Independent and indistinguishable particles

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Density matrix in quantum mechanics

- A quantum mechanical (micro)state is characterized in terms of the eigenstates of a complete set of commuting observables
- An ensemble can be seen as the set of probabilities of finding the system in one of such eigenstates
- The density matrix provides a formally elegant solution to computing ensemble averages in quantum mechanics. E.g. the canonical density matrix is

$$\boldsymbol{\rho} = e^{-\beta \hat{H}}$$

  - The partition function is the trace of $\boldsymbol{\rho}$

$$\operatorname{Tr} \boldsymbol{\rho} = \sum_\nu \langle \nu | \, e^{-\beta \hat{H}} \, | \nu \rangle = \sum_\nu e^{-\beta E_\nu} = Q$$

  - The value of any observable can be obtained as a trace

$$\frac{1}{Q} \operatorname{Tr} \boldsymbol{\rho} \hat{A} = \frac{1}{Q} \sum_\nu \langle \nu | \, e^{-\beta \hat{H}} \hat{A} \, | \nu \rangle = \frac{1}{Q} \sum_\nu A_\nu e^{-\beta E_\nu} = \langle A \rangle$$

The origin of quantum statistics

- Consider the quantum mechanical partition function in the position representation

$$Q = \mathrm{Tr}\, e^{-\beta\hat{H}} = \int \mathrm{d}\mathbf{q} \langle\mathbf{q}| e^{-\beta\hat{H}} |\mathbf{q}\rangle$$

  - Now, let's pretend that $\left[\hat{T}, \hat{V}\right] = 0$, so we can write $e^{-\beta\hat{H}} = e^{-\beta\hat{T}} e^{-\beta\hat{V}}$

$$\int \mathrm{d}\mathbf{q} \langle\mathbf{q}| e^{-\beta\hat{T}} e^{-\beta\hat{V}} |\mathbf{q}\rangle = \int \mathrm{d}\mathbf{q} e^{-\beta V(\mathbf{q})} \langle\mathbf{q}| e^{-\beta\hat{T}} |\mathbf{q}\rangle$$

  - We need to insert a **p** projector $\int \mathrm{d}\mathbf{p} |\mathbf{p}\rangle \langle\mathbf{p}|$

$$\int \mathrm{d}\mathbf{q} \int \mathrm{d}\mathbf{p} e^{-\beta V(\mathbf{q})} \langle\mathbf{q}| e^{-\beta\hat{T}} |\mathbf{p}\rangle \langle\mathbf{p}|\mathbf{q}\rangle = \int \mathrm{d}\mathbf{q} \int \mathrm{d}\mathbf{p} e^{-\beta\left[V(\mathbf{q}) + \frac{p^2}{2m}\right]} \langle\mathbf{q}|\mathbf{p}\rangle \langle\mathbf{p}|\mathbf{q}\rangle$$

  - We are left with the *classical* canonical partition function. QM behavior arises from non-commuting operators!

Remember: $\langle\mathbf{p}|\mathbf{q}\rangle \propto e^{i\mathbf{p}\cdot\mathbf{q}}$, so $\langle\mathbf{q}|\mathbf{p}\rangle \langle\mathbf{p}|\mathbf{q}\rangle = \mathrm{cnst.}$

A more formal look at independent particles

- Let's look at the canonical partition function of two non-interacting subsystems considered as a whole
  - Let ν_i^A and ν_i^B be the microstates of subsystems A and B respectively, so

$$Q^A = \sum_i e^{-\beta E_i^A}, \quad Q^B = \sum_i e^{-\beta E_i^B}$$

  now, if we consider the composite system, its states correspond to the Cartesian product of $\left\{\nu_i^A\right\} \times \left\{\nu_j^B\right\}$, so

$$Q^{AB} = \sum_{ij} e^{-\beta E_i^A} e^{-\beta E_j^B} = Q^A Q^B$$

  - The observables of the composite systems are similarly easy to obtain,

$$\langle E \rangle = \left\langle E^A \right\rangle + \left\langle E^B \right\rangle$$

  and observables of individual systems are uncorrelated as they should

$$\left\langle E^A E^B \right\rangle = \frac{1}{Q} \sum_{ij} E_i^A E_j^B e^{-\beta\left(E_i^A + E_j^B\right)} = \frac{\left[\sum_i E_i^A e^{-\beta E_i^A}\right]\left[\sum_i E_i^B e^{-\beta E_i^B}\right]}{Q_A Q_B} = \left\langle E^A \right\rangle \left\langle E^B \right\rangle$$

Many-particle states: stat-mech gets QM

- Consider a system with N particles. They will be described by the many-body wavefunction

$$\langle \mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_N | \nu \rangle = \Psi_\nu \left(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_N \right)$$

  - This is a formidable problem! How are we going to write this wavefunction, and to label states??

- In many cases we can make a factorization ansatz, that is equivalent to assuming that (quasi)particles behave independently of each other

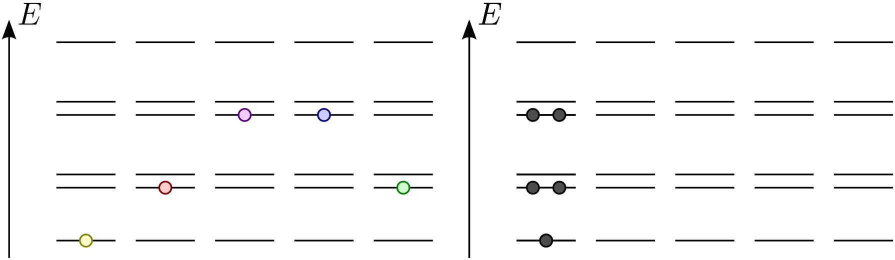
$$\Psi_\nu \left(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_N \right) = \prod_{i=1}^{N} \psi_{\nu_i}^{(i)} \left(\mathbf{x}_i \right)$$

- If the particles are all subject to a sum of single-particle Hamiltonians, then everything pans out nicely, and the density matrix and partition function are just products of single-particle DM and PF

$$\boldsymbol{\rho} = e^{-\beta \hat{H}} = e^{-\beta \sum_i \hat{H}_i} = \prod_i e^{-\beta \hat{H}_i} = \prod_i \boldsymbol{\rho}_i$$

$$Q = \mathrm{Tr}\, e^{-\beta \hat{H}} = \prod_i \sum_{\nu_i} \langle \nu_i | \, e^{-\beta \hat{H}_i} \, | \nu_i \rangle = \prod_i Q_i$$

- Now consider what should happen if all the Hamiltonians are identical, but the different particles are somehow distinguishable (e.g. because they are very far from each other)
- If particles are all the same, some states are indistinguishable, and we must avoid double-counting!
- A very effective formalism: using *occupation numbers* for the different levels



Indistinguishability - the wavefunction

- Quantum mechanically, the observables must not change if we swap indices of identical particles, e.g.

$$\left|\Psi\left(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_N\right)\right|^2 = \left|\Psi\left(\mathbf{x}_2, \mathbf{x}_1, \ldots \mathbf{x}_N\right)\right|^2$$

in fact, there are only two possibilities:

1. bosons: $\Psi\left(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_N\right) = \Psi\left(\mathbf{x}_2, \mathbf{x}_1, \ldots \mathbf{x}_N\right)$

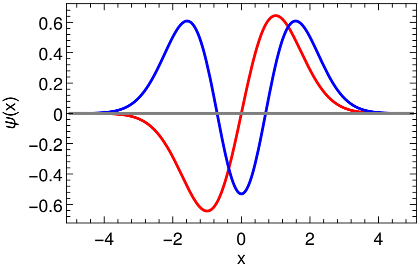
$$\Psi = \frac{1}{\sqrt{N!}} \sum_\pi \prod_{i=1}^N \psi_{\nu_i}\left(\mathbf{x}_{\pi_i}\right)$$

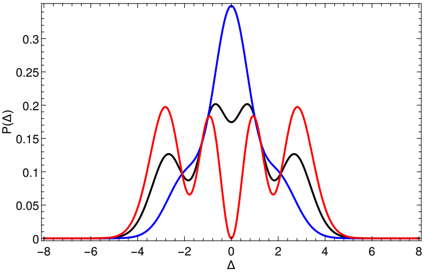
2. fermions: $\Psi\left(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_N\right) = -\Psi\left(\mathbf{x}_2, \mathbf{x}_1, \ldots \mathbf{x}_N\right)$

$$\Psi = \frac{1}{\sqrt{N!}} \sum_\pi \operatorname{sign} \pi \prod_{i=1}^N \psi_{\nu_i}\left(\mathbf{x}_{\pi_i}\right)$$

- Exclusion principle: Ψ_F is zero if two systems are in the same quantum state, so each state can be occupied at most once!

- Two identical oscillators, resp. in the first and second excited states
- Product ansatz is not invariant to particle exchanges
- Symmetrized wavefunctions introduce new correlations





$$\psi_1(x), \qquad \psi_2(x), P(\Delta) = \int |\Psi(x, x+\Delta)|^2 \, dx$$

- For N *distinguishable* particles with single-particle energy levels ϵ_i

$$Q = q^N = \left[\sum_i e^{-\beta\epsilon_i}\right]^N$$

where q is the partition function for a single particle

- For indistinguishable particles it is better to work in terms of the occupation numbers $\{n_\nu\}$

  1. bosons: $Q = \sum_{\{n_i\}} \delta\left(\sum_i n_i - N\right) e^{-\beta\sum_i n_i\epsilon_i}$
  2. fermions $Q = \sum_{\{n_i\}} \delta\left(\sum_i n_i - N\right) \left[\prod_i \left(\delta_{n_i 0} + \delta_{n_i 1}\right)\right] e^{-\beta\sum_i n_i\epsilon_i}$

- It is far from trivial to work analytically in constant-N ensembles

- How about we use the grand-canonical formalism?

$$\Xi = \sum_{\{n_i\}} e^{-\beta\left[\sum_i n_i \epsilon_i - \mu \sum_i n_i\right]} = \sum_{\{n_i\}} \prod_i e^{-\beta n_i (\epsilon_i - \mu)} = \prod_i \sum_{n_i=0}^{\infty} e^{-\beta n_i (\epsilon_i - \mu)}$$

- Summing up the geometric series we get

$$\Xi = \prod_i \frac{1}{1 - e^{-\beta(\epsilon_i - \mu)}}, \quad \ln \Xi = -\sum_i \ln\left(1 - e^{-\beta(\epsilon_i - \mu)}\right)$$

from which we get mean occupation numbers

$$\langle n_j \rangle = -\frac{\partial \ln \Xi}{\partial (\beta \epsilon_j)} = \frac{e^{-\beta(\epsilon_j - \mu)}}{1 - e^{-\beta(\epsilon_j - \mu)}} = \frac{1}{e^{\beta(\epsilon_j - \mu)} - 1}$$

- Total particle number can be enforced by computing $\langle N \rangle$ and self-consistently adjusting μ

Fermi statistics

- Also when considering Fermions it helps working grand-canonical

$$\Xi = \sum_{\{n_i\}} e^{-\beta\left[\sum_i n_i\epsilon_i - \mu\sum_i n_i\right]} = \sum_{\{n_i\}}\prod_i e^{-\beta n_i(\epsilon_i-\mu)} = \prod_i \sum_{n_i=0}^{1} e^{-\beta n_i(\epsilon_i-\mu)}$$

- Getting the PF is a piece of cake

$$\Xi = \prod_i 1 + e^{-\beta(\epsilon_i-\mu)}, \quad \ln\Xi = \sum_i \ln\left(1+e^{-\beta(\epsilon_i-\mu)}\right)$$

an so is obtaining the mean occupation numbers

$$\langle n_j\rangle = -\frac{\partial\ln\Xi}{\partial(\beta\epsilon_j)} = \frac{e^{-\beta(\epsilon_j-\mu)}}{1+e^{-\beta(\epsilon_j-\mu)}} = \frac{1}{e^{\beta(\epsilon_j-\mu)}+1}$$

- Also in this case, in the thermodynamic limit, constant-$\langle N\rangle$ can be set by adjusting μ

- Re-consider the distinguishable particles case in the grand-canonical ensemble

$$\Xi = \sum_N q^N e^{\beta\mu N} = \frac{1}{1 - qe^{\beta\mu}}, \qquad \ln \Xi = -\ln 1 - qe^{\beta\mu}$$

- It is easy to get $\langle n_j \rangle$ by differentiating the G-C PF

$$\langle n_j \rangle = -\frac{\partial \ln \Xi}{\partial \beta\epsilon_j} = \frac{e^{\beta\mu} \left(\partial q / \beta\epsilon_j\right)}{1 - qe^{\beta\mu}} = \frac{e^{\beta\mu} e^{-\beta\epsilon_j}}{1 - qe^{\beta\mu}} = \frac{e^{-\beta(\epsilon_j - \mu)}}{1 - e^{\beta\mu} q} = \frac{e^{-\beta\epsilon_j}}{e^{-\beta\mu} - q}$$

- Guess how you can enforce the desired value for $\langle N \rangle$...

High-T limits

- In the high-T limit, for a system with an infinite number of energy levels, the number of levels gets much larger than $\langle N\rangle$. Then,

$$\langle n_j\rangle = \frac{1}{e^{\beta(\epsilon_j-\mu)}\pm 1} \ll 1$$

which implies that $e^{\beta(\epsilon_j-\mu)} \gg 1$.

  - Then, one can write $\langle n_j\rangle \approx e^{-\beta\left(\epsilon_j-\mu\right)}$, so

$$\langle N\rangle = \sum_j \langle n_j\rangle = e^{\beta\mu}\sum_j e^{-\beta\epsilon_j} \quad \rightarrow \quad \beta\mu = \ln\langle N\rangle - \ln\sum_j e^{-\beta\epsilon_j}$$

  - Let's now apply a few thermodynamic relations

$$\ln Q = -\langle N\rangle \ln\langle N\rangle + \langle N\rangle \ln\sum_j e^{-\beta\epsilon_j} + \langle N\rangle \approx -N! + \langle N\rangle \ln q$$

- The high-temperature partition function equals the Boltzmann case, with a correction to account for the indistinguishability of particles

$$\boxed{Q = \frac{q^N}{N!}}$$