A linear harmonic oscillator

$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial q^2} + \frac{1}{2}m\omega^2 q^2$$

$$E_n = (n + \frac{1}{2})\hbar\omega$$

$$\phi_n(q) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{H_n(\xi)}{(2^n n!)^{1/2}} e^{-(1/2)\xi^2}$$

$$\xi = \left(\frac{m\omega}{\hbar}\right)^{1/2} q$$

$$H_n(\xi) = (-1)^n e^{\xi^2} \left(\frac{d}{d\xi}\right)^n e^{-\xi^2}$$

$$\langle q|e^{-\beta\hat{H}}|q'\rangle = \sum_{n=0}^{\infty} e^{-\beta E_n}\phi_n(q)\phi_n(q') = \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} e^{-(1/2)(\xi^2+\xi'^2)} \sum_{n=0}^{\infty}\left\{e^{-(n+1/2)\beta\hbar\omega}\frac{H_n(\xi)H_n(\xi')}{2^n n!}\right\}$$

The mathematical details of this derivation can be found in Kubo (1965), pp. 175-177.

$$= \left[\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}\right]^{1/2} \times \exp\left[-\frac{m\omega}{4\hbar}\left\{(q+q')^2\tanh\left(\frac{\beta\hbar\omega}{2}\right) + (q-q')^2\coth\left(\frac{\beta\hbar\omega}{2}\right)\right\}\right]$$

$$\mathrm{Tr}\,(e^{-\beta\hat{H}}) = \int_{-\infty}^{\infty}\langle q|e^{-\beta\hat{H}}|q\rangle\,dq = \left[\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}\right]^{1/2}\int_{-\infty}^{\infty}\exp\left[-\frac{m\omega q^2}{\hbar}\tanh\left(\frac{\beta\hbar\omega}{2}\right)\right]dq$$

Partition function

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

$$\langle q|\hat{\rho}|q\rangle = \left[\frac{m\omega\tanh\left(\frac{1}{2}\beta\hbar\omega\right)}{\pi\hbar}\right]^{1/2}\exp\left[-\frac{m\omega q^2}{\hbar}\tanh\left(\frac{\beta\hbar\omega}{2}\right)\right] \qquad q_{\mathrm{r.m.s.}} = \left[\frac{\hbar}{2m\omega\tanh\left(\frac{1}{2}\beta\hbar\omega\right)}\right]^{1/2}$$

In the classical limit ($\beta\hbar\omega << 1$), the distribution becomes purely thermal-free from quantum

$$\langle q|\hat{\rho}|q\rangle \approx \left(\frac{m\omega^2}{2\pi kT}\right)^{1/2} \exp\left[-\frac{m\omega^2 q^2}{2kT}\right] \quad \text{with dispersion } (kT/m\omega^2)^{1/2}$$

At the other extreme ($\beta\hbar\omega >> 1$), the distribution becomes purely quantum-mechanical -free from thermal effects:

$$\langle q|\hat{\rho}|q\rangle \approx \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \exp\left[-\frac{m\omega q^2}{\hbar}\right] \quad \text{with dispersion } (\hbar/2m\omega)^{1/2}$$

Note that the above limiting distribution is precisely the one expected for an oscillator in its ground state (n = 0):

$$\langle q|\rho|q\rangle = \Phi_0^2(q)$$

$$\langle H\rangle = -\frac{\partial}{\partial\beta}\ln \mathrm{Tr}\,(e^{-\beta\hat{H}}) = \tfrac{1}{2}\hbar\omega\coth\left(\tfrac{1}{2}\beta\hbar\omega\right)$$

we observe that the temperature dependence of the distribution (25) is *solely* determined through the expectation value $\langle H\rangle$. Actually, we can write

$$\langle q|\hat{\rho}|q\rangle = \left[\frac{m\omega\tanh\left(\frac{1}{2}\beta\hbar\omega\right)}{\pi\hbar}\right]^{1/2}\exp\left[-\frac{m\omega q^2}{\hbar}\tanh\left(\frac{\beta\hbar\omega}{2}\right)\right] \qquad q_{\text{r.m.s.}} = \left[\frac{\hbar}{2m\omega\tanh\left(\frac{1}{2}\beta\hbar\omega\right)}\right]^{1/2}$$

$$\langle q|\hat{\rho}|q\rangle = \left(\frac{m\omega^2}{2\pi\langle H\rangle}\right)^{1/2}\exp\left[-\frac{m\omega^2 q^2}{2\langle H\rangle}\right] \qquad q_{\text{r.m.s.}} = \left(\frac{\langle H\rangle}{m\omega^2}\right)^{1/2}$$

It is now straightforward to see that the mean value of the potential energy ($\frac{1}{2}m\omega^2q^2$) of the oscillator is $\frac{1}{2}\langle H\rangle$; accordingly, the mean value of the kinetic energy ($p^2/2m$) must also be the same.

Systems composed of indistinguishable particles

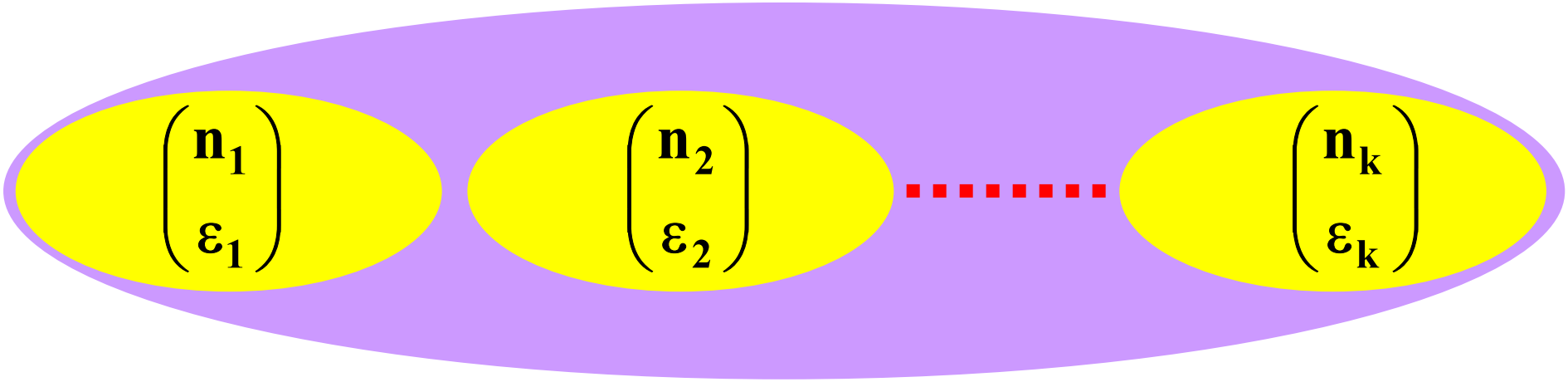
We shall now formulate the quantum-mechanical description of a system of N identical particles. To fix ideas, we consider a gas of *non-interacting* particles; the findings of this study will be of considerable relevance to other systems as well.

$$H\Psi_E(q_1, q_2, \ldots, q_N) = E\Psi_E(q_1, q_2, \ldots, q_N)$$

$$\Psi_E(q_1, q_2, \ldots, q_N) = \prod_{i=1}^{N} U_{\varepsilon_i}(q_i)$$

$$HU_{\varepsilon_i}(q_i) = \varepsilon_i U_{\varepsilon_i}(q_i)$$

$$\sum_i n_i = N \qquad \sum_i n_i \varepsilon_i = E$$

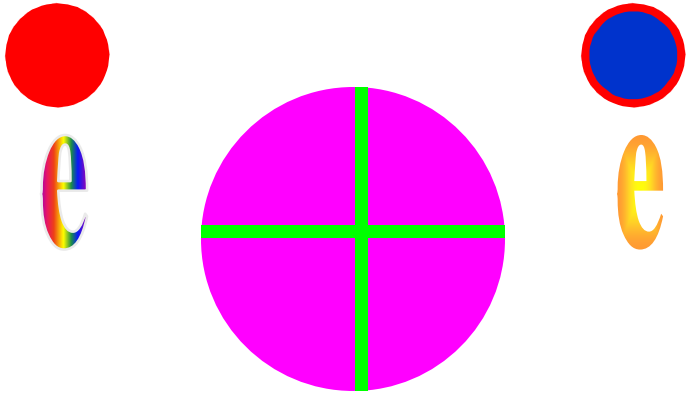


$$\Psi_E(q_1, q_2, \ldots, q_N) = \prod_{i=1}^{N} U_{\varepsilon_i}(q_i)$$

$$= \prod_{i=1}^{n_1} U_1(m) \prod_{i=n_1+1}^{n_1+n_2} U_2(m) \prod_{i=n_1+n_2+1}^{n_1+n_2+n_3} U_3(m) \ldots$$

We would like to be all the electrons in quantum mechanics indistinguishable.

How can we do it?



$$H = \frac{P_1^2}{2m} + \frac{P_2^2}{2m} + V(x_1, x_2)$$

$$H(1,2) = H(2,1)$$

$$H(1,2)\Psi_E(1,2) = E\Psi_E(1,2)$$

$$H(2,1)\Psi_E(2,1) = E\Psi_E(2,1)$$

$$P\Psi_E(1,2) = \Psi_E(2,1)$$

$$H(1,2)\Psi_E(2,1) = E\Psi_E(2,1)$$

$$H(1,2)P\Psi_E(1,2) = EP\Psi_E(1,2)$$

$$H(1,2)P\Psi_E(1,2) = PE\Psi_E(1,2)$$

$$H(1,2)P\Psi_E(1,2) = PH\Psi_E(1,2)$$

$$HP = PH \Rightarrow [H, P] = 0$$

Permutation is conserved

$$[H, P] = 0$$

P and H have common eigenstates

$$P\Psi(1,2) = \lambda\Psi(1,2)$$

$$P^2\Psi(1,2) = \lambda P\Psi(1,2)$$

$$\Psi(1,2) = \lambda^2\Psi(1,2)$$

$$\lambda = \pm 1$$

Bosons

Fermions

Always we can separate a wavefunction into symmetric and asymmetric parts

For two particles we have

$$\Psi(1,2)=\frac{1}{2}\big(\Psi(1,2)+\Psi(2,1)\big)+\frac{1}{2}\big(\Psi(1,2)-\Psi(2,1)\big)$$

$$\Psi(1,2)=\frac{1}{2}\sqrt{2}\Psi^{(S)}(1,2)+\frac{1}{2}\sqrt{2}\Psi^{(A)}(1,2)$$

$$\Psi(1,2)=\frac{\sqrt{2}}{2}\left\{\Psi^{(S)}(1,2)+\Psi^{(A)}(1,2)\right\}$$

For three particles we can write

$$\Psi^{(S)}(1,2,3)=\frac{1}{\sqrt{6}}\left[\Psi(1,2,3)+\Psi(2,1,3)+\Psi(2,3,1)+\Psi(3,2,1)+\Psi(3,1,2)+\Psi(1,3,2)\right]$$

$$\Psi^{(A)}(1,2,3)=\frac{1}{\sqrt{6}}\left[\Psi(1,2,3)-\Psi(2,1,3)+\Psi(2,3,1)-\Psi(3,2,1)+\Psi(3,1,2)-\Psi(1,3,2)\right]$$

For non-interacting particles

$$\Psi^{(A)}(1,2) = \frac{1}{\sqrt{2}}\left[\Psi_{\varepsilon_1}(1)\Psi_{\varepsilon_2}(2) - \Psi_{\varepsilon_1}(2)\Psi_{\varepsilon_2}(1)\right]$$

$$\Psi^{(S)}(1,2) = \frac{1}{\sqrt{2}}\left[\Psi_{\varepsilon_1}(1)\Psi_{\varepsilon_2}(2) + \Psi_{\varepsilon_1}(2)\Psi_{\varepsilon_2}(1)\right]$$

$$\Psi^{(A)}(1,2,\ldots,N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \Psi_{\varepsilon_1}(1) & \Psi_{\varepsilon_1}(2) & \ldots & \Psi_{\varepsilon_1}(N) \\ \Psi_{\varepsilon_2}(1) & \Psi_{\varepsilon_2}(2) & \ldots & \Psi_{\varepsilon_2}(N) \\ \ldots & \ldots & \ldots & \ldots \\ \Psi_{\varepsilon_N}(1) & \Psi_{\varepsilon_N}(2) & & \Psi_{\varepsilon_N}(N) \end{vmatrix}_{N\times N}$$


$$\Psi^{(A)}(1,2,\ldots,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \Psi_{\varepsilon_1}(1) & \Psi_{\varepsilon_1}(2) & \ldots & \Psi_{\varepsilon_1}(N) \\ \Psi_{\varepsilon_2}(1) & \Psi_{\varepsilon_2}(2) & \ldots & \Psi_{\varepsilon_2}(N) \\ \ldots & \ldots & \ldots & \ldots \\ \Psi_{\varepsilon_N}(1) & \Psi_{\varepsilon_N}(2) & & \Psi_{\varepsilon_N}(N) \end{vmatrix}_{N\times N}$$

$$= -\frac{1}{\sqrt{N!}} \begin{vmatrix} \Psi_{\varepsilon_1}(2) & \Psi_{\varepsilon_1}(1) & \ldots & \Psi_{\varepsilon_1}(N) \\ \Psi_{\varepsilon_2}(2) & \Psi_{\varepsilon_2}(1) & \ldots & \Psi_{\varepsilon_2}(N) \\ \ldots & \ldots & \ldots & \ldots \\ \Psi_{\varepsilon_N}(2) & \Psi_{\varepsilon_N}(1) & & \Psi_{\varepsilon_N}(N) \end{vmatrix}_{N\times N}$$

Antisymmetric property is satisfied.

$$\Psi^{(A)}(1,2,\ldots,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \Psi_{\varepsilon_1}(1) & \Psi_{\varepsilon_1}(2) & \ldots & \Psi_{\varepsilon_1}(N) \\ \Psi_{\varepsilon_2}(1) & \Psi_{\varepsilon_2}(2) & \ldots & \Psi_{\varepsilon_2}(N) \\ \ldots & \ldots & \ldots & \ldots \\ \Psi_{\varepsilon_N}(1) & \Psi_{\varepsilon_N}(2) & & \Psi_{\varepsilon_N}(N) \end{vmatrix}_{N\times N}$$

$$= \frac{1}{\sqrt{N!}} \begin{vmatrix} \Psi_{\varepsilon_1}(1) & \Psi_{\varepsilon_1}(2) & \ldots & \Psi_{\varepsilon_1}(N) \\ \Psi_{\varepsilon_1}(1) & \Psi_{\varepsilon_1}(2) & \ldots & \Psi_{\varepsilon_1}(N) \\ \ldots & \ldots & \ldots & \ldots \\ \Psi_{\varepsilon_N}(1) & \Psi_{\varepsilon_N}(2) & & \Psi_{\varepsilon_N}(N) \end{vmatrix}_{N\times N} = 0$$

Pauli's exclusion principle is also satisfied.

Regardless of spin in each state only one electron can be found

$$W_{\text{F.D.}}\{n_i\} = \begin{cases} 1 & \text{if} \quad \sum_i n_i^2 = N, \\ 0 & \text{if} \quad \sum_i n_i^2 > N. \end{cases} \qquad W_{\text{B.E.}}\{n_i\} = 1; \quad n_i = 0, 1, 2, \ldots.$$

$$W\{n_i\} = \frac{1}{\mathrm{n}_1\ !\mathrm{n}_2\ !\ldots\mathrm{n}_\mathrm{k}\ !} = \begin{cases} 1 \\ 0 \end{cases}$$

Therefore, this is why Gibbs correction yields correct answer:

$$\frac{1}{N\ !}\frac{N\ !}{1\ !1\ !1\ !0!0\ !\ldots1\ !} = 1$$

From now on instead of Slater's determinants we will use the following form just for simplicity:

$$\psi_S(\boldsymbol{q}) = \text{const.} \sum_P P\psi_{\text{Boltz}}(\boldsymbol{q})$$

$$\psi_A(\boldsymbol{q}) = \text{const.} \sum_P \delta_P P\psi_{\text{Boltz}}(\boldsymbol{q})$$

$$\delta_P = \begin{cases} +1 & \text{For even permutation P} \\ -1 & \text{For odd permutation P} \end{cases}$$

Or simply for both Bosons and Fermions we can use only one expression:

$$\psi_{\boldsymbol{K}}(1,\ldots,N) = (N!)^{-1/2} \sum_{P} \delta_P P \left\{ u_{\boldsymbol{k}_1}(1) \ldots u_{\boldsymbol{k}_N}(N) \right\}$$

$$\delta_P = \begin{cases} +1 \;\; \text{Bosons} \quad \text{(For even permutation P)} \\ +1 \;\; \text{Fermions (For even permutation P)} \\ -1 \;\; \text{Fermions (For odd permutation P)} \end{cases} \equiv (\pm)^{[P]}$$

The density matrix and the partition function of a system of free particles

Suppose that the given system, which is composed of N indistinguishable, non-interacting particles confined to a cubical box of volume V, is a member of a canonical ensemble characterized by the temperature parameter β. The *density matrix* of the system in the coordinate representation will be given by

$$\langle \boldsymbol{r}_1, \ldots, \boldsymbol{r}_N | \hat{\rho} | \boldsymbol{r}'_1, \ldots, \boldsymbol{r}'_N \rangle = \frac{1}{Q_N(\beta)} \langle \mathbf{r}_1, \ldots, \boldsymbol{r}_N | e^{-\beta \hat{H}} | \boldsymbol{r}'_1, \ldots, \boldsymbol{r}'_N \rangle$$

$$Q_N(\beta) = \mathrm{Tr}\,(e^{-\beta \hat{H}}) = \int \langle \boldsymbol{r}_1, \ldots, \boldsymbol{r}_N | e^{-\beta \hat{H}} | \boldsymbol{r}_1, \ldots, \boldsymbol{r}_N \rangle \, d^{3N} r$$

$$\langle 1, 2, \ldots, N | e^{-\beta H} | 1', 2', \ldots, N' \rangle = \sum_E \langle 1, 2, \ldots, N | E \rangle \langle E | e^{-\beta H} | E \rangle \langle E | 1', 2', \ldots, N' \rangle$$

$$= \sum_E e^{-\beta E} \left[\psi_E(1, \ldots, N) \psi_E^*(1', \ldots, N') \right]$$

Since the particles constituting the given system are non-interacting, we may express the eigenfunctions $\psi_E(1, \ldots, N)$ and the eigenvalues E in terms of the single-particle wave functions $u_i(m)$ and the single-particle energies ε_i. Moreover, we find it advisable to work with the wave vectors $\boldsymbol{k}_i$ rather than the energies ε_i; so we write

$$E = \frac{\hbar^2 K^2}{2m} = \frac{\hbar^2}{2m}(k_1^2 + k_2^2 + \cdots + k_N^2)$$

$$u_{\boldsymbol{k}}(\boldsymbol{r}) = V^{-1/2} \exp\{i(\boldsymbol{k} \cdot \boldsymbol{r})\},$$

$$\boldsymbol{k} = 2\pi V^{-1/3} \boldsymbol{n};$$

$$\psi_{\boldsymbol{K}}(1, \ldots, N) = (N!)^{-1/2} \sum_P \delta_P P \left\{ u_{\boldsymbol{k}_1}(1) \ldots u_{\boldsymbol{k}_N}(N) \right\}$$

$$\delta_P = (\pm 1)^{[P]}$$

$$\psi_K(1,\ldots,N) = (N!)^{-1/2} \sum_P \delta_P P \left\{ u_{k_1}(1) \ldots u_{k_N}(N) \right\}$$

Permutation P acts on particles:

$$\psi_K(1,\ldots,N) = (N!)^{-1/2} \sum_P \delta_P \left\{ u_{k_1}(P1) \ldots u_{k_N}(PN) \right\}$$

But due to symmetry we can rewrite:

$$= (N!)^{-1/2} \sum_P \delta_P \left\{ u_{Pk_1}(1) \ldots u_{Pk_N}(N) \right\}$$

$$\left\langle 1,2,...,N\left|e^{-\beta H}\right|1',2',...,N'\right\rangle = \sum_E e^{-\beta E}\left[\psi_E(1,\ldots,N)\psi_E^*(1',\ldots,N')\right]$$

$$\langle 1,\ldots,N|e^{-\beta\hat{H}}|1',\ldots,N'\rangle = (N!)^{-1}\sum_K e^{-\beta\hbar^2K^2/2m}\times\left[\sum_P \delta_P\left\{u_{k_1}(P1)\ldots u_{k_N}(PN)\right\}\sum_{\tilde{P}}\delta_{\tilde{P}}\left\{u^*_{\tilde{P}k_1}(1')\ldots u^*_{\tilde{P}k_N}(N')\right\}\right]$$

where P and $\tilde{P}$ are any of the $N!$ possible permutations. Now, since a permutation among the k_i changes the wave function ψ at most by a sign, the quantity $[\psi\psi^*]$ in (11) is insensitive to such a permutation; the same holds for the exponential factor as well. The summation over $\boldsymbol{K}$ is, therefore, equivalent to $(1/N!)$ times a summation over all the vectors $\boldsymbol{k}_1,\ldots,\boldsymbol{k}_N$ *independently of one another*. Next, in view of the N-fold summation over the k_i, all the permutations $\tilde{P}$ will make equal contributions towards the sum (because they differ from one another only in the ordering of the k_i). Therefore, we may consider only one of these permutations, say the one for which $\tilde{P}\boldsymbol{k}_1 = \boldsymbol{k}_1,\ldots,\tilde{P}\boldsymbol{k}_N = \boldsymbol{k}_N$ (and hence $\delta_{\tilde{P}} = 1$ for both kinds of statistics), and include a factor of $(N!)$ along. The net result is

$$\langle 1,\ldots,N|e^{-\beta\hat{H}}|1',\ldots,N'\rangle = (N!)^{-1}\sum_{k_1,\ldots,k_N} e^{-\beta\hbar^2(k_1^2+\cdots+k_N^2)/2m}\left[\sum_P \delta_P\left\{u_{k_1}(P1)u^*_{k_1}(1')\right\}\ldots\left\{u_{k_N}(PN)u^*_{k_N}(N')\right\}\right]$$

$$= \frac{1}{N!(2\pi)^{3N}}\sum_P \delta_P\left[\int e^{-\beta\hbar^2k_1^2/2m+i\boldsymbol{k}_1\cdot(P1-1')}\,d^3k_1\ldots\int e^{-\beta\hbar^2k_N^2/2m+i\boldsymbol{k}_N\cdot(PN-N')}\,d^3k_N\right]$$

$$\langle 1,\ldots,N|e^{-\beta\hat{H}}|1',\ldots,N'\rangle = \frac{1}{N!}\left(\frac{m}{2\pi\beta\hbar^2}\right)^{3N/2}\sum_P \delta_P[f(P1-1')\ldots f(PN-N')]$$

$$f(\boldsymbol{\xi}) = \exp\left(-\frac{m}{2\beta\hbar^2}\xi^2\right)$$

Here you may remember the procedure for a single particle:

$$\langle \boldsymbol{r}|e^{-\beta\hat{H}}|\boldsymbol{r}'\rangle = \frac{1}{L^3}\sum_{\boldsymbol{k}} \exp\left[-\frac{\beta\hbar^2}{2m}k^2 + i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')\right]$$

1/V

$$\approx \frac{1}{(2\pi)^3}\int \exp\left[-\frac{\beta\hbar^2}{2m}k^2 + i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')\right] d^3k$$

$$= \left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2} \exp\left[-\frac{m}{2\beta\hbar^2}|\boldsymbol{r}-\boldsymbol{r}'|^2\right];$$

$$\mathrm{Tr}\left(e^{-\beta\hat{H}}\right) = \int \langle \boldsymbol{r}|e^{-\beta\hat{H}}|\boldsymbol{r}\rangle\, d^3r$$

$$= V\left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2}.$$

Introducing the *mean thermal wavelength*

$$\lambda = \frac{h}{(2\pi mkT)^{1/2}} = \hbar \left(\frac{2\pi\beta}{m} \right)^{1/2}$$

$$\langle \boldsymbol{r}_1, \ldots, \boldsymbol{r}_N | e^{-\beta \hat{H}} | \boldsymbol{r}_1, \ldots, \boldsymbol{r}_N \rangle = \frac{1}{N! \lambda^{3N}} \sum_P \delta_P [f(P\boldsymbol{r}_1 - \boldsymbol{r}_1) \ldots f(P\boldsymbol{r}_N - \boldsymbol{r}_N)]$$

$$f(\boldsymbol{r}) = \exp(-\pi r^2/\lambda^2)$$

$$\sum_P = 1 \pm \sum_{i<j} f_{ij} f_{ji} + \sum_{i<j<k} f_{ij} f_{jk} f_{ki} \pm \cdots$$

where $f_{ij} \equiv f(\boldsymbol{r}_i - \boldsymbol{r}_j)$; again note that the upper (lower) signs in this expansion pertain to a system of bosons (fermions). Now, the function f_{ij} vanishes rapidly as the distance r_{ij} becomes much larger than the mean thermal wavelength λ.

It follows that if the mean interparticle distance, $(V/N)^{1/3}$, in the system is much larger than the mean thermal wavelength, i.e. if

$$\frac{nh^3}{(2\pi mkT)^{3/2}} \ll 1$$

Then we may use the following approximation

$$\sum_P = 1 \pm \sum_{i<j} f_{ij} f_{ji} + \sum_{i<j<k} f_{ij} f_{jk} f_{ki} \pm \cdots \approx 1$$

Accordingly, the partition function of the system becomes:

$$Q_N(V, T) \equiv \mathrm{Tr}\,(e^{-\beta \hat{H}}) \approx \frac{1}{N!\lambda^{3N}} \int 1\,(d^{3N} r) = \frac{1}{N!} \left(\frac{V}{\lambda^3}\right)^N$$

$$Q_N(V,T) \equiv \mathrm{Tr}\,(e^{-\beta\hat{H}}) \approx \frac{1}{N!\lambda^{3N}} \int 1\,(d^{3N}r) = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N$$

This is precisely the result obtained earlier for the classical ideal gas; see eqn. (3.5.9). Thus, we have obtained from our quantum-mechanical treatment the precise classical limit for the partition function $Q_N(V,T)$. Incidentally, we have achieved something more. Firstly, we have automatically recovered here the Gibbs correction factor $(1/N!)$ which was introduced into the classical treatment on an *ad hoc*, semi-empirical basis. We, of course, tried to understand its origin in terms of the inherent indistinguishability of the particles. Here, on the other hand, we see it coming in a very natural manner and its source indeed lies in the symmetrization of the wave functions of the system (which is ultimately related to the indistinguishability of the particles); cf. Problem 5.4. Secondly, we find here a formal justification for computing the number of microstates of a system corresponding to a given region of its phase space by dividing the volume of that region into cells of a "suitable" size and then counting instead the number of these cells. This correspondence becomes all the more transparent by noting that formula (21) is exactly equivalent to the classical expression

$$Q_N(V,T) = \frac{1}{N!}\int e^{-\beta(p_1^2+\cdots+p_N^2)/2m}\left(\frac{d^{3N}q\,d^{3N}p}{\omega_0}\right) \qquad \text{with } \omega_0 = h^{3N}$$

Thirdly, in deriving the classical limit we have also evolved a criterion which enables us to determine whether a given physical system can be treated classically; mathematically, this criterion is given by following condition:

$$\frac{nh^3}{(2\pi mkT)^{3/2}} \ll 1$$

Next, we note that, in the classical limit, the diagonal elements of the density matrix are given by

$$\langle \boldsymbol{r}_1, \ldots, \boldsymbol{r}_N | \hat{\rho} | \boldsymbol{r}_1, \ldots, \boldsymbol{r}_N \rangle \approx \left(\frac{1}{V}\right)^N \rightarrow \frac{1}{N!\lambda^{3N}}$$

which is simply a product of N factors, each equal to $(1/V)$. Recalling that for a single particle in a box of volume V, $\langle \mathbf{r} | \hat{\rho} | \boldsymbol{r} \rangle = (1/V)$, see eqn. (5.3.16), we infer that in the classical limit there is no spatial correlation among the various particles of the system.

In general, however, spatial correlations exist even if the particles are supposedly non-interacting; they arise from the symmetrization of the wave functions and their magnitude is quite significant if the interparticle distances in the system are comparable with the mean thermal wavelength of the particles. To see this more clearly, we consider the simplest relevant case, namely the one with $N = 2$. The sum $\sum_P$ is now exactly equal to $1 \pm [f(r_{12})]^2$. Accordingly,

$$\langle \boldsymbol{r}_1, \boldsymbol{r}_2 | e^{-\beta \hat{H}} | \boldsymbol{r}_1, \boldsymbol{r}_2 \rangle = \frac{1}{2\lambda^6} [1 \pm \exp(-2\pi r_{12}^2/\lambda^2)]$$

$$Q_2(V, T) = \frac{1}{2\lambda^6} \int\int [1 \pm \exp(-2\pi r_{12}^2/\lambda^2] \, d^3 r_1 \, d^3 r_2$$

$$= \frac{1}{2} \left(\frac{V}{\lambda^3} \right)^2 \left[1 \pm \frac{1}{V} \int_0^\infty \exp(-2\pi r^2/\lambda^2) \, 4\pi r^2 \, dr \right]$$

$$= \frac{1}{2} \left(\frac{V}{\lambda^3} \right)^2 \left[1 \pm \frac{1}{2^{3/2}} \left(\frac{\lambda^3}{V} \right) \right] \approx \frac{1}{2} \left(\frac{V}{\lambda^3} \right)^2 = 1$$

$$\langle \boldsymbol{r}_1, \boldsymbol{r}_2 | \hat{\rho} | \boldsymbol{r}_1, \boldsymbol{r}_2 \rangle \approx \frac{1}{V^2} [1 \pm \exp(-2\pi r_{12}^2/\lambda^2)]$$

$$\langle \boldsymbol{r}_1, \boldsymbol{r}_2 | \hat{\rho} | \boldsymbol{r}_1, \boldsymbol{r}_2 \rangle \approx \frac{1}{V^2}[1 \pm \exp(-2\pi r_{12}^2/\lambda^2)]$$

Deviation from classical treatment

Probability density 2 classical particles $\langle r_1, r_2 | \rho | r_1, r_2 \rangle = \frac{1}{V^2}$

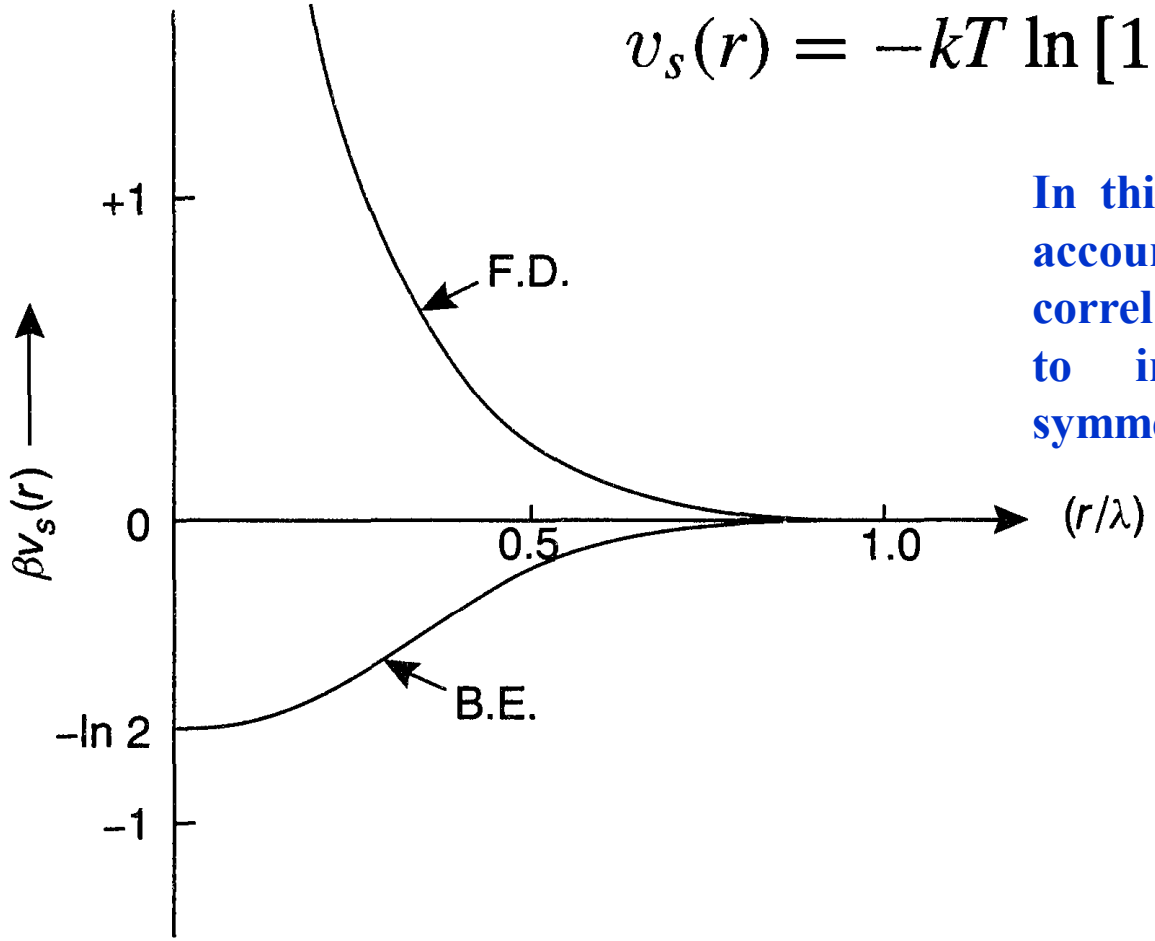
Probability density of Bosons $\langle r_1, r_2 | \rho | r_1, r_2 \rangle = \frac{1}{V^2}\left[1 + e^{-2\pi r_{12}^2}\right]$

Probability density of Fermions $\langle r_1, r_2 | \rho | r_1, r_2 \rangle = \frac{1}{V^2}\left[1 - e^{-2\pi r_{12}^2}\right]$

$$\left(\frac{1}{V^2}\left[1 + e^{-2\pi r_{12}^2}\right]\right)_{Bosons} > \left(\frac{1}{V^2}\right)_{Class.} > \left(\frac{1}{V^2}\left[1 - e^{-2\pi r_{12}^2}\right]\right)_{Fermions}$$

In conclusion, another way to treat quantum mechanically a system composed of bosons/Fermions is adding the following effective potential to the Hamiltonian and solve the problem classically:

$$v_s(r) = -kT \ln\left[1 \pm \exp\left(-2\pi r^2/\lambda^2\right)\right]$$



In this case correlation is taking into account. It should be noticed that this correlation is not due to spin. It is due to indistinguishability or existed symmetry in the wavefunctions.