

* Reminder to submit #1 from Wed's worksheet (4A) on gradescope

* How many have started problem set?

- I fixed one missing part yesterday... make sure you have latest version

Last time

Fund. thermo. relation: $dE = -pdV + \tau d\sigma$

$$\Rightarrow dF = -pdV - \sigma dT$$

* Let's us determine p, σ from derivatives of free energy

* $F = -T \ln Z$ is easy to calculate if we can write down partition function

Today: derive ideal gas law & understand what we mean by "ideal"

EXERCISE 4B: STATISTICAL DERIVATION OF THE IDEAL GAS LAW*Objectives:*

- Derive the **ideal gas law** from first principles (quantum and statistical mechanics)
- Calculate the **energy** and **entropy** of an ideal (non-interacting) gas

Reading: Kittel & Kroemer, Ch. 3*Useful past results:*

- $dF = -pdV - \sigma d\tau$
- $F = -\tau \ln Z$

1. *Partition function of an ideal gas.* Consider a gas of N non-interacting particles in a cubic box of volume $V = L^3$. Recall that the energy eigenstates of a single particle in a three-dimensional box are given by

$$\varepsilon(n_x, n_y, n_z) = \frac{\pi^2 \hbar^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2). \quad (1)$$

- a. Let z_1 denote the partition function of a single particle in a one-dimensional box of length L (which we will calculate below). Find an expression for the partition function of N particles in a box of dimensions $L \times L \times L$ in terms of z_1 ...

- i. ...assuming that the particles are distinguishable.



$$Z = z_1^{3N}$$

Check:
$$Z = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} e^{-\beta \cdot \frac{\pi^2 \hbar^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2)}$$

$$= \left(\sum_{n=1}^{\infty} e^{-\beta \frac{\pi^2 \hbar^2}{2mL^2} n^2} \right)^{3N} = z_1^{3N}, \text{ where } z_1 = \sum_{n=1}^{\infty} e^{-\beta \frac{\pi^2 \hbar^2}{2mL^2} n^2}$$

- ii. ...assuming that the particles are indistinguishable.

We have overcounted by a factor $N!$.

i.e., each configuration of indistinguishable particles appeared $N!$ times in the sum in (i)

$$\Rightarrow Z = z_1^{3N} / N!$$

Assumption: terms w/ 2 particles in same orbital (n_x, n_y, n_z) are negligible. Should be valid except at very low temperature...

- b. Write out the partition function z_1 for a single particle in a 1D box and simplify it by approximating the sum as an integral.

$$z_1 = \sum_{n=1}^{\infty} e^{-\beta \epsilon_n} \approx \frac{1}{2} \int_{-\infty}^{\infty} e^{-\beta \epsilon_n} dn = \frac{1}{2} \sqrt{\frac{\pi}{\alpha \beta}} = \frac{L}{2} \sqrt{\frac{\pi \tau \cdot 2m}{\pi^2 \hbar^2}}$$

$$= L \cdot \frac{\sqrt{2\pi m \tau}}{h}$$

Used: $\mathcal{I} \equiv \int_{-\infty}^{\infty} e^{-Ax^2} dx \Rightarrow \mathcal{I}^2 = \int_0^{\infty} 2\pi r dr e^{-Ar^2} = -\frac{\pi}{A} e^{-Ar^2} \Big|_0^{\infty} = \pi/A$

$$\Rightarrow \mathcal{I} = \sqrt{\pi/A}$$

- c. The partition function z_1 can be expressed as $z_1 = L/\lambda_T$, where λ_T is a temperature-dependent length-scale. What is the value of λ_T ? Can you give a physical interpretation for λ_T ?

$$z_1 = \frac{L}{\lambda_T} \quad \text{where} \quad \lambda_T = \frac{h}{\sqrt{2\pi m \tau}}$$

This is the de Broglie wavelength of particles w/ momentum $\sqrt{2\pi m \tau}$,
a characteristic momentum scale @ temperature τ .

- d. Based on parts a.-c., write down the full partition function for the gas of N indistinguishable, non-interacting particles in terms of L , λ_T , and N .

$$Z = \frac{z_1^N}{N!} = \left(\frac{L}{\lambda_T} \right)^N / N!$$

2. Quantum mechanical derivation of the ideal gas law.

 $N \gg 1$

- a. Calculate the Helmholtz free energy F of the ideal gas of N particles in a three-dimensional box of volume V .

$$F = -\tau \ln Z \approx -3N\tau \ln[L/\lambda_\tau] + N\tau \ln N - N\tau,$$

where we have used Stirling's approximation:

$$\ln N! \approx N \ln N - N$$

$$\Rightarrow \boxed{F = -N\tau \ln(V/\lambda_\tau^3) + N\tau \ln N - N\tau} \quad (\text{in terms of } V)$$

- b. Calculate the pressure $p(N, T, V)$.

$$dF = -p dV + \tau dN \Rightarrow p = -\left(\frac{\partial F}{\partial V}\right)_\tau$$

$$\begin{aligned} \left[p = -\left(\frac{\partial F}{\partial V}\right)_\tau = \frac{\partial}{\partial V} [N\tau \ln V + \text{const}] \right] \\ = \boxed{\frac{N\tau}{V}} \end{aligned}$$

$$\text{or, } \boxed{pV = N\tau}$$

- c. While we are at it, let's also calculate the energy E of the ideal gas from the partition function Z .

$$E = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial}{\partial \beta} [3N \ln(L/\lambda_\tau) - N \ln N + N]$$

$$= -\frac{\partial}{\partial \beta} \left[3N \ln \left(\frac{\sqrt{2\pi m \tau}}{h} \right) + \text{const} \right]$$

$$= -\frac{\partial}{\partial \beta} \left[\frac{3}{2} N \ln \tau + \text{const} \right] = +\frac{\partial}{\partial \beta} \left(\frac{3}{2} N \ln \beta \right)$$

$$\boxed{E = \frac{3}{2} \frac{N}{\beta} = \frac{3}{2} N\tau}$$

Comment: equipartition theorem $\frac{1}{2}\tau$ of kinetic energy for each translational d.o.f. We will come back to proving and seeing conditions for validity.

3. Entropy of the ideal gas.

- a. Express the entropy of a generic system at known particle number N , temperature τ , and volume V as a derivative of the Helmholtz free energy $F(N, \tau, V)$.

$$dF = -pdV - \sigma d\tau$$

$$\Rightarrow \sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V$$

- b. Calculate the entropy of a gas of N non-interacting *identical* particles.
(You already wrote down the Helmholtz free energy F in problem 2.)

Express your results in terms of the ^{N, V , and} **thermal de Broglie wavelength**

$$\lambda_\tau = \frac{h}{\sqrt{2\pi m \tau}}. \quad (2)$$

$$F = -N\tau \ln(V/\lambda_\tau^3) + N\tau \ln N - N\tau$$

$$= -N\tau [-\ln V + \ln N - 1] + N\tau \underbrace{\ln \lambda_\tau^3}_{= 3 \ln \lambda_\tau}$$

$$\left(\frac{\partial F}{\partial \tau}\right)_V = N [\ln(N/V) - 1] + N \ln \lambda_\tau^3 + 3N\tau \frac{\partial \ln \lambda_\tau}{\partial \tau}$$

$$= N \ln\left(\frac{N \lambda_\tau^3}{V}\right) - N + 3N\tau \frac{\partial}{\partial \tau} \left(-\frac{1}{2} \ln \tau + \text{const}\right)$$

$$= N \ln\left(\frac{N \lambda_\tau^3}{V}\right) - N - \frac{3}{2} N\tau \cdot \frac{1}{\tau}$$

$$= N \ln\left(\frac{N \lambda_\tau^3}{V}\right) - \frac{5}{2} N$$

$$\therefore \boxed{\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V = N \ln\left(\frac{V}{N \lambda_\tau^3}\right) + \frac{5}{2} N}$$

- c. Your result from 3.b. is the Sackur-Tetrode equation for the entropy of a monatomic ideal gas. Subject it to ~~another~~ sanity check: does it violate any laws of thermodynamics? Explain.

Let's check the 3rd law:

$$\text{As } T \rightarrow 0, \lambda_T^{-3} \propto T^{3/2} \rightarrow 0 \Rightarrow \ln\left(\frac{V}{N\lambda_T^3}\right) \rightarrow -\infty$$

$$\text{So } S \rightarrow N(-\infty) + \frac{5}{2}N \rightarrow -\infty$$

This is inconsistent with the 3rd law and even with our definition of entropy, which is always positive...

- d. In what parameter regime must the Sackur-Tetrode equation (3.b.) break down? Why does it break down?

The Sackur-Tetrode equation must break down for

$$\frac{V}{N\lambda_T^3} \lesssim 1, \text{ where } N \ln\left(\frac{V}{N\lambda_T^3}\right) < 0$$

We can think of λ_T^3 as the smallest volume within which a particle can be localized. (Defining a smaller wave-packet would require a larger spread of momenta than compatible w/ temperature T .)

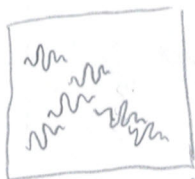
Thus, for $V \lesssim N\lambda_T^3$, we start to have multiple particles in the same microstate. Here, our approximation $Z \approx z_1^N/N!$ breaks down.

We will come back to this regime later in the term.

- e. In summary: what conditions must be satisfied for a gas to be considered **ideal**?

* Classical regime: low density $\frac{N\lambda_T^3}{V} \ll 1$ (or high temperature)

* Non-interacting \Rightarrow also a good approximation at sufficiently low density



↑ wavefunctions start to overlap

f. Estimate the thermal de Broglie wavelength for...

$$\lambda_T = \frac{h}{\sqrt{2\pi m k_B T}}$$

i. ...nitrogen gas (28 amu) at room temperature. Compare your result with the typical intermolecular spacing at 1 atmosphere of pressure.

$$h = 6.63 \times 10^{-34} \text{ J}\cdot\text{s}, \quad k_B = 1.38 \times 10^{-23} \text{ J/K}, \quad m = 28 \times 1.67 \times 10^{-27} \text{ kg}$$

$$\Rightarrow \lambda_T = 19 \text{ pm}$$

$$\text{Compare: } pV = Nk_B T \Rightarrow \frac{V}{N} = \frac{k_B T}{p} \Rightarrow (V/N)^{1/3} \approx 3 \text{ nm}$$

So $\lambda_T \ll \text{intermolecular spacing} \Rightarrow \text{classical gas.}$

ii. ...atomic sodium (23 amu) at a temperature of 100 nK.

$$\lambda_T \approx 1 \mu\text{m}$$

\therefore can be in quantum regime even for a comparatively dilute gas (under vacuum — collected from vapor pressure of laser-cooled...).

iii. ...an electron at room temperature. Compare your result with the lattice constant of a typical metal.

$$\lambda_T = 4.3 \text{ nm} @ T = 300 \text{ K} \quad (\text{using } m_e = 9.1 \times 10^{-31} \text{ kg})$$

Well, actually using Wolfram alpha...

For comparison, copper has a lattice constant of $4 \text{ \AA} = 0.4 \text{ nm} \ll \lambda_T$

\Rightarrow Electrons at room temperature can be viewed as a quantum gas. Crucial foundation for solid-state physics.

We'll come back to this later in the term.