

# Physics 415 - Lecture 23: Classical Limit, Equipartition Theorem

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## Summary

- Canonical Ensemble (CE): Fixed  $T, V, N$ .  $P_r = e^{-\beta E_r} / Z$ ,  $Z = \sum_r e^{-\beta E_r}$  ( $\beta = 1/T$ ).  $F = -T \ln Z$ .
- Classical Partition Function ( $N$  identical particles):

$$Z = \frac{1}{N!} \int \prod_{i=1}^N \frac{d^3 q_i d^3 p_i}{(2\pi\hbar)^3} e^{-\beta E(q,p)}$$
$$Z = \frac{1}{N!} \xi^N \int \prod_{i=1}^N \frac{d^3 q_i}{V} e^{-\beta U(q)}$$

where  $\xi = V/\lambda_{th}^3$  is related to the single-particle partition function, and  $\lambda_{th} = h/\sqrt{2\pi mT}$  is the thermal de Broglie wavelength.  $U(q)$  is potential energy (for ideal gas  $U = 0$ ).

## Validity of the Classical Approach

We have seen that a sensible partition function in classical statistical mechanics requires ingredients from Quantum Mechanics (QM): the phase space cell volume  $(2\pi\hbar)^S$  and the  $N!$  factor for indistinguishable particles. Question: When is the classical approach valid? When must we resort to a full quantum treatment?

We can use the Heisenberg uncertainty relation  $\Delta x \Delta p \sim \hbar$  to make some estimates of the "classical regime". (Note: This mixes classical and quantum reasoning, but gives the correct estimate. A more careful calculation uses a full QM treatment). Estimate the typical momentum spread  $\Delta p$ : Average kinetic energy per DOF is  $\sim T/2$ , so  $\overline{p^2/(2m)} \sim T/2 \implies \overline{p^2} \sim mT$ . Assume the spread is roughly the typical momentum magnitude:  $\Delta p \sim \sqrt{\overline{p^2}} \sim \sqrt{mT}$ . This momentum uncertainty determines a minimum "size" or position uncertainty of the particle via QM:

$$\Delta x \sim \frac{\hbar}{\Delta p} \sim \frac{\hbar}{\sqrt{mT}}$$

This leads to a characteristic length scale:

$$\lambda_{th} \equiv \sqrt{\frac{2\pi\hbar^2}{mT}} = \frac{h}{\sqrt{2\pi mT}}$$

This is the **thermal de Broglie wavelength**, roughly the quantum "size" of a particle at temperature  $T$ . Note that  $\lambda_{th}$  already appeared in the classical partition function:

$$\xi = V \left( \frac{mT}{2\pi\hbar^2} \right)^{3/2} = V \left( \frac{h^2}{2\pi mT(2\pi\hbar)^2} \right)^{3/2} ?$$

Let's re-check  $\xi = V(m/(2\pi\hbar^2\beta))^{3/2} = V(mT/(2\pi\hbar^2))^{3/2}$ .  $\lambda_{th}^2 = h^2/(2\pi mT) = (2\pi\hbar)^2/(2\pi mT) = 2\pi\hbar^2/(mT)$ .  $mT/(2\pi\hbar^2) = 1/\lambda_{th}^2$ . So  $\xi = V(1/\lambda_{th}^2)^{3/2} = V/\lambda_{th}^3$ . Correct.

$$Z = \frac{1}{N!} \left( \frac{V}{\lambda_{th}^3} \right)^N \int \prod \frac{d^3 q_i}{V} e^{-\beta U(q)} \quad (\text{Ideal gas } U = 0 \implies \text{integral} = V^N)$$

It is reasonable to expect the classical treatment to be appropriate when the average distance 'a' between particles is much larger than their thermal wavelength  $\lambda_{th}$ :

$$a \gg \lambda_{th} \quad (\text{Classical Regime})$$

When  $a \sim \lambda_{th}$ , quantum mechanical effects (wave nature, interference, identity) become important. We can rephrase this condition in terms of the particle density  $n = N/V$ . The average volume per particle is  $1/n$ , so  $a \sim (1/n)^{1/3}$ . The condition becomes:  $n^{-1/3} \gg \lambda_{th}$ , or  $1 \gg n^{1/3} \lambda_{th}$ , or  $1 \gg n \lambda_{th}^3$ .

$$n \lambda_{th}^3 \ll 1 \quad (\text{Classical Limit})$$

The classical limit is reached if the density  $n$  is sufficiently low or the temperature  $T$  is sufficiently high ( $\lambda_{th} \propto 1/\sqrt{T}$ ).

**Example 1:** He gas at  $T = 300$  K and  $p = 1$  atm.  $n \approx 3 \times 10^{19} \text{ cm}^{-3}$ . Average distance  $a = n^{-1/3} \approx 3 \times 10^{-7} \text{ cm}$ . Mass  $m_{He} \approx 4 \times 1.67 \times 10^{-24} \text{ g}$ .  $\lambda_{th} = h/\sqrt{2\pi mT} \approx 0.5 \times 10^{-8} \text{ cm}$ . Here  $a \gg \lambda_{th}$ . Classical treatment is valid.

**Example 2:** Electrons ( $e^-$ ) in a typical metal.  $m_e \ll m_{He}$ . Density  $n \sim 10^{22} - 10^{23} \text{ cm}^{-3}$ .  $a \sim \text{few} \times 10^{-8} \text{ cm}$  (lattice spacing).  $\lambda_{th} \sim 50 \times 10^{-8} \text{ cm}$  at  $T = 300$  K. Here  $\lambda_{th} \gtrsim a$ . Electrons in a metal form a highly quantum system even at room temperature.

## Equipartition Theorem

This is an important general result in classical statistical mechanics. In many situations, the energy  $E$  contains terms that are quadratic in momenta and/or coordinates.

- Ideal gas kinetic energy:  $K = \sum_{i=1}^N \frac{1}{2m} (p_{ix}^2 + p_{iy}^2 + p_{iz}^2)$ . (Quadratic in momenta).
- Harmonic oscillator:  $E = \frac{p^2}{2m} + \frac{1}{2} k q^2$ . (Quadratic in  $p$  and  $q$ ).

**Theorem Statement:** In classical statistical mechanics, for a system in thermal equilibrium at temperature  $T$ , each degree of freedom (coordinate or momentum) that enters the Hamiltonian quadratically contributes, on average,  $\frac{1}{2}T$  to the internal energy  $\bar{E}$ . (Using  $T$  in energy units; otherwise  $\frac{1}{2}k_B T$ ). It also contributes  $\frac{1}{2}$  (or  $\frac{1}{2}k_B$ ) to the heat capacity.

**Derivation:** Suppose the energy  $\tilde{E}$  contains a term  $\epsilon = \frac{1}{2}\kappa u^2$ , where  $u$  is some coordinate or momentum variable, and  $E = \epsilon(u) + \tilde{E}(\text{other vars})$ , where  $\tilde{E}$  is independent of  $u$ . The classical partition function  $Z$  (ignoring  $N!$  for simplicity here, as it won't affect averages) is:

$$Z = \int \frac{dq dp}{(2\pi\hbar)^S} e^{-\beta E} = \left( \int' \frac{dq' dp'}{(2\pi\hbar)^{S-1}} e^{-\beta \tilde{E}} \right) \left( \int_{-\infty}^{\infty} \frac{du}{2\pi\hbar \text{ or } 1?} e^{-\beta \kappa u^2/2} \right)$$

$$Z = \tilde{Z} \times \xi_u$$

where  $\tilde{Z}$  involves integration over all variables except  $u$ , and  $\xi_u$  is the factor from integrating over  $u$ :

$$\xi_u = C' \int_{-\infty}^{\infty} du e^{-\beta \kappa u^2/2} = C' \sqrt{\frac{2\pi}{\beta \kappa}}$$

The average energy associated with the variable  $u$  is  $\bar{\epsilon} = \frac{1}{2}\kappa \bar{u}^2$ . We can calculate this using the formula  $\bar{E} = -\partial(\ln Z)/\partial\beta$ . The total average energy  $\bar{E} = \tilde{\bar{E}} + \bar{\epsilon}$ .  $\ln Z = \ln \tilde{Z} + \ln \xi_u$ .

$\bar{E} = -\frac{\partial}{\partial\beta}(\ln \tilde{Z}) - \frac{\partial}{\partial\beta}(\ln \xi_u)$ . The first term is the average energy from all other degrees of freedom. The second term is the contribution from  $u$ :

$$\bar{\epsilon} = -\frac{\partial}{\partial\beta}(\ln \xi_u) = -\frac{\partial}{\partial\beta}(\ln C' + \ln \sqrt{2\pi/(\beta\kappa)}) = -\frac{\partial}{\partial\beta}(\text{const} - \frac{1}{2} \ln \beta)$$

$$\bar{\epsilon} = -(-\frac{1}{2} \frac{1}{\beta}) = \frac{1}{2\beta} = \frac{1}{2}T$$

So, each quadratic term  $\frac{1}{2}\kappa u^2$  contributes  $\frac{1}{2}T$  to the average energy. The contribution to the heat capacity is  $C_u = \partial\bar{\epsilon}/\partial T = \partial(\frac{1}{2}T)/\partial T = 1/2$ . (Or  $k_B/2$ ).

**Note:** This theorem is only true in classical statistical mechanics.

## Simple Applications

- Single molecule (or atom) in gas at  $T$ : Translational kinetic energy  $K = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$ . Three quadratic terms. Contribution to average energy  $= 3 \times (\frac{1}{2}T) = \frac{3}{2}T$ .
- Monatomic ideal gas ( $N$  particles):  $E = \sum_{i=1}^N K_i$ . Total  $3N$  quadratic terms.  $\bar{E} = 3N \times (\frac{1}{2}T) = \frac{3}{2}NT$ . ✓
- Classical 1D Harmonic Oscillator:  $E = \frac{p^2}{2m} + \frac{1}{2}kq^2$ . Two quadratic terms.  $\bar{E} = 2 \times (\frac{1}{2}T) = T$ . Note that the average kinetic energy  $\bar{K} = \overline{p^2/(2m)} = T/2$  and average potential energy  $\bar{U} = \overline{kq^2/2} = T/2$ . Thus  $\bar{K} = \bar{U} = \bar{E}/2$ .

## Quantum Harmonic Oscillator Revisited

It is interesting to see how the harmonic oscillator result is modified in QM. Energy levels:  $E_n = (n + 1/2)\hbar\omega$ ,  $n = 0, 1, 2, \dots$ . Partition function:  $Z = \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_{n=0}^{\infty} e^{-\beta(n+1/2)\hbar\omega} = e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} (e^{-\beta\hbar\omega})^n$ . This is a geometric series  $\sum_{n=0}^{\infty} x^n = 1/(1-x)$  with  $x = e^{-\beta\hbar\omega}$ .

$$Z = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}$$

Average energy:  $\bar{E} = -\frac{\partial}{\partial\beta}(\ln Z)$ .  $\ln Z = -\frac{\beta\hbar\omega}{2} - \ln(1 - e^{-\beta\hbar\omega})$ .

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

$$\bar{E} = \frac{\hbar\omega}{2} + \frac{\hbar\omega e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

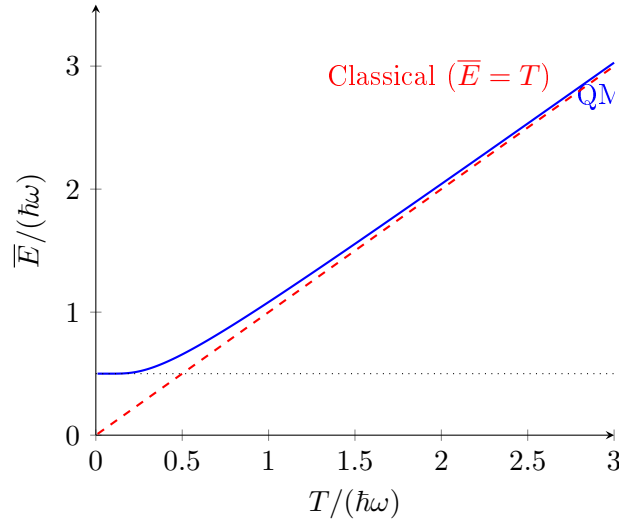
$$\bar{E} = \hbar\omega \left( \frac{1}{2} + \frac{1}{e^{\hbar\omega/T} - 1} \right)$$

(Includes zero-point energy  $\hbar\omega/2$ ).

### Limits:

- High T limit ( $T \gg \hbar\omega \implies \beta\hbar\omega \ll 1$ ): Let  $x = \beta\hbar\omega = \hbar\omega/T$ .  $e^x \approx 1 + x$ .  $\bar{E} \approx \hbar\omega(\frac{1}{2} + \frac{1}{(1+x)-1}) = \hbar\omega(\frac{1}{2} + \frac{1}{x}) = \hbar\omega(\frac{1}{2} + \frac{T}{\hbar\omega}) = \frac{\hbar\omega}{2} + T$ . Excluding the zero-point energy,  $\bar{E} - E_0 \approx T$ . This recovers the classical equipartition result ( $\bar{E}_{\text{classical}} = T$ ).
- Low T limit ( $T \ll \hbar\omega \implies \beta\hbar\omega \gg 1$ ):  $e^{\beta\hbar\omega} \gg 1$ .  $\bar{E} \approx \hbar\omega(\frac{1}{2} + e^{-\beta\hbar\omega}) = \frac{\hbar\omega}{2} + \hbar\omega e^{-\hbar\omega/T}$ . As  $T \rightarrow 0$ ,  $\bar{E} \rightarrow \hbar\omega/2$  (ground state energy).

Sketch of  $\bar{E}$  vs  $T$ :



Heat Capacity  $C = \partial \bar{E} / \partial T$ .

$$C = \frac{\partial}{\partial T} \left[ \hbar\omega \left( \frac{1}{2} + \frac{1}{e^{\hbar\omega/T} - 1} \right) \right] = \hbar\omega \frac{-1}{(e^{\hbar\omega/T} - 1)^2} \left( e^{\hbar\omega/T} \right) \left( -\frac{\hbar\omega}{T^2} \right)$$

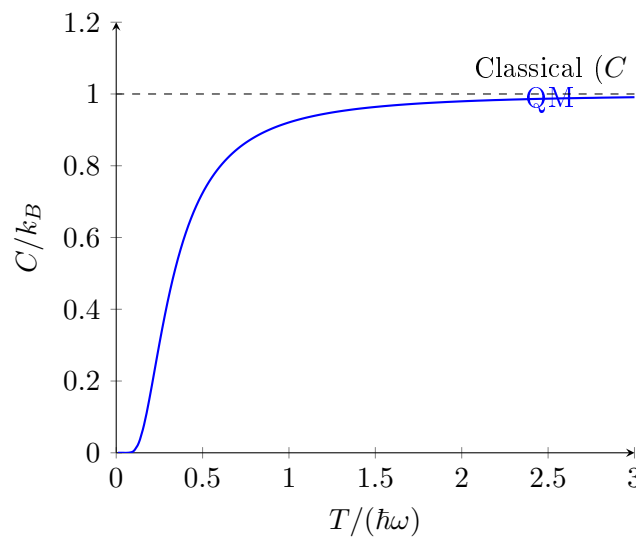
$$C = \left( \frac{\hbar\omega}{T} \right)^2 \frac{e^{\hbar\omega/T}}{(e^{\hbar\omega/T} - 1)^2}$$

(Using  $T$  in energy units, so  $C$  is dimensionless, equivalent to  $C/k_B$ ).

**Limits:**

- High T limit ( $x = \hbar\omega/T \ll 1$ ):  $e^x \approx 1 + x$ .  $C \approx x^2 \frac{1+x}{((1+x)-1)^2} = x^2 \frac{1+x}{x^2} \approx 1$ . Agrees with classical  $C = 1$  (or  $k_B$ ).
- Low T limit ( $x = \hbar\omega/T \gg 1$ ):  $e^x \gg 1$ .  $C \approx x^2 \frac{e^x}{(e^x)^2} = x^2 e^{-x} = \left(\frac{\hbar\omega}{T}\right)^2 e^{-\hbar\omega/T}$ . Goes to 0 exponentially as  $T \rightarrow 0$ .

Sketch of  $C$  vs  $T$ :



Quantized energy levels lead to a dramatic reduction ("freezing out") of the heat capacity at low temperatures ( $T \ll \hbar\omega$ ).