

EXERCISE 5A: CLASSICAL STATISTICAL MECHANICS*Objectives:*

- Apply the classical formulation of the partition function to an ideal gas particle
- Derive the **Maxwell-Boltzmann velocity distribution**
- Derive the **Equipartition Theorem**

Useful past results:

- Partition for a single particle in a 1D box: $z_1 = L/\lambda_\tau$
- Thermal de Broglie wavelength: $\lambda_\tau \equiv h/\sqrt{2\pi m\tau}$
- Gaussian integral $\int_{-\infty}^{\infty} du e^{-\alpha u^2} = \sqrt{\pi/\alpha}$.

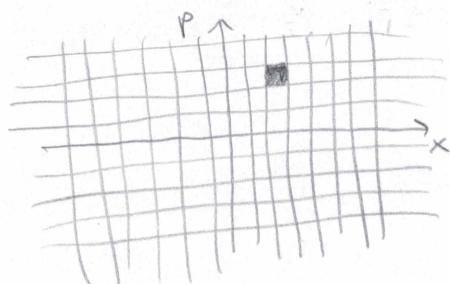
Boltzmann's formulation of statistical mechanics predates quantum mechanics. How did Boltzmann describe microstates? Let \mathbf{x} and \mathbf{p} denote the position and momentum of a classical particle of mass m and $U(\mathbf{x})$ its potential energy. Classically, the **partition function** in a D -dimensional system is given by

$$Z = \xi^{-D} \int d^D \mathbf{x} \int d^D \mathbf{p} e^{-\beta H(\mathbf{x}, \mathbf{p})}, \quad (1)$$

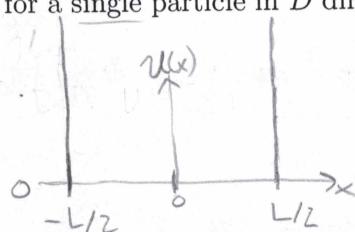
where $H(\mathbf{x}, \mathbf{p}) = \mathbf{p}^2/(2m) + U(\mathbf{x})$ is the particle's total energy, $\beta = 1/\tau$ is the inverse temperature, and ξ is a normalization factor.

1. *A classical gas particle.*

- a. Calculate the partition function for a single particle in D dimensions confined to a box of volume L^D .



ξ^D = volume of each microstate in phase space



$$\begin{aligned} Z &= \xi^{-D} \prod_{i=1}^D \int_{-L/2}^{L/2} dx_i \int_{-\infty}^{\infty} dp_i e^{-\beta p_i^2/(2m)} \\ &= \xi^{-D} \cdot L^D \left[\int_{-\infty}^{\infty} dp e^{-\beta p^2/(2m)} \right]^D \\ &= \xi^{-D} \cdot L^D \cdot \sqrt{\frac{2\pi m\tau}{\beta}}^D = \left(\frac{L}{\xi} \sqrt{\frac{2\pi m\tau}{\beta}} \right)^D \end{aligned}$$

- b. No classical physical quantities you calculate based on Z will depend on the normalization factor ξ . Nevertheless, determine the value of ξ by comparing the partition function Z calculated in Part a. to our previous quantum mechanical expression. How do you interpret your result?

$$\xi = h \text{ (Planck's constant)}$$

- * So the area (volume) of a microstate in D -dimensional phase space is set by Planck's constant (h^D).
- * Makes sense: $\Delta x \Delta p \gtrsim h \Rightarrow h$ sets the smallest phase-space volume to which a particle can be localized.

Comment: also generalizes to N particles: $Z = \frac{(L/\lambda_r)^{ND}}{N!}$ as before,

- c. Calculate the following quantities in $D=3$ dimensions: (check for $D=3$)

- i. The particle's mean energy E

$$E = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial}{\partial \beta} [D \ln(L/\lambda_r)] = D \frac{\partial}{\partial \beta} \ln \lambda_r$$

$$\lambda_r \propto \beta^{1/2} \Rightarrow \boxed{E = D \frac{\partial}{\partial \beta} (\frac{1}{2} \ln \beta) = \frac{D}{2\beta} = \frac{D}{2} \cdot \tau}$$

$$D=3 \Rightarrow E = \frac{3}{2} \tau$$

- ii. The particle's rms velocity $v_{\text{rms}} = \sqrt{\langle v_x^2 + v_y^2 + v_z^2 \rangle}$

$$E = \frac{1}{2} m \langle v^2 \rangle, \text{ since } U=0 \text{ (no potential energy)}$$

$$\Rightarrow \langle v^2 \rangle = \frac{2E}{m} \Rightarrow \boxed{v_{\text{rms}} = \sqrt{\frac{2E}{m}} = \sqrt{\frac{D\tau}{m}}}$$

$$3D \Rightarrow v_{\text{rms}} = \sqrt{\frac{3\tau}{m}}$$

See attached.

d. Find the following probability distributions:

- i. ...the distribution $P(v)$ for the particle's velocity v in $D = 1$ dimension.
Sketch $P(v)$.

- ii. ...the distribution $P(\mathbf{v})$ for the particle's velocity \mathbf{v} in $D = 3$ dimensions.

- iii. ...the distribution $P(|v|)$ for the particle's speed $|v|$ in $D = 3$ dimensions.
Sketch $P(|v|)$.

Note on 1(d): we could also use the partition function for normalization:

$$P(p_x, p_y, p_z) dp_x dp_y dp_z = \frac{1}{Z} \cdot \int_{-L/2}^{L/2} d^3x \cdot e^{-\beta(p_x^2 + p_y^2 + p_z^2)/(2m)} \cdot dp_x dp_y dp_z / \xi^3$$

This is an alternative approach, using the partition function.

$$P(|p|) dp = \frac{L^3}{Z} e^{-\beta|p|^2/(2m)} \cdot 4\pi|p|^2 dp$$

$$|p| = mv \Rightarrow dp = m dv, \quad P(|p|) dp = P(|v|) dv$$

$$P(|v|) \cdot dv = \frac{L^3}{Z} e^{-\frac{\beta}{2} \cdot mv^2} \cdot 4\pi m^3 |v|^2 dv / \xi^3$$

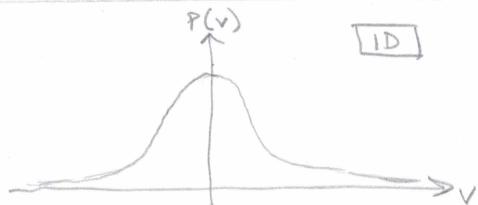
$$\begin{aligned} P(|v|) &= \frac{L^3}{\xi^3 Z} \cdot m^3 |v|^2 e^{-\frac{\beta}{2} \cdot mv^2} = 4\pi \left(\frac{1}{\sqrt{2\pi m}} \right)^3 m^3 |v|^2 e^{-\frac{\beta}{2} mv^2} \\ &= 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} |v|^2 e^{-\frac{\beta}{2} mv^2} \end{aligned}$$

1(d) starts below:

1d)

Start with velocity in 1D:

$$i) P(v) = e^{-\beta \cdot \frac{1}{2} mv^2} / \int_{-\infty}^{\infty} dv e^{-\beta \cdot \frac{1}{2} mv^2} = e^{-mv^2/(2kT)} / \sqrt{\frac{2\pi kT}{m}}$$



In 3D:

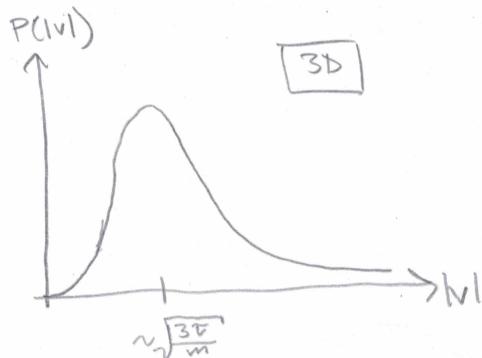
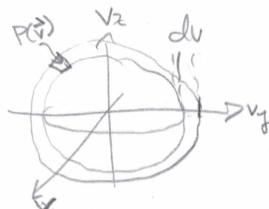
$$ii) P(\vec{v}) = P(v_x)P(v_y)P(v_z) = \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-m|\vec{v}|^2/(2kT)}$$

Probability distribution for speed in 3D?

$$iii) P(|v|) dv = 4\pi|v|^2 P(\vec{v}) dv$$

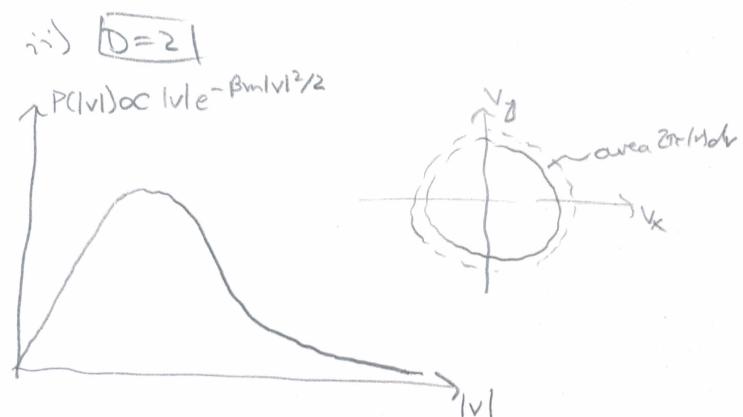
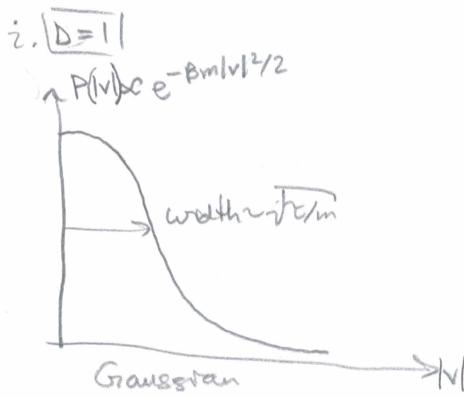
$$P(|v|) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} |v|^2 e^{-m|v|^2/(2kT)}$$

- Maxwell-Boltzmann Distribution



1e) Return to worksheet...

- e. Your result in d.iii. is the **Maxwell-Boltzmann** velocity distribution. Without doing detailed math, sketch analogous distribution functions for the speed of:
- A particle in $D = 1$ dimension
 - A particle in $D = 2$ dimensions



The functional form depends on dimension b/c we need to consider a shell of radius $|v|$.

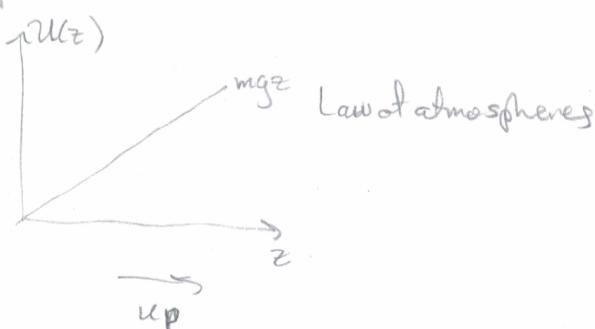
- f. You could have done the entirety of this problem equally well starting from the quantum mechanical description of a particle in a box. Under what circumstances is it valid to use a classical description, in which the microstates are cells in phase space?

For sufficiently large V , energy level spacing becomes small...
so for a dilute gas at high temperature, the classical description is valid.

- g. Under what circumstances might it be *advantageous* to use a classical description instead of a quantum mechanical one?

Suppose particles are in a potential $U(x)$ for which we cannot easily calculate the energy spectrum — can still write out partition function in phase space.

Ex. on HW, e.g.



2. *Equipartition Theorem*

Consider quite generally a classical Hamiltonian of the form $H = \sum_{i=1}^f a_i u_i^2$, where u_i represent independent degrees of freedom, e.g., coordinates or their conjugate momenta.

- a. Give at least two examples of physical systems that can be described in the form above.

Free particle: $H = \sum_i \frac{p_i^2}{2m}$



Harmonic oscillator: $H = \frac{1}{2} m \omega^2 x^2 + \frac{p^2}{2m}$



Rotor: $H = \frac{L^2}{2mR^2}$

- b. Calculate the mean energy E for a system described by the generic Hamiltonian above at temperature τ .

- i. First, show that the partition function is of the form $Z \propto \tau^{f/2}$.

$$Z \propto \prod_i \int_{-\infty}^{\infty} du_i e^{-a_i \beta u_i^2} = \prod_{i=1}^f \sqrt{\frac{\pi \tau}{a_i}} \propto \tau^{f/2} \propto \beta^{-f/2}$$

$$\Rightarrow E = -\frac{\partial \ln Z}{\partial \beta} = +\frac{f}{2} \cdot \frac{1}{\beta} = \boxed{\frac{f\tau}{2}}$$

$Z \propto \beta^\alpha$ $\alpha = -f/2$

- ii. Calculate the mean energy E from the partition function.

See above.

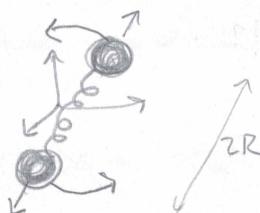
- c. Your derivation should show that each of the f degrees of freedom makes the same contribution to the energy. What is the energy per degree of freedom?

$$E = \frac{f\tau}{2} \Rightarrow \frac{\tau}{2} \text{ per degree of freedom}$$

3. Application of Equipartition: Gas of Diatomic Molecules

Apply the *equipartition theorem* to determine the mean energy of a dilute gas of N homonuclear diatomic molecules, accounting for translational, vibrational, and rotational degrees of freedom in the classical limit.

- a) Sketch the molecule, label its degrees of freedom, and write down the resulting total energy H . Don't worry about the precise numerical prefactors in H —just give the general form including all terms.



$$H = \underbrace{\frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}}_{\text{translation}} + \underbrace{\frac{1}{2}mc\omega^2(R-R_0)^2}_{\text{vibration}} + \underbrace{\frac{L_1^2}{2mR^2} + \frac{L_2^2}{2mR^2}}_{\text{rotation}}$$

- b). Based on your sketch, what is the mean energy $\langle E \rangle$ in the high- T limit?

$$f = 7N \Rightarrow E = \frac{7}{2}N\tau$$