Quantum occupations and limits of equipartition

GRE undergraduate preparation · local supported objectives

Quantum occupations and the limits of equipartition

- Use fermion and boson **occupation numbers 占据数** with the **chemical potential 化学势**.
- Count arrangements of **identical particles 全同粒子**.
- Recognise the classical limit.
- Know when equipartition holds and when it fails, as in the **Einstein solid 爱因斯坦固体**.

Mean occupations

- Fermions: between 0 and 1. Bosons: can be larger than 1.
- A level with g states holds $g\bar{n}$ on average. A level with five states can hold up to five fermions.
- Photons have $\mu = 0$ because their number is not conserved.

$$\bar{n}_{\mathrm{FD}} = \frac{1}{e^x + 1}, \qquad \bar{n}_{\mathrm{BE}} = \frac{1}{e^x - 1}$$

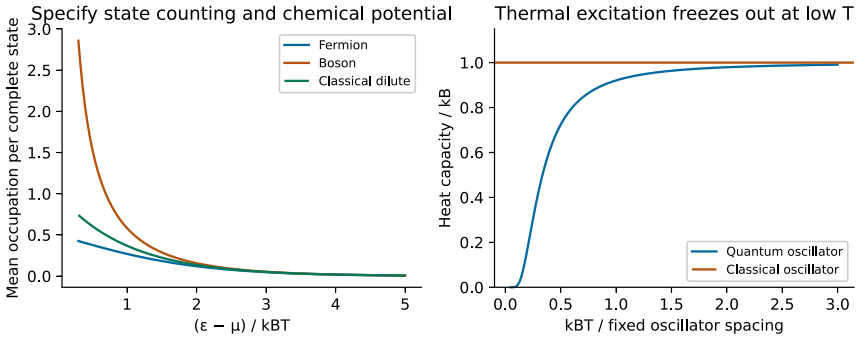
Counting two particles

- Two identical fermions: $\binom{4}{2} = 6$ ways (no state used twice).
- Two identical bosons: $\binom{5}{2} = 10$ ways (sharing allowed).
- Two labelled (distinguishable) particles: $4^2 = 16$ ways.
- Two electrons with opposite spins can share one spatial orbital, because they are in different complete states.

The classical limit

- At $x = \ln 4$: fermions $\frac{1}{5}$, bosons $\frac{1}{3}$, classical $\frac{1}{4}$, still clearly different.
- Fermions at low temperature fill every state below μ and none above, with $\overline{n} = \frac{1}{2}$ at $\varepsilon = \mu$.

Figure: The classical limit



- All three distributions agree when $(\varepsilon - \mu) \gg \mathrm{kT}$; quantum heat capacity freezes out at low T
- Read the axes and units first.

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Equipartition and its limits

- Monatomic gas: $C_V = \frac{3}{2} N k_B$. One oscillator (kinetic plus potential): $C = k_B$.
- A quantum oscillator with $x = \hbar\omega / k_B T$ has $\dfrac{C}{k_B} = \dfrac{x^2 e^x}{(e^x - 1)^2}$.
- When $k_B T \ll \hbar\omega$, $C \to 0$: molecular vibrations at room temperature add almost nothing to the heat capacity of air.

The Einstein solid

- At high temperature, $C \to 3Nk_B = 3R$ per mole (the Dulong–Petit law).
- At low temperature, C falls towards zero. Diamond's stiff bonds give a high frequency, so it is still frozen out at room temperature.

Worked example: occupations and counting

- At $x = \ln 4$: $\bar{n}_{\mathrm{FD}} = 1/(4+1) = 0.20$; $\bar{n}_{\mathrm{BE}} = 1/(4-1) = 0.33$; classical $e^{-x} = 0.25$.
- A quantum oscillator at $x = \ln 2$: mean excitation $\hbar\omega/(e^{x}-1) = \hbar\omega$, and $C/k_B = 2(\ln 2)^2 = 0.96$, just below the classical 1.
- Two identical fermions in 4 states: 6 arrangements, against 16 for labelled particles.

Worked example: diamond at room temperature

- $x = 1320/300 = 4.4$ and $e^x = 81.5$.
- $C/k_B = \dfrac{(4.4)^2(81.5)}{(80.5)^2} = 0.24$ per oscillator, so $C = 0.24 \times 3R = 6.1$ J/(mol K).
- This matches the measured value, about a quarter of the classical 24.9 J/(mol K).

Common errors

- Applying the Pauli limit per energy level instead of per complete state.
- Using $\mu \neq 0$ for photons.
- Counting **identical particles** as if they were labelled.

Common errors (2)

- Using equipartition for vibrations whose spacing is much larger than $k_B T$.
- Forgetting the factor 3 (three directions) in the **Einstein solid**.

Key terms

- **equipartition**: Each quadratic energy term has an average of $\frac{1}{2}k_B T$ in classical equilibrium.
- **freeze out**: A degree of freedom stops taking up heat when $k_B T$ is much smaller than its level spacing.
- **occupation number**: The mean number of particles in one quantum state.
- **chemical potential**: The energy cost of adding one particle; it sets the occupations.

Check yourself

- Two identical bosons share 3 states. How many arrangements are there? And for fermions?
- What is the fermion occupation at $\varepsilon = \mu$?
- What is the heat capacity of one quantum oscillator at very high temperature?