

$$= \frac{1}{(2\pi\hbar)^3} (2\pi m k_B T)^{3/2} \left(2\pi m k_B T \frac{1}{m^2 \omega^2} \right)^{3/2} \quad (54)$$

$$= \left(\frac{k_B T}{\hbar \omega} \right)^3 \quad (55)$$

where we used the Gaussian integral identity:

$$\int_{-\infty}^{\infty} dx e^{-ax^2} = \sqrt{\frac{\pi}{a}} \quad , \quad \text{Re}(a) > 0. \quad (56)$$

This integral is worth memorizing. There is a trick for evaluating it which you should know about. Write

$$I = \int_{-\infty}^{\infty} dx e^{-\alpha x^2}. \quad (57)$$

Then square it:

$$I^2 = \int_{-\infty}^{\infty} dx e^{-\alpha x^2} \int_{-\infty}^{\infty} dy e^{-\alpha y^2} \quad (58)$$

$$= \int dx dy e^{-\alpha(x^2+y^2)}. \quad (59)$$

This is an integral over the whole $x - y$ plane. Write it in polar coordinates:

$$I^2 = \int_0^{2\pi} d\phi \int_0^{\infty} r dr e^{-\alpha r^2} \quad (60)$$

$$= 2\pi \int_0^{\infty} r dr e^{-\alpha r^2} \quad (61)$$

$$= 2\pi \int_0^{\infty} \frac{du}{2\alpha} e^{-u} \quad u \equiv \alpha r^2 \quad (62)$$

$$= \frac{\pi}{\alpha}. \quad (63)$$

(b) The energy is then

$$U = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \quad (64)$$

$$= -(\beta \hbar \omega)^3 \times -3 \frac{1}{(\beta \hbar \omega)^4} \hbar \omega \quad (65)$$

$$= \frac{3}{\beta}, \quad (66)$$

or equivalently

$$U = 3k_B T. \quad (67)$$

This agrees with the equipartition theorem, which tells us that the 6 quadratic terms in the Hamiltonian each contribute an average energy of $\frac{1}{2}k_B T$.

(c) What we are about to do is a special case of a more general procedure, so let me first illustrate it with an abstract example. Suppose you have two continuous random variables A and B . That is, A or B are things you can measure; when you measure them, you get results a and b which can be any real number. But the values you get for a and b are correlated with each other. That is, knowing a gives you some extra information about what b will be. A situation like this is described by a so-called joint probability distribution $p(a, b)$ which is a function of a and b . Namely, the probability of measuring A and getting a result between a and $a + da$ and *simultaneously* measuring B and getting a result between b and $b + db$ is $p(a, b)da db$.

Suppose I don't care about the value of B , or maybe I'm not even able to measure it. I just want to know the probability of measuring A and getting a result between a and $a + da$ regardless of what b is. I can denote this probability as $P(a)da$. To compute $P(a)da$, I need to take the probability of simultaneously getting A between a and $a + da$ and B between b and $b + db$, and add it up over all the possible values of b . In other words, I need to integrate:

$$P(a)da = \left(\int_{-\infty}^{\infty} p(a, b)db \right) da. \quad (68)$$

Now back to our problem. Look out for the similarities with the abstract situation above. As argued above, and using the Z from part (a), the probability that the oscillator will occupy a small region $d^3q d^3p$ in phase space around the point (\vec{q}, \vec{p}) is

$$P(\vec{q}, \vec{p}) d^3q d^3p = \left(\frac{\hbar\omega}{k_B T} \right)^3 \exp \left[-\beta \left(\frac{1}{2m} \vec{p}^2 + \frac{1}{2} m \omega^2 \vec{q}^2 \right) \right] \frac{d^3q d^3p}{(2\pi\hbar)^3}. \quad (69)$$

Integrating this expression over the position degrees of freedom gives us the probability $P(\vec{p}) d^3p$ that the oscillator's momentum is in a small region d^3p around \vec{p} :

$$P(\vec{p}) d^3p = \left(\frac{\hbar\omega}{k_B T} \right)^3 \left\{ \int d^3q \exp \left(-\beta \frac{1}{2} m \omega^2 \vec{q}^2 \right) \right\} \exp \left(-\beta \frac{1}{2m} \vec{p}^2 \right) \frac{d^3p}{(2\pi\hbar)^3} \quad (70)$$

Doing these integrals requires we use the same Gaussian identity from when we calculated the partition function in part (a). The result is that

$$P(\vec{p}) d^3p = \left(\frac{1}{2\pi m k_B T} \right)^{3/2} \exp \left(-\beta \frac{1}{2m} \vec{p}^2 \right) d^3p \quad (71)$$

Now we can write $d^3p = p^2 dp d\Omega_p$ in spherical coordinates (p, θ_p, ϕ_p) , where $d\Omega_p = \sin \theta_p d\theta_p d\phi_p$ is a tiny elementary of solid angle of the momentum vector. We will now integrate this expression over momentum orientations (i.e integrate over the solid angle $d\Omega_p$ in spherical coordinates) to get the probability $P(p) dp$ that the magnitude of the oscillator's momentum is between p and $p + dp$. Note that in (71), $P(\vec{p})$ doesn't depend on the angle of p (it only depends on $\vec{p}^2 = p^2$). So

$$P(p) dp = \left(\frac{1}{2\pi m k_B T} \right)^{3/2} p^2 dp e^{-\beta p^2/2m} \int d\Omega_p \quad (72)$$

$$= \left(\frac{1}{2\pi m k_B T} \right)^{3/2} p^2 dp e^{-\beta p^2/2m} 4\pi \quad (73)$$

Note: If we then change variables from momentum to velocity, $p = mv$, we obtain the **Maxwell velocity distribution**:

$$f(v) dv = P(p) dp \quad (74)$$

where

$$f(v) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 \exp \left(-\frac{mv^2}{2k_B T} \right). \quad (75)$$

Remarkably, this is the same distribution of velocities that is found in an ideal gas. In particular, the velocity distribution doesn't depend on the frequency of the oscillator ω . Would this also happen for a particle in a potential more complicated than $V(\vec{q}) = \frac{1}{2} m \omega^2 \vec{q}^2$?