Lesson 5- Applications Canonical Ensemble

Ideal monoatomic gas and Gibbs paradox

Consider the **ideal monotomic gas as a classical system** so that the partition function for the N-fixed molecules is

$$\mathcal{Z} = \int e^{-\beta E} d^3\mathbf{r}_1 \ldots d^3\mathbf{r}_N d^3\mathbf{p}_1 \ldots d^3\mathbf{p}_N \frac{1}{\hbar^{3N}}$$

with

$$E = \sum_{i=1}^{N} \frac{|\mathbf{p}_i|^2}{2m} + U(r_1, \ldots, r_N)$$

Therefore,

$$\mathcal{Z} = \frac{1}{\hbar^{3N}} \left(\int e^{-\frac{\beta |\mathbf{p}|^2}{2m}} d^3\mathbf{p} \right)^N \left(\int e^{-\beta U(\mathbf{r}_1, \ldots, \mathbf{r}_N)} d^3\mathbf{r}_1 \ldots d^3\mathbf{r}_N \right)$$

where the term $U(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ can be complicated in general.

If $U = 0$ (diluted) or $U = \begin{cases} 0 & \text{inside box} \\ \infty & \text{outside box} \end{cases}$ then

$$\int e^{-\beta U(r_1, \ldots, r_N)} d^{3n} r_1 \ldots d^{3n} r_N = V^N \Rightarrow \mathcal{Z} = \left(\frac{V}{\hbar^3} \int e^{-\frac{\beta |\mathbf{p}|^2}{2m}} d^3 p \right)^N = \left[V \left(\frac{2m\pi}{\beta \hbar^2} \right)^{\frac{3}{2}} \right]^N$$

Ideal monoatomic gas and Gibbs paradox

$$\mathscr{Z} = \xi^N = \left[V \left(\frac{2m\pi}{\beta \hbar^2} \right)^{\frac{3}{2}} \right]^N \implies \ln \mathscr{Z} = N \ln \left[V \left(\frac{2\pi mkT}{\hbar^2} \right)^{\frac{3}{2}} \right] = N \left[\ln V - \frac{3}{2} \ln \beta + \frac{3}{2} \ln \left(\frac{2\pi m}{\hbar^2} \right) \right]$$

equipped with the partition function $\mathscr{Z}$ we can compute the thermodynamical mean values and the equation of state:

Pressure: $\langle P \rangle = \left(\frac{1}{\beta} \frac{\partial \ln \mathscr{Z}}{\partial V} \right) = \frac{1}{\beta} \frac{N}{V} \Rightarrow \bar{P}V = NkT$ "Eq. of state"

Internal energy: $\langle E \rangle = -\frac{\partial \ln \mathscr{Z}}{\partial \beta} = \frac{3}{2} \frac{N}{\beta} = \frac{3}{2} NkT = N\bar{\varepsilon}$

where $\bar{\varepsilon} = \frac{3}{2} kT =$ mean energy/molecule

Heat capacity: $C_v = \left(\frac{\partial E}{\partial T} \right)_V = \frac{3}{2} Nk = \frac{3}{2} nR \Rightarrow c_v = \frac{3}{2} R$

(molar specific heat)

Energy dispersion: $\langle \Delta E^2 \rangle = -\frac{\partial \langle E \rangle}{\partial \beta} = \frac{3}{2} N\beta^{-2} = kC_v T^2$

Ideal monoatomic gas and Gibbs paradox

Entropy: $S = k \left[\ln Z + \beta E \right]$

$$= kN \left[\ln V - \frac{3}{2} \ln \beta + \frac{3}{2} \ln \left(\frac{2\pi m}{h_0^2} \right) + \frac{3}{2} \right]$$

$$= kN \left[\ln V + \frac{3}{2} \ln T + \sigma \right]$$

(where σ is independent of T, V, N)

But this is **not correct!** Entropy must be an extensive quantity:

$V \to \gamma V, \quad N \to \gamma N \implies S \to \gamma S$ 　　moreover

$S \to -\infty$ when $T \to 0$ it should go to $S_0 = $ cte by 3rd law thermo.

Gibbs paradox

Ideal monoatomic gas and Gibbs paradox

The question is: what is going wrong?

Ideal monoatomic gas and Gibbs paradox

The question is: what is going wrong?
Answer: we treated the gas molecules as individually **distinguishable**
This is wrong.

This is a consequence of the classical treatment we applied. If we had done a quantum mechanical treatment **we should have considered the molecules as completely indistinguishable**. Correct!
Therefore we must use

$$Z = \frac{\mathscr{Z}}{N!} = \frac{\xi^N}{N!} \implies \ln Z = N \ln \xi - \ln N! \text{ applying Stirling}$$
$$(N \gg 1) \qquad \ln Z \approx N \ln \xi - N \ln N + N$$

Note that only the entropy is affected by this

$$S = kN \left[\ln V + \frac{3}{2} \ln T + \sigma \right] + k(-N \ln N + N)$$

Ideal monoatomic gas and Gibbs paradox

Then the entropy reads now:

$$S = kN \left[\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln T + \sigma_0 \right] \text{ with } \sigma_O \equiv \sigma + 1$$

Now the entropy is extensive and additive.

$S \to -\infty$ when $T \to 0$ Classical approximation not valid at low T few quantum states.

Validity of classical approximation: Is it valid to use classical physics to study gases?

Ideal monoatomic gas and Gibbs paradox

Criterion: amount of action involved $\Delta q \Delta p \geq \hbar$? (Heisenberg)
Estimating Δq and Δp:

$\Delta q \sim$ mean separation between molecules L

$\Delta p \sim$ mean value of momentum $\overline{p}$

Classical behaviour

$$\bar{L} \cdot \overline{p} \gg \bar{h} \Rightarrow \bar{L} \gg \frac{\bar{h}}{\overline{p}} = \frac{h}{2\pi p} = \frac{1}{2\pi}\bar{\lambda}$$

where $\bar{\lambda}$ is de Broglie wavelength. This is an approximation.

Important: When $L \gg \bar{\lambda}$, the quantum description is equivalent to the motion of wave packets describing individual particles which move independently in a quasi-classical manner. If $L \ll \bar{\lambda}$ then the whole gas is described by a single wave function encoding the quantum correlations between particles even if no forces exist between them.

Ideal monoatomic gas and Gibbs paradox

Let us do some calculations:

i) $\bar{L}$: Each molecule is viewed as a cube of size $\bar{L}$.

$$\text{Volume} = \bar{L}^3 \Rightarrow N \cdot \bar{L}^3 = V \Rightarrow \bar{L} = \left(\frac{V}{N}\right)^{\frac{1}{3}}$$

ii) $\bar{p}$: we estimate it from the mean energy

$$\frac{\bar{p}^2}{2m} = \bar{\epsilon} = \frac{3}{2}kT \Rightarrow \bar{p} \sim \sqrt{3mkT}$$

therefore we have that

$$\bar{\lambda} = \frac{h}{\bar{p}} \approx \frac{h}{\sqrt{3mkT}}, \quad L = \left(\frac{V}{N}\right)^{\frac{1}{3}}$$

and

$$\bar{L} \gg \bar{\lambda} \Leftrightarrow \left(\frac{V}{N}\right)^{\frac{1}{3}} \gg \frac{h}{\sqrt{3mkT}}$$

Ideal monoatomic gas and Gibbs paradox

Important:The classical approximation is valid at:

Low density $\left(\dfrac{N}{V}\right)$ **and High temperature** T **and** m **not too small**

- Numerical estimations:

  1-Let us consider **He gas at room temperature** T **and pressure** $\bar{P}$

  $\left.\begin{array}{l} T = 300\text{K} \Rightarrow kT \approx 4.14 \times 10^{-21}\text{J.} \\ \bar{p} = 760\text{mm Hg} \end{array}\right\}$ $\dfrac{N}{V} = \dfrac{\bar{P}}{kT} \approx 2.5 \times 10^{19}\dfrac{\text{molecules}}{\text{cm3}}$

  molecular mass $m = \dfrac{4}{6 \times 10^{23}} \approx 7 \times 10^{-24}\text{grams}$

  $\Rightarrow \left.\begin{array}{l} \bar{L} = 34 \times 10^{-8}\text{cm} \\ \bar{\lambda} = 6 \times 10^{-9}\text{cm} \end{array}\right\}$ $\Rightarrow \bar{L} \gg \bar{\lambda} \text{ (classical)}$

Ideal monoatomic gas and Gibbs paradox

- Numerical estimations:

  2- **Electrons in a typical metal** (non interaction $\approx$ ideal gas)

  Electron mass $m = 10^{-28}$ grams

  $$\Rightarrow \left. \begin{array}{l} \bar{L} = 2 \times 10^{-8}\text{cm} \\ \bar{\lambda} = 5 \times 10^{-7}\text{cm} \end{array} \right\} \quad \Rightarrow \bar{L} \ll \bar{\lambda} \text{ (non classical)}$$

Real monoatomic gas

Our starting point now is the classical partition function from the previous section:

$$\mathcal{Z} = \frac{1}{N!} \left(\frac{2m\pi}{\hbar^2} \right)^{\frac{3N}{2}} \left(\int e^{-\beta U(\mathbf{r}_1, \ldots, \mathbf{r}_N)} d^3\mathbf{r}_1 \ldots d^3\mathbf{r}_N \right)$$

This time we address the problem of having $U(\mathbf{r}_1, \ldots, \mathbf{r}_N) \neq 0$. The potential can be modelled by

$$U = u_{11} + u_{12} + \ldots + u_{MN} = \sum_{i<j} u_{ij} = \frac{1}{2} \sum_{i,j} u_{ij} \quad \text{with} \quad u_{ij} = u(|\mathbf{r}_i - \mathbf{r}_j|)$$
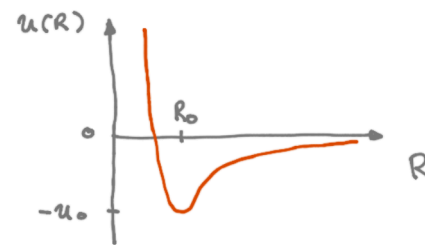
The potential between two molecules at distance R has a semi-empirical form:

$$u(R) = u_0 \left[\left(\frac{R_0}{R} \right)^{12} - 2 \left(\frac{R_0}{R} \right)^6 \right] \quad \text{(Lennard-Jones potential)}$$

Real monoatomic gas

The Lennard-Jones potential) $\quad u(R) = u_0 \left[\left(\dfrac{R_0}{R} \right)^{12} - 2 \left(\dfrac{R_0}{R} \right)^6 \right]$ has the form:
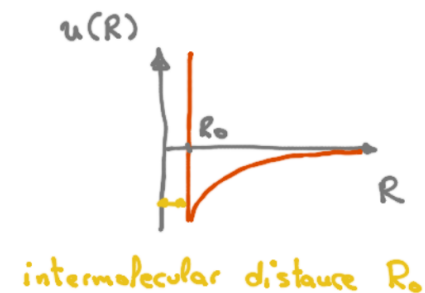

$R < R_0 \implies$ strong electronic repulsion

$R > R_0 \implies$ weak gravitational attraction

The potential $u(R)$ can be less accurately modeled as:

$$u(R) = \begin{cases} \infty & \text{if } R < R_0 \\ -u_0 \left(\dfrac{R_0}{R} \right)^s & \text{if } R \geq R_0 \end{cases}$$

intermolecular distance R_0

Note: the choice s=6 is usually the most realistic

Real monoatomic gas

To compute $\mathscr{Z}_U$, let us consider the effective potential U_e felt by a molecule as a consequence of the rest. Separability $\Longleftrightarrow$ canonical ensemble. Then:

$$\mathscr{Z}_U = \left[\int e^{-\beta U_e(\mathbf{r})} d^3\mathbf{r} \right]^N \quad \text{This implies } N \text{ independent molecules!}$$

- There is a region of space V_x (per molecule) which is excluded in the integral. For each pair of molecules, one of them cannot be where the other is.
- In the region $(V - V_x)$, the potential is smooth: $U_e \approx \overline{U_e}$

Therefore,

$$\mathscr{Z}_U \approx \left[(V - V_x) e^{-\beta U_e} \right]^N \text{ where } (V_x, U_e) \text{ are to be determined by some self-consistency checks.}$$

Determination of $\overline{U_e}$:

Total mean potential: $\qquad\qquad N\overline{U_e} = \dfrac{1}{2}N(N-1)\tilde{u} \approx \dfrac{1}{2}N^2\tilde{u}$

Here, $\tilde{u}$ is the mean intermolecular potential.

Real monoatomic gas

Thus,

$$\overline{U_e} = \frac{1}{2}N\tilde{u} = \frac{1}{2}N\int_{R_0}^{R_*} \left(\frac{dV}{V}\right) u(R) = \frac{1}{2}N\int_{R_0}^{R_*} \frac{4\pi R^2 dR}{V} u(R)$$

Inside the integral represents the probability of the intermolecular distance to be between R and $R + dR$.

Note: $V = \frac{4}{3}\pi R^3 \implies dV = 4\pi R^2\, dR$

Therefore,

$$\frac{1}{2}\frac{N}{V}\int_{R_0}^{R_*} 4\pi R^2 u(R)\, dR = -\frac{1}{2}\frac{N}{V}\int_{R_0}^{R_*} 4\pi u_0 R^2 \left(\frac{R_0}{R}\right)^s dR = -\frac{1}{2}\frac{N}{V}4\pi u_0 R_0^s \left[\frac{R_*^{3-s}}{3-s} - \frac{R_0^{3-s}}{3-s}\right]$$

$$= \frac{1}{2}\frac{N}{V}4\pi u_0 R_0^s \frac{1}{s-3}\left[\frac{R_0^s R_*^{3-s} - R_0^3}{R_0^s}\right]$$

Given that $s > 3$ and $R_* \to \infty$

$$= -\frac{N}{V}\left(\frac{2\pi}{3}R_0^3 u_0 \frac{3}{s-3}\right) = -\frac{N}{V}a' = \bar{U}_e$$

Real monoatomic gas

Determination of V_x:

# of pairs of interacting molecules x Region enclosed for each interacting pair of molecules = Total excluded volume

$$\frac{1}{2}N(N-1) \times \frac{4}{3}\pi R^3 \approx \frac{2}{3}\pi N^2 R_0^3 = NV_x$$

$\Rightarrow \frac{4}{3}\pi R_0^3$

$$\Rightarrow V_x = N\left(\frac{2\pi}{3}R_0^3\right) = N4\left(\frac{4}{3}\pi\left(\frac{R_0}{2}\right)^3\right) = Nb'$$

molecule volume

Now, we can readily compute the equation of state for the real gas using the partition function:

$$Z = \frac{1}{N!}\left[\left(\frac{2\pi m}{\beta h^2}\right)^{3/2}(V - V_x)e^{-\beta U_e}\right]^N$$

Real monoatomic gas

One finds

$$\bar{p} = \frac{1}{\beta} \frac{\partial \ln \mathscr{Z}}{\partial V} = \frac{1}{\beta} \frac{\partial}{\partial V} \left[N \ln(V - V_x) - N\beta \overline{U_e} \right]$$

$$= \frac{NkT}{V - Nb'} - \frac{N^2 a'}{V^2} \Rightarrow \bar{p} + \frac{a'N^2}{V^2} = \frac{NkT}{V - Nb'}$$

$$\Rightarrow \left(\bar{p} + \frac{aN^2}{V^2} \right) (V - Nb') = kT$$

Equivalently,

$$\left(\bar{p} + \frac{a}{v^2} \right)(v - b) = RT \qquad \text{"van der Waals law, 1873"}$$

with $a = a' N_A^2$, $b = b' N_A$, $N = n N_A$ (where n is number of mols) and $V = \frac{V}{n}$.

Real monoatomic gas

Critical point:

The van der Waals equation of state predicts a the existence of a **critical point** located at $(T_c, \bar{p}_c, v_c)$. This is found by performing the partials respect to volume

$$\left(\frac{\partial \bar{p}}{\partial v} \right)_{T_c, \bar{p}_c, v_c} = 0 \quad , \quad \left(\frac{\partial^2 \bar{p}}{\partial v^2} \right)_{T_c, \bar{p}_c, v_c} = 0$$

The equation of state $\left(\bar{p} + \dfrac{a}{v^2} \right)(v - b) = RT$ doing the partials we obtain:

$$-\frac{RT_c}{(V_c - b)^2} + 2\frac{a}{V_c^3} = 0 \qquad \text{and} \qquad 2\frac{RT_c}{(V_c - b)^3} - 6\frac{a}{V_c^4} = 0$$

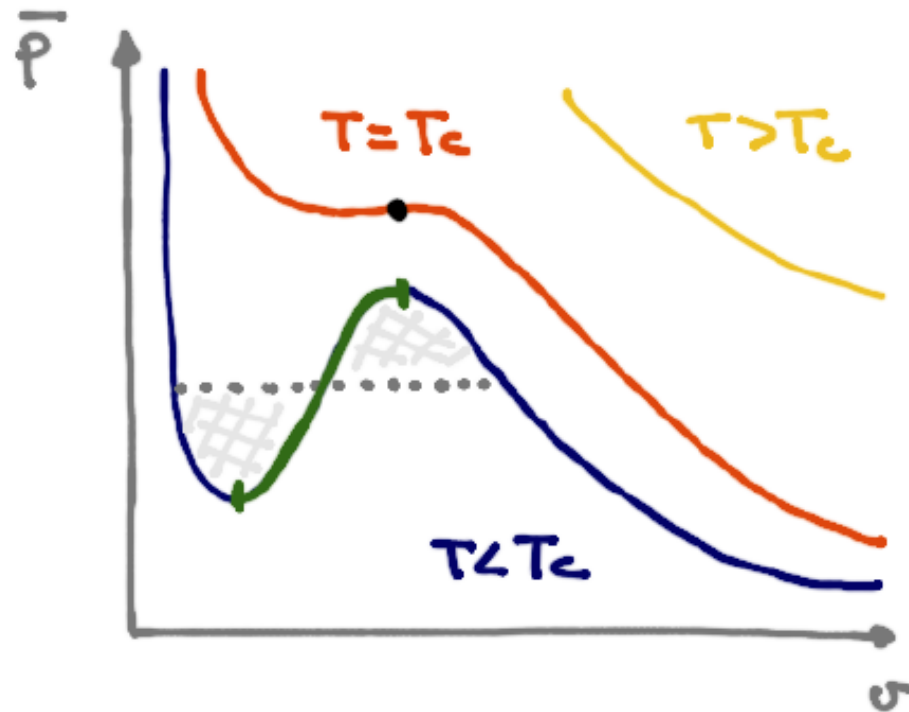rearranging terms: $T_c = 2\dfrac{a}{R}\dfrac{(V_c - b)^2}{V_c^3}$ and substituting in the second

$$4\frac{a}{R(V_c - b)} = 6\frac{a}{V_c} \text{ yielding } \Rightarrow V_c = 3b, \quad T_c = \frac{8a}{27Rb}, \quad \bar{p}_c = \frac{a}{27b^2}$$
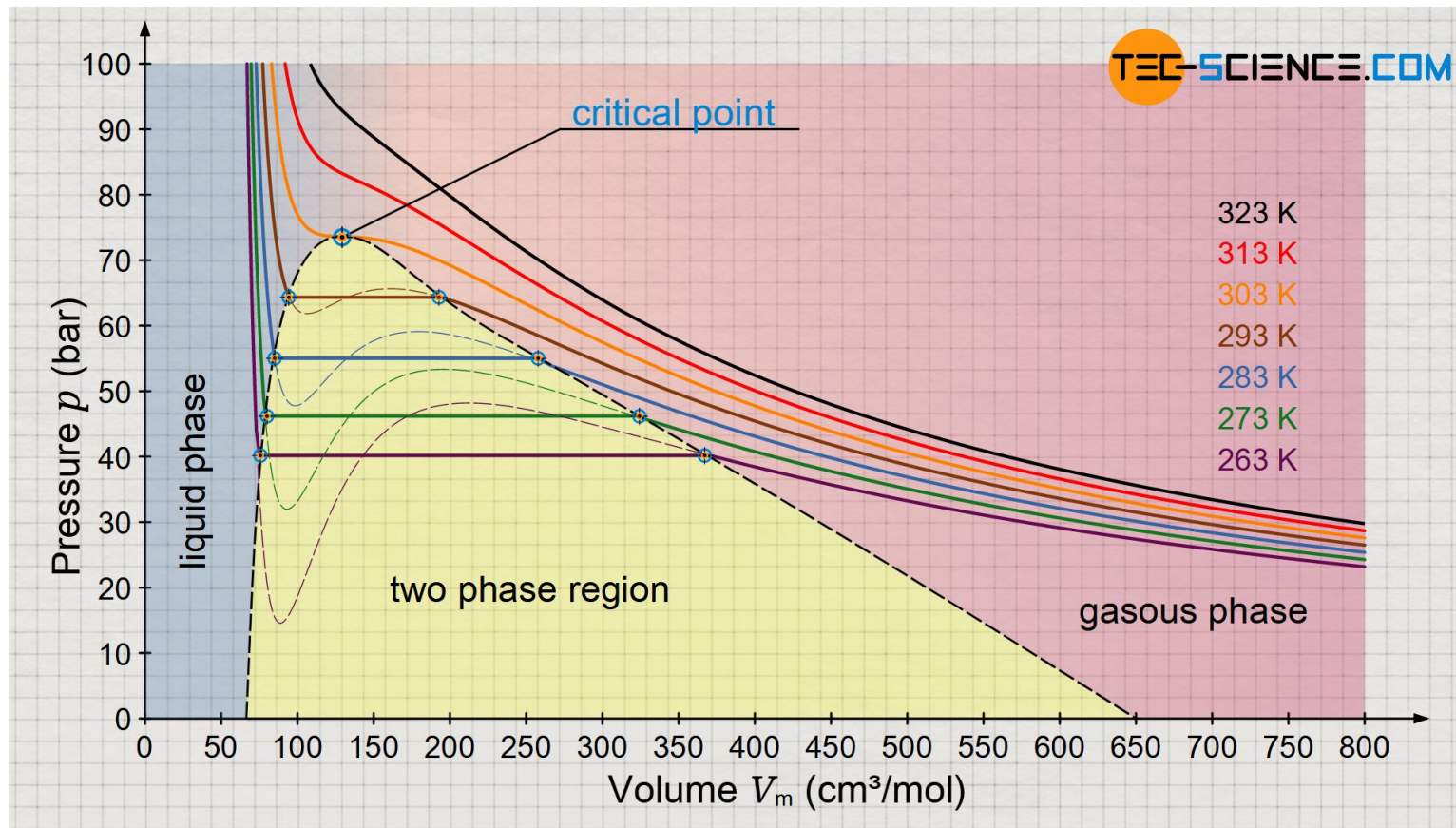
Real monoatomic gas

Critical point:

Explains the phase transition from the gaseous state to the liquid state at high pressures.

Real monoatomic gas

Critical point:

Example of liquefaction for CO_2

Equipartition theorem and simple applications

Theorem in classical physics about the mean value $\bar{E}_i$ of the energy associated with a quadratic generalized coordinate/momentum. If the energy is a quadratic function:

$$E = E(q_1, \ldots, q_f; p_1, \ldots, p_f) = \begin{cases} cp_i^2 + E'(q_1, \ldots, p_f) \\ cq_i^2 + E'(q_1, \ldots, p_f) \end{cases}$$

If the classical system is in equilibrium at temperature T, and $\beta = (kT)^{-1}$, then

$$\bar{E}_i = \frac{\int_{-\infty}^{\infty} e^{-\beta E} E_i \, dq_1 \cdots dp_f}{\int_{-\infty}^{\infty} e^{-\beta E} \, dq_1 \cdots dp_f} = \frac{\int_{-\infty}^{\infty} e^{-\beta(E_i + E')} \bar{E}_i \, dq_1 \cdots dp_f}{\int_{-\infty}^{\infty} e^{-\beta(E_i + E')} \, dq_1 \cdots dp_f}$$

$$\int \text{independent of } p_i \text{ cancel out} = \frac{\int_{-\infty}^{\infty} e^{-\beta E_i} E_i \, dp_i}{\int_{-\infty}^{\infty} e^{-\beta E_i} \, dp_i} = -\frac{\partial}{\partial \beta} \ln \left(\int_{-\infty}^{\infty} e^{-\beta E_i} \, dp_i \right)$$

$$= -\frac{\partial}{\partial \beta} \ln \left(\int_{-\infty}^{\infty} e^{-\beta c p_i^2} \, dp_i \right) = -\frac{\partial}{\partial \beta} \ln \left(\sqrt{\frac{\pi}{\beta c}} \right) = -\frac{\partial}{\partial \beta} \ln \left(\sqrt{\frac{1}{\beta}} \sqrt{\frac{\pi}{c}} \right) = \frac{1}{2\beta} = \frac{1}{2} kT$$

$$\bar{E}_i = \frac{1}{2} kT$$

Equipartition theorem and simple applications

Message: The mean value of each independent quadratic term in the energy is equal to $\frac{1}{2}kT$ for classical systems.

Comment: The classical approximation is justified whenever $\Delta E \ll \beta^{-1} = kT$, which represents the separation of quantum energy levels and the thermal energy, so that E acts like a continuous quantity instead of a discrete (quantized) one.

Simple applications:
- Mean kinetic energy of a molecule in a gas:

$$K = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) \Rightarrow \bar{K} = \sum_{i=1}^{3} \frac{1}{2m} \bar{p_i^2} = \frac{3}{2}kT$$

- Brownian motion:
Consider a macroscopic particle of mass \(m \) immersed in a fluid at temperature T. Since the motion is random then $\bar{v}_x = \bar{v}_y = 0$ due to gravity along z axis. However, according to the equipartition theorem $K = \frac{1}{2}m\bar{v}_{x,y}^2 = \frac{1}{2}kT \Rightarrow \bar{v}_{x,y}^2 = \frac{kT}{m}$ then

- Heavy particles with $m \gg kT$ appear at rest.
- Light particles with $m \approx kT$ perpetually move in a random manner $\rightarrow$ Brownian motion

Equipartition theorem and simple applications

Simple applications:

- **Harmonic oscillator:**

Consider a 1D classical harmonic oscillator with $E = \dfrac{p^2}{2m} + \dfrac{1}{2}k_0 x^2$ so that

$\bar{E} = \dfrac{1}{2m}\bar{p}^2 + \dfrac{1}{2}k_0\bar{x}^2 = kT$ which is the classical result, with $\bar{E}$ being the mean energy, $\bar{p}^2$ and $\bar{x}^2$ are the mean squared momentum and position, respectively.

Now let us see what happens in the quantum case, remember:

$$\hat{H} = \frac{1}{2m}\hat{p}^2 + \frac{1}{2}m\omega^2\hat{x}^2$$

the time-independent Schrödinger equation gives:

$$-\frac{\hbar}{2m}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2}m\omega^2 x^2\psi(x) = E\psi(x)\,.$$

Solving this equation we find the energy spectrum

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \quad \text{with} \quad \omega^2 = \frac{k_0}{m}$$

Equipartition theorem and simple applications

- **Harmonic oscillator:**

the canonical partition function for the quantum oscillator reads:

$$Z = \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_{n=0}^{\infty} e^{-(n+\frac{1}{2})\beta\hbar\omega} = e^{-\frac{1}{2}\beta\hbar\omega} \cdot \sum_{n=0}^{\infty} e^{-n\beta\hbar\omega}$$

$$= e^{-\frac{1}{2}\beta\hbar\omega} \left[1 + e^{-\beta\hbar\omega} + e^{-2\beta\hbar\omega} + \cdots \right] = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} = \frac{1}{2}\,\mathrm{csch}\left(\frac{\beta\hbar\omega}{2}\right)$$

hence

$$\ln Z = -\frac{1}{2}\beta\hbar\omega - \ln\left[1 - e^{-\beta\hbar\omega}\right]$$

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta} = \hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\right) \qquad \Rightarrow \qquad \text{Quantum result}$$

How do we reconcile classical vs quantum results?

Equipartition theorem and simple applications

- **Harmonic oscillator:**

Let us explore the limit $\beta\hbar\omega = \dfrac{\hbar\omega}{kT} = \dfrac{\Delta E}{kT} \ll 1$ (High T): This is a classical limit
$\Delta E \ll kT$ consequently

$$\bar{E} = \hbar\omega \left(\frac{1}{2} + \frac{1}{(1 + \beta\hbar\omega + \ldots) - 1} \right)$$

$$\approx \hbar\omega \left(\frac{1}{2} + \frac{kT}{\hbar\omega} \right)$$

$$\approx kT \quad \Rightarrow \quad \bar{E} \approx kT$$

In agreement with the equipartition theorem !!

Equipartition theorem and simple applications

- **Harmonic oscillator:**

Let us explore the limit $\beta\hbar\omega = \frac{\hbar\omega}{kT} = \frac{\Delta E}{kT} \gg 1$ (Low T): This is not a classical limit
$\Delta E \gg kT$ consequently

$$\bar{E} = \hbar\omega \left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right) \approx \hbar\omega \left(\frac{1}{2} + e^{-\beta\hbar\omega} \right)$$

Different from equipartition theorem.
Approaches the ``zero point'' energy $\bar{E} = \frac{1}{2}\hbar\omega$ when $T = 0$.