CHAPTER 5

FORMULATION OF QUANTUM STATISTICS

THE scope of the ensemble theory developed in Chapters 2–4 is extremely general, though the applications considered so far were confined either to classical systems or to quantum-mechanical systems composed of *distinguishable* entities. When it comes to quantum-mechanical systems composed of *indistinguishable* entities, as most physical systems are, considerations of the preceding chapters have to be applied with care. One finds that in this case it is advisable to rewrite ensemble theory in a language that is more natural to a quantum-mechanical treatment, namely the language of the operators and the wave functions. Insofar as statistics are concerned, this rewriting of the theory may not seem to introduce any new physical ideas as such; nonetheless, it provides us with a tool which is highly suited for studying typical quantum systems. And once we set out to study these systems in detail, we encounter a stream of new, and altogether different, physical concepts. In particular, we find that the behavior of even a non-interacting system, such as the ideal gas, departs considerably from the pattern set by the classical treatment. In the presence of interactions, the pattern becomes even more complicated. Of course, in the limit of high temperatures and low densities, the behavior of all physical systems tends *asymptotically* to what we expect on classical grounds. In the process of demonstrating this point, we automatically obtain a criterion which tells us whether a given physical system may or may not be treated classically. At the same time, we obtain rigorous evidence in support of the procedure, employed in the previous chapters, for computing the number, Γ, of microstates (corresponding to a given macrostate) of a given system from the volume, ω, of the relevant region of its phase space, viz. $\Gamma \approx \omega/h^f$, where f is the number of "degrees of freedom" in the problem.

5.1. Quantum-mechanical ensemble theory: the density matrix

We consider an ensemble of $\mathcal{N}$ identical systems, where $\mathcal{N} \gg 1$. These systems are characterized by a (common) Hamiltonian, which may be denoted by the operator $\hat{H}$. At time t, the physical states of the various systems in the ensemble will be characterized by the wave functions $\psi(r_i, t)$, where r_i denote the position coordinates relevant to the system under study. Let $\psi^k(r_i, t)$ denote the (normalized) wave function characterizing the physical state in which the kth system of the

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ensemble hap_ .is to be at time t; naturally, $k = 1, 2, \ldots, \, . \, !$. The time variation of the function $\psi^k(t)$ will be determined by the Schrödinger equation[1]

$$\hat{H}\psi^k(t) = i\hbar\dot{\psi}^k(t).$$

(1)

Introducing a complete set of orthonormal functions ϕ_n, the wave functions $\psi^k(t)$ may be written as

$$\psi^k(t) = \sum_n a_n^k(t)\phi_n,$$

(2)

where

$$a_n^k(t) = \int \phi_n^* \psi^k(t)\,d\tau;$$

(3)

here, ϕ_n^* denotes the complex conjugate of ϕ_n while $d\tau$ denotes the volume element of the coordinate space of the given system. Clearly, the physical state of the kth system can be described equally well in terms of the coefficients $a_n^k(t)$. The time variation of these coefficients will be given by

$$i\hbar\dot{a}_n^k(t) = i\hbar \int \phi_n^* \dot{\psi}^k(t)\,d\tau = \int \phi_n^* \hat{H}\psi^k(t)\,d\tau$$

$$= \int \phi_n^* \hat{H} \left\{ \sum_m a_m^k(t)\phi_m \right\} d\tau$$

$$= \sum_m H_{nm}a_m^k(t),$$

(4)

where

$$H_{nm} = \int \phi_n^* \hat{H}\phi_m\,d\tau.$$

(5)

The physical significance of the coefficients $a_n^k(t)$ is evident from eqn. (2). They are the *probability amplitudes* for the various systems of the ensemble to be in the various states ϕ_n; to be practical, the number $|a_n^k(t)|^2$ represents the probability that a measurement at time t finds the kth system of the ensemble to be in the particular state ϕ_n. Clearly, we must have

$$\sum_n |a_n^k(t)|^2 = 1 \quad \text{(for all } k\text{).}$$

(6)

We now introduce the *density operator* $\hat{\rho}(t)$, as defined by the matrix elements

$$\rho_{mn}(t) = \frac{1}{. \, !} \sum_{k=1}^{. \, !} \{a_m^k(t)a_n^{k*}(t)\};$$

(7)

Clearly, the matrix element $\rho_{mn}(t)$ is the ensemble average of the quantity $a_m(t)a_n^*(t)$ which, as a rule, varies from member to member in the ensemble. In particular, the diagonal element $\rho_{nn}(t)$ is the ensemble average of the probability $|a_n(t)|^2$, the latter itself being a (quantum-mechanical) average. Thus, we encounter here a double-averaging process—once due to the probabilistic aspect of the wave functions and again due to the statistical aspect of the ensemble. The quantity $\rho_{nn}(t)$ now represents the probability that a system, chosen *at random* from the ensemble, at time t, is found to be in the state ϕ_n. In view of eqns (6) and (7).

$$\sum_n \rho_{nn} = 1.$$

(8)

We shall now determine the equation of motion for the density matrix $\rho_{mn}(t)$. We obtain, with the help of the foregoing equations,

$$i\hbar\dot{\rho}_{mn}(t) = \frac{1}{i\Gamma}\sum_{k=1}^{\cdot\Gamma}\left[i\hbar\left\{\dot{a}_m^k(t)a_n^{k*}(t) + a_m^k(t)\dot{a}_n^{k*}(t)\right\}\right]$$

$$= \frac{1}{i\Gamma}\sum_{k=1}^{\cdot\Gamma}\left[\left\{\sum_l H_{ml}a_l^k(t)\right\}a_n^{k*}(t) - a_m^k(t)\left\{\sum_l H_{nl}^* a_l^{k*}(t)\right\}\right]$$

$$= \sum_l\{H_{ml}\rho_{ln}(t) - \rho_{ml}(t)H_{ln}\}$$

$$= (\hat{H}\hat{\rho} - \hat{\rho}\hat{H})_{mn}; \tag{9}$$

here, use has been made of the fact that, in view of the Hermitian character of the operator $\hat{H}$, $H_{nl}^* = H_{ln}$. Using the commutator notation, eqn. (9) may be written as

$$i\hbar\dot{\hat{\rho}} = [\hat{H}, \hat{\rho}]_- \tag{10}$$

Equation (10) is the quantum-mechanical analogue of the classical equation (2.2.10) of Liouville. As expected in going from a classical equation of motion to its quantum-mechanical counterpart, the Poisson bracket $[\rho, H]$ has given place to the commutator $(\hat{\rho}\hat{H} - \hat{H}\hat{\rho})/i\hbar$.

If the given system is known to be in a state of equilibrium, the corresponding ensemble must be *stationary*, i.e. $\dot{\rho}_{mn} = 0$. Equations (9) and (10) then tell us that, for this to be the case, (i) the density operator $\hat{\rho}$ must be an explicit function of the Hamiltonian operator $\hat{H}$ (for then the two operators will necessarily commute) and (ii) the Hamiltonian must not depend explicitly on time, i.e., we must have (i) $\hat{\rho} = \hat{\rho}(\hat{H})$ and (ii) $\dot{\hat{H}} = 0$. Now, if the basis functions ϕ_n were the eigenfunctions of the Hamiltonian itself, then the matrices H and ρ would be diagonal:

$$H_{mn} = E_n\delta_{mn}, \quad \rho_{mn} = \rho_n\delta_{mn}. \tag{11}^2$$

The diagonal element ρ_n, being a measure of the probability that a system, chosen *at random* (and at *any* time) from the ensemble, is found to be in the eigenstate ϕ_n, will naturally depend upon the corresponding eigenvalue E_n of the Hamiltonian; the precise nature of this dependence is, however, determined by the "kind" of ensemble we wish to construct.

In any other representation, the density matrix may or may not be diagonal. However, quite generally, it will be symmetric:

$$\rho_{mn} = \rho_{nm}. \tag{13}$$

The physical reason for this symmetry is that, in statistical equilibrium, the tendency of a physical system to switch from one state (in the new representation) to another must be counterbalanced by an equally strong tendency to switch between the same states in the reverse direction. T' ʼ\ condition of *detailed balancing* is essential for the maintenance of an equʼ ɪum distribution within the ensemble.

Finally, we consider the expectation value of a physical quantity G, which is dynamically represented by an operator $\hat{G}$. This will be given by

$$\langle G \rangle = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} \int \psi^{k*} \hat{G} \psi^k \, d\tau.$$ (14)

In terms of the coefficients a_n^k,

$$\langle G \rangle = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} \left[\sum_{m,n} a_n^{k*} a_m^k G_{nm} \right],$$ (15)

where

$$G_{nm} = \int \phi_n^* \hat{G} \phi_m \, d\tau.$$ (16)

Introducing the density matrix ρ, eqn. (15) becomes

$$\langle G \rangle = \sum_{m,n} \rho_{mn} G_{nm} = \sum_m (\hat{\rho}\hat{G})_{mm} = \mathrm{Tr}\,(\hat{\rho}\hat{G}).$$ (17)

Taking $\hat{G} = \hat{1}$, where $\hat{1}$ is the unit operator, we have

$$\mathrm{Tr}\,(\hat{\rho}) = 1.$$ (18)

which is identical with (8). It should be noted here that if the original wave functions ψ^k were not normalized then the expectation value $\langle G \rangle$ would be given by the formula

$$\langle G \rangle = \frac{\mathrm{Tr}\,(\hat{\rho}\hat{G})}{\mathrm{Tr}\,(\hat{\rho})}$$ (19)

instead. In view of the mathematical structure of the formulae (17) and (19), the expectation value of any given physical quantity G is *manifestly* independent of the choice of the basis $\{\phi_n\}$, as it indeed should be.

5.2. Statistics of the various ensembles

A. The microcanonical ensemble

The construction of the microcanonical ensemble is based on the premise that the systems constituting the ensemble are characterized by a fixed number of particles N, a fixed volume V and an energy lying within the interval $(E - \frac{1}{2}\Delta, E + \frac{1}{2}\Delta)$, where $\Delta \ll E$. The total number of distinct microstates accessible to a system is then denoted by the symbol $\Gamma(N, V, E; \Delta)$ and, by assumption, any one of these microstates is as likely to occur as any other. This assumption enters into our theory in the nature of a postulate, and is often referred to as the postulate of *equal a priori probabilities* for the various accessible states. Accordingly, the density matrix   (which, in the energy representation, must be a diagonal matrix) will be of the   n

$$\rho_{mn} = \rho_n \delta_{mn}.$$ (1)

with

$$p_n = \begin{cases} 1/\Gamma & \text{for each of the accessible states,} \\ 0 & \text{for all other states;} \end{cases} \tag{2}$$

the normalization condition (5.1.18) is clearly satisfied. As we already know, the thermodynamics of the system is completely determined from the expression for its entropy which, in turn, is given by

$$S = k \ln \Gamma. \tag{3}$$

Since Γ, the total number of distinct, accessible states, is supposed to be computed quantum-mechanically, taking due account of the indistinguishability of the particles right from the beginning, no paradox, such as Gibbs', is now expected to arise. Moreover, if the quantum state of the system turns out to be unique ($\Gamma = 1$), the entropy of the system would identically vanish. This provides us with a sound theoretical basis for the hitherto empirical theorem of Nernst (also known as the *third law of thermodynamics*).

The situation corresponding to the case $\Gamma = 1$ is usually referred to as a *pure* case. In such a case, the construction of an ensemble is essentially superfluous, because every system in the ensemble has got to be in one and the same state. Accordingly, there is only one diagonal element p_{nn} which is nonzero (actually equal to unity), while all others are zero. The density matrix, therefore, satisfies the condition

$$\rho^2 = \rho. \tag{4}$$

In a different representation, the pure case will correspond to

$$\rho_{mn} = \frac{1}{\Gamma} \sum_{k=1}^{\prime} a_m^k a_n^{k*} = a_m a_n^* \tag{5}$$

because all values of k are now literally equivalent. We then have

$$\rho_{mn}^2 = \sum_l \rho_{ml} \rho_{ln} = \sum_l a_m a_l^* a_l a_n^*$$

$$= a_m a_n^* \quad \left(\text{because } \sum_l a_l^* a_l = 1 \right)$$

$$= \rho_{mn}. \tag{6}$$

Condition (4) thus holds in all representations.

A situation in which $\Gamma > 1$ is usually referred to as a *mixed* case. The density matrix, in the energy representation, is then given by eqns (1) and (2). If we now change over to any other representation, the general form of the density matrix should remain the same, namely (i) the off-diagonal elements should continue to be zero, while (ii) the diagonal elements (over the allowed range) should continue to be equal to one another. Now, had we constructed our ensemble on a representation other than the energy representation right from the beginning, how could we have possibly anticipated *ab initio* property (i) of the density matrix, though property (ii) could have been easily invoked through a postulate of *equal a priori probabilities*? To ensure that property (i), as well as property (ii), holds in *every* representation,

we must invoₐ yet another postulate, viz. the postulate of *random a priori phases* for the probability amplitudes a_n^k, which in turn implies that the wave function ψ^k, for all k, is an *incoherent* superposition of the basis $\{\phi_n\}$. As a consequence of this postulate, coupled with the postulate of equal *a priori* probabilities, we would have in any representation

$$\rho_{mn} \equiv \frac{1}{\Gamma} \sum_{k=1}^{\Gamma} a_m^k a_n^{k*} = \frac{1}{\Gamma} \sum_{k=1}^{\Gamma} |a|^2 e^{i(\theta_m^k - \theta_n^k)}$$

$$= c \langle e^{i(\theta_m^k - \theta_n^k)} \rangle$$

$$= c \delta_{mn}, \tag{7}$$

as it should be for a microcanonical ensemble.

Thus, contrary to what might have been expected on customary thought, to secure the physical situation corresponding to a microcanonical ensemble, we require in general two postulates instead of one! The second postulate arises solely from quantum-mechanics and is intended to ensure noninterference (and hence a complete absence of correlations) among the member systems; this, in turn, enables us to form a mental picture of each system, one at a time, completely disentangled from other systems in the ensemble.

B. The canonical ensemble

In this ensemble the macrostate of a member system is defined through the parameters N, V and T; the energy E is now a variable quantity. The probability that a system, chosen *at random* from the ensemble, possesses an energy E_r is determined by the Boltzmann factor $\exp(-\beta E_r)$, where $\beta = 1/kT$; see Secs 3.1 and 3.2. The density matrix in the energy representation is, therefore, taken as

$$\rho_{mn} = \rho_n \delta_{mn}, \tag{8}$$

with

$$\rho_n = C \exp(-\beta E_n); \quad n = 0, 1, 2, \ldots \tag{9}$$

The constant C is determined by the normalization condition (5.1.18), whence

$$C = \frac{1}{\sum_n \exp(-\beta E_n)} = \frac{1}{Q_N(\beta)}, \tag{10}$$

where $Q_N(\beta)$ is the *partition function* of the system. In view of eqn. (5.1.12). see Note 2 the density operator in this ensemble may be written as

$$\hat{\rho} = \sum_n |\phi_n\rangle \frac{1}{Q_N(\beta)} e^{-\beta E_n} \langle \phi_n|$$

$$= \frac{1}{Q_N(\beta)} e^{-\beta \hat{H}} \sum_n |\phi_n\rangle \langle \phi_n|$$

$$= \frac{1}{Q_N(\beta)} e^{-\beta \hat{H}} = \frac{e^{-\beta \hat{H}}}{\text{Tr}(e^{-\beta \hat{H}})}, \tag{11}$$

for the operator $\sum_n |\phi_n\rangle\langle\phi_n|$ is identically the unit operator. It is understood th the operator $\exp(-\beta\hat{H})$ in eqn. (11) stands for the sum

$$\sum_{j=0}^{\infty}(-1)^j\frac{(\beta\hat{H})^j}{j!}.$$ (1:

The expectation value $\langle G\rangle_N$ of a physical quantity G, which is represented by · operator $\hat{G}$, is now given by

$$\langle G\rangle_N = \mathrm{Tr}\,(\hat{\rho}\hat{G}) = \frac{1}{Q_N(\beta)}\,\mathrm{Tr}\,(\hat{G}e^{-\beta\hat{H}})$$

$$= \frac{\mathrm{Tr}\,(\hat{G}e^{-\beta\hat{H}})}{\mathrm{Tr}\,(e^{-\beta\hat{H}})};$$ (13

the suffix N here emphasizes the fact that the averaging is being done over · ensemble *with N fixed*.

C. The grand canonical ensemble

In this ensemble the density operator $\hat{\rho}$ operates on a Hilbert space with indefinite number of particles. The density operator must therefore commute n only with the Hamiltonian operator $\hat{H}$ but also with a number operator $\hat{n}$ who eigenvalues are $0, 1, 2, \ldots$. The precise form of the density operator can now be obtained by a straightforward generalization of the preceding case, with the res

$$\hat{\rho} \propto e^{-\beta\hat{H}-\alpha\hat{n}} = \frac{1}{\mathscr{Q}(\mu, V, T)}e^{-\beta(\hat{H}-\mu\hat{n})},$$ (1⊥

where

$$\mathscr{Q}(\mu, V, T) = \sum_{r,s}e^{-\beta(E_r-\mu N_s)} = \mathrm{Tr}\left\{e^{-\beta(\hat{H}-\mu\hat{n})}\right\}.$$ (1:

The ensemble average $\langle G\rangle$ is now given by

$$\langle G\rangle = \frac{1}{\mathscr{Q}(\mu, V, T)}\,\mathrm{Tr}\left(\hat{G}e^{-\beta\hat{H}}e^{\beta\mu\hat{n}}\right)$$

$$= \frac{\displaystyle\sum_{N=0}^{\infty}z^N\langle G\rangle_N Q_N(\beta)}{\displaystyle\sum_{N=0}^{\infty}z^N Q_N(\beta)},$$ (1

where $z\,(\equiv e^{\beta\mu})$ is the *fugacity* of the system while $\langle G\rangle_N$ is the canonical-ensem average, as given by eqn. (13). The quantity $\mathscr{Q}(\mu, V, T)$ appearing in th formulae is, clearly, the *grand partition function* of the system.

5.3. Examples

A. An electron in a magnetic field

Let us consider, for illustration, the case of a single electron which possesses an intrinsic spin $\frac{1}{2}\hbar\hat{\sigma}$ and a magnetic moment μ_B, where $\hat{\sigma}$ is the Pauli spin operator and $\mu_B = e\hbar/2mc$. The spin of the electron can have two possible orientations, ↑ or ↓, with respect to an applied magnetic field B. If the applied field is taken to be in the direction of the z-axis, the configurational Hamiltonian of the spin takes the form

$$\hat{H} = -\mu_B(\hat{\sigma} \cdot B) = -\mu_B B \hat{\sigma}_z. \tag{1}$$

In the representation that makes $\hat{\sigma}_z$ diagonal, namely

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{2}$$

the density matrix in the canonical ensemble would be

$$\langle \hat{\rho} \rangle = \frac{(e^{-\beta\hat{H}})}{\mathrm{Tr}\,(e^{-\beta\hat{H}})}$$

$$= \frac{1}{e^{\beta\mu_B B} + e^{-\beta\mu_B B}} \begin{pmatrix} e^{\beta\mu_B B} & 0 \\ 0 & e^{-\beta\mu_B B} \end{pmatrix} \tag{3}$$

We thus obtain for the expectation value σ_z

$$\langle \sigma_z \rangle = \mathrm{Tr}\,(\hat{\rho}\hat{\sigma}_z) = \frac{e^{\beta\mu_B B} - e^{-\beta\mu_B B}}{e^{\beta\mu_B B} + e^{-\beta\mu_B B}} = \tanh\,(\beta\mu_B B), \tag{4}$$

in agreement with the findings of Secs 3.9 and 3.10.

B. A free particle in a box

We now consider the case of a free particle, of mass m, in a cubical box of side L. The Hamiltonian of the particle is given by

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right), \tag{5}$$

while the eigenfunctions of the Hamiltonian, which satisfy periodic boundary conditions

$$\phi(x + L, y, z) = \phi(x, y + L, z) = \phi(x, y, z + L)$$

$$= \phi(x, y, z), \tag{6}$$

are given by

$$\phi_E(r) = \frac{1}{L^{3/2}}\exp\,(i\mathbf{k} \cdot \mathbf{r}), \tag{7}$$

the corresponding eigenvalues E being

$$E = \frac{\hbar^2 k^2}{2m}, \tag{8}$$

with

$$k \equiv (k_x, k_y, k_z) = \frac{2\pi}{L}(n_x, n_y, n_z); \tag{9}$$

the quantum numbers n_x, n_y and n_z must be integers (positive, negative or zero). Symbolically, we may write for the wave vector k

$$k = \frac{2\pi}{L}n, \tag{10}$$

where n is a vector with integral components $0, \pm 1, \pm 2, \dots$.

We now proceed to evaluate the density matrix $(\hat{\rho})$ of this system in the canonical ensemble; we shall do so in the *coordinate* representation. In view of eqn. (5.2.11), we have

$$\langle r|e^{-\beta\hat{H}}|r'\rangle = \sum_E \langle r|E\rangle e^{-\beta E}\langle E|r'\rangle$$

$$= \sum_E e^{-\beta E}\phi_E(r)\phi_E^*(r'). \tag{11}$$

Substituting from (7) and making use of (8) and (10), we obtain

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

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

$$= \left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2}\exp\left[-\frac{m}{2\beta\hbar^2}|r - r'|^2\right]; \tag{12}$$

see eqns (B.41, 42). It follows that

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

$$= V\left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2}. \tag{13}$$

Expression (13) is indeed the partition function, $Q_1(\beta)$, of a single particle confined to a box of volume V; see eqn. (3.5.19). Combining (12) and (13), we obtain for the density matrix in the coordinate representation

$$\langle r|\hat{\rho}|r'\rangle = \frac{1}{V}\exp\left[-\frac{m}{2\beta\hbar^2}|r - r'|^2\right]. \tag{14}$$

As expected, the matrix $\rho_{r,r'}$ is symmetric between the states r and r'. Moreover, the diagonal element $\langle r|\rho|r\rangle$, which represents the *probability density* for the particle to be in the neighborhood of the point r, is independent of r; this means that, in the case of a single free particle, *all* positions within the box are equally likely to obtain. A nondiagonal element $\langle r|\rho|r'\rangle$, on the other hand, is a measure of the probability of "spontaneous transition" between the position coordinates r and r' and is therefore a measure of the relative "intensity" of the wave

packet (assoc. d with the particle) at a distance $|r - r'|$ from the centre of the packet. The spatial extent of the wave packet, which in turn is a measure of the uncertainty involved in locating the position of the particle, is clearly of order $\hbar/(mkT)^{1/2}$; the latter is also a measure of the *mean thermal wavelength* of the particle. The spatial spread found here is a purely quantum-mechanical effect; quite expectedly, it tends to vanish at high temperatures. In fact, as $\beta \to 0$, the behavior of the matrix element (14) approaches that of a delta function, which implies a return to the classical picture of a *point* particle.

Finally, we determine the expectation value of the Hamiltonian itself. From eqns (5) and (14), we obtain

$$
\langle H \rangle = \mathrm{Tr}\,(\hat{H}\hat{\rho}) = -\frac{\hbar^2}{2mV} \int \left\{ \nabla^2 \exp\left[-\frac{m}{2\beta\hbar^2}|r - r'|^2 \right] \right\}_{r=r'} d^3 r
$$

$$
= \frac{1}{2\beta V} \int \left\{ \left[3 - \frac{m}{\beta\hbar^2}|r - r'|^2 \right] \exp\left[-\frac{m}{2\beta\hbar^2}|r - r'|^2 \right] \right\}_{r=r'} d^3 r
$$

$$
= \frac{3}{2\beta} = \frac{3}{2}kT, \tag{15}
$$

which was indeed expected. Otherwise, too,

$$
\langle H \rangle = \frac{\mathrm{Tr}\,(\hat{H}e^{-\beta\hat{H}})}{\mathrm{Tr}\,(e^{-\beta\hat{H}})} = -\frac{\partial}{\partial\beta}\ln\mathrm{Tr}\,(e^{-\beta\hat{H}}) \tag{16}
$$

which, on combination with (13), leads to the same result.

C. A linear harmonic oscillator

Next, we consider the case of a linear harmonic oscillator, whose Hamiltonian is given by

$$
\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial q^2} + \frac{1}{2}m\omega^2 q^2, \tag{17}
$$

with eigenvalues

$$
E_n = \left(n + \tfrac{1}{2}\right)\hbar\omega; \quad n = 0, 1, 2, \ldots \tag{18}
$$

and eigenfunctions

$$
\phi_n(q) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{H_n(\xi)}{(2^n n!)^{1/2}} e^{-(1/2)\xi^2}, \tag{19}
$$

where

$$
\xi = \left(\frac{m\omega}{\hbar}\right)^{1/2} q \tag{20}
$$

and

$$
H_n(\xi) = (-1)^n e^{\xi^2} \left(\frac{d}{d\xi}\right)^n e^{-\xi^2}. \tag{21}
$$

The matrix elements of the operator exp $(-\beta\hat{H})$ in the q-representation are given by

$$\langle q|e^{-\beta\hat{H}}|q'\rangle = \sum_{n=0}^{\infty} e^{-\beta E_n}\phi_n(q)\phi_n(q')$$

$$= \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} e^{-(1/2)(\xi^2+\xi'^2)}\sum_{n=0}^{\infty}\left\{e^{-(n+1/2)\beta\hbar\omega}\frac{H_n(\xi)H_n(\xi')}{2^n n!}\right\}. \quad (22$$

The summation over n is somewhat difficult to evaluate; nevertheless, the fin result is[3]

$$\langle q|e^{-\beta\hat{H}}|q'\rangle = \left[\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}\right]^{1/2}$$

$$\times \exp\left[-\frac{m\omega}{4\hbar}\left\{(q+q')^2\tanh\left(\frac{\beta\hbar\omega}{2}\right)+(q-q')^2\coth\left(\frac{\beta\hbar\omega}{2}\right)\right\}\right], \quad (23$$

whence

$$\text{Tr}\,(e^{-\beta\hat{H}}) = \int_{-\infty}^{\infty}\langle q|e^{-\beta\hat{H}}|q\rangle\,dq$$

$$= \left[\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}\right]^{1/2}\int_{-\infty}^{\infty}\exp\left[-\frac{m\omega q^2}{\hbar}\tanh\left(\frac{\beta\hbar\omega}{2}\right)\right]dq$$

$$= \frac{1}{2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)} = \frac{e^{-(1/2)\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}. \quad (24$$

Expression (24) is indeed the *partition function* of a linear harmonic oscillat see eqn. (3.8.14). At the same time, we find that the *probability density* for oscillator coordinate to be in the vicinity of the value q is given by

$$\langle q|\hat{\rho}|q\rangle = \left[\frac{m\omega\tanh\left(\frac{1}{2}\beta\hbar\omega\right)}{\pi\hbar}\right]^{1/2}\exp\left[-\frac{m\omega q^2}{\hbar}\tanh\left(\frac{\beta\hbar\omega}{2}\right)\right]; \quad (25$$

we note that this is a Gaussian distribution in q, with mean value zero and r. mean-square deviation

$$q_{\text{r.m.s.}} = \left[\frac{\hbar}{2m\omega\tanh\left(\frac{1}{2}\beta\hbar\omega\right)}\right]^{1/2} \qquad ($$

The probability distribution (25) was first derived by Bloch in 1932. In the c sical limit ($\beta\hbar\omega \ll 1$), the distribution becomes *purely thermal*—free from quan effects:

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

with dispersion $(kT/m\omega^2)^{1/2}$. At the other extreme $(\beta\hbar\omega \gg 1)$, the distribution becomes *purely quantum-mechanical* – free from thermal effects:

$$\langle q|\hat{\rho}|q\rangle \approx \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \exp\left[-\frac{m\omega q^2}{\hbar}\right]$$ (28)

with dispersion $(\hbar/2m\omega)^{1/2}$. Note that the limiting distribution (28) is precisely the one expected for an oscillator in its ground state $(n = 0)$, viz. one with probability density $\phi_0^2(q)$; see eqns (19)–(21).

In view of the fact that the mean energy of the oscillator is given by

$$\langle H \rangle = -\frac{\partial}{\partial\beta} \ln \mathrm{Tr}\,(e^{-\beta\hat{H}}) = \tfrac{1}{2}\hbar\omega \coth\left(\tfrac{1}{2}\beta\hbar\omega\right),$$ (29)

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

$$\langle q|\hat{\rho}|q\rangle = \left(\frac{m\omega^2}{2\pi\langle H\rangle}\right)^{1/2} \exp\left[-\frac{m\omega^2 q^2}{2\langle H\rangle}\right]$$ (30)

with

$$q_{\mathrm{r.m.s.}} = \left(\frac{\langle H\rangle}{m\omega^2}\right)^{1/2}$$ (31)

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

5.4. 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.

Now, the Hamiltonian of a system of N non-interacting particles is simply a sum of the individual single-particle Hamiltonians:

$$\hat{H}(q,p) = \sum_{i=1}^{N} \hat{H}_i(q_i, p_i);$$ (1)

here, (q_i, p_i) are the coordinates and momenta of the ith particle while $\hat{H}_i$ is its Hamiltonian.[4] Since the particles are identical, the Hamiltonians $\hat{H}_i (i = 1, 2, \ldots, N)$ are *formally* the same; they only differ in the values of their arguments. The time-independent Schrödinger equation for the system is

$$\hat{H}\psi_E(q) = E\psi_E(q),$$ (2)

where E is an eigenvalue of the Hamiltonian and $\psi_E(q)$ the corresponding eigenfunction. In view of (1), we can write a straightforward solution of the Schrödinger

equation, namely

$$\psi_E(q) = \prod_{i=1}^{N} u_{\varepsilon_i}(q_i),$$ (3)

with

$$E = \sum_{i=1}^{N} \varepsilon_i;$$ (4)

the factor $u_{\varepsilon_i}(q_i)$ in (3) is an eigenfunction of the single-particle Hamiltonian $\hat{H}_i(q_i, p_i)$, with eigenvalue ε_i:

$$\hat{H}_i u_{\varepsilon_i}(q_i) = \varepsilon_i u_{\varepsilon_i}(q_i).$$ (5)

Thus, a stationary state of the given system may be described in terms of the single-particle states of the constituent particles. In general, we may do so by specifying the set of numbers $\{n_i\}$ to represent a particular state of the system; this would imply that there are n_i particles in the eigenstate characterized by the energy value ε_i. Clearly, the distribution set $\{n_i\}$ must conform to the conditions

$$\sum_i n_i = N$$ (6)

and

$$\sum_i n_i \varepsilon_i = E.$$ (7)

Accordingly, the wave function of this state may be written as

$$\psi_E(q) = \prod_{m=1}^{n_1} u_1(m) \prod_{m=n_1+1}^{n_1+n_2} u_2(m) \ldots,$$ (8)

where the symbol $u_i(m)$ stands for the single-particle wave function $u_{\varepsilon_i}(q_m)$.

Now, suppose we effect a permutation among the coordinates appearing on the right-hand side of (8); as a result, the coordinates $(1, 2, \ldots, N)$ get replaced by $(P1, P2, \ldots, PN)$, say. The resulting wave function, which we shall call $P\psi_E(q)$, will be

$$P\psi_E(q) = \prod_{m=1}^{n_1} u_1(Pm) \prod_{m=n_1+1}^{n_1+n_2} u_2(Pm) \ldots.$$ (9)

In classical physics, where the particles of a given system, even though identical, are regarded as mutually *distinguishable*, any permutation that brings about an interchange of particles in two *different* single-particle states is recognized to have led to a *new, physically distinct* microstate of the system. For example, classical physics regards a microstate in which the so-called 5th particle is in the state u_i and the so-called 7th particle in the state $u_j (j \neq i)$ as distinct from a microstate in which the 7th particle is in the state u_i and the 5th in the state u_j. This leads to

$$\frac{N!}{n_1! n_2! \ldots}$$ (10)

(supposedly d: ct) microstates of the system, corresponding to a given mode of distribution $\{n_i\}$. The number (10) would then be ascribed as a "statistical weight factor" to the distribution set $\{n_i\}$. Of course, the "correction" applied by Gibbs, which has been discussed in Secs 1.5 and 1.6, reduces this weight factor to

$$W_c\{n_i\} = \frac{1}{n_1! n_2! \ldots}.$$ (11)

And the only way one could understand the physical basis of that "correction" was in terms of the inherent *indistinguishability* of the particles.

According to quantum physics, however, the situation remains unsatisfactory even after the Gibbs correction has been incorporated, for, strictly speaking, an interchange among identical particles, *even* if they are in different single-particle states, should not lead to a new microstate of the system! Thus, if we want to take into account the indistinguishability of the particles properly, we must not regard a microstate in which the "5th" particle is in the state u_i and the "7th" in the state u_j as distinct from a microstate in which the "7th" particle is in the state u_i and the "5th" in the state u_j (even if $i \neq j$), for the labeling of the particles as No. 1, No. 2, etc. (which one often resorts to) is at most a matter of convenience–it is not a matter of reality. In other words, all that matters in the description of a particular state of the given system is the set of numbers n_i which tell us "*how many* particles there are in the various single-particle states u_i"; the question "*which* particle is in *which* single-particle state" has no relevance at all. Accordingly, the microstates resulting from any permutation P among the N particles (so long as the numbers n_i remain the same) must be regarded as *one and the same* microstate. For the same reason, the weight factor associated with a distribution set $\{n_i\}$, provided that the set is not disallowed on some other physical grounds, should be identically equal to unity, whatever the values of the numbers n_i:

$$W_q\{n_i\} \equiv 1$$ (12)[5]

Indeed, if for some physical reason the set $\{n_i\}$ is disallowed, the weight factor W_q for that set should be identically equal to zero; see, for instance, eqn. (19).

At the same time, a wave function of the type (8), which we may call *Boltzmannian* and denote by the symbol $\psi_{\text{Boltz}}(q)$, is inappropriate for describing the state of a system composed of indistinguishable particles because an interchange of arguments among the factors u_i and u_j, where $i \neq j$, would lead to a wave function which is both mathematically and physically different from the one we started with. Now, since a mere interchange of the particle coordinates must not lead to a new microstate of the system, the wave function $\psi_E(q)$ must be constructed in such a way that, for all practical purposes, it is insensitive to any interchange among its arguments. The simplest way to do this is to set up a linear combination of all the $N!$ functions of the type (9) which obtain from (8) by all possible permutations among its arguments; of course, the combination must be such that if a permutation of coordinates is carried out in it, then the wave functions ψ and $P\psi$ must satisfy the property

$$|P\psi|^2 = |\psi|^2.$$ (13)

This leads to the following possibilities:

(i) $P\psi = \psi$ for all P,   (14)

which means that the wave function is symmetric in all its arguments, or

(ii) $P\psi = \begin{cases} +\psi & \text{if } P \text{ is an } even \text{ permutation,} \\ -\psi & \text{if } P \text{ is an } odd \text{ permutation,} \end{cases}$ $(15)^6$

which means that the wave function is *antisymmetric* in its arguments. We call these wave functions ψ_S and ψ_A, respectively; their mathematical structure is given by

$$\psi_S(q) = \text{const.} \sum_P P\psi_{\text{Boltz}}(q)$$ (16)

and

$$\psi_A(q) = \text{const.} \sum_P \delta_P P\psi_{\text{Boltz}}(q).$$ (17)

where δ_P in the expression for ψ_A is $+1$ or -1 according as the permutation P is even or odd.

We note that the function $\psi_A(q)$ can be written in the form of a *Slater determinant*:

$$\psi_A(q) = \text{const.} \begin{vmatrix} u_i(1) & u_i(2) & & u_i(N) \\ u_j(1) & u_j(2) & & u_j(N) \\ & & & \\ & & & \\ u_l(1) & u_l(2) & \ldots & u_l(N) \end{vmatrix},$$ (18)

where the leading diagonal is precisely the Boltzmannian wave function while the other terms of the expansion are the various permutations thereof; positive and negative signs in the combination (17) appear automatically as we expand the determinant. On interchanging a pair of arguments (which amounts to interchanging the corresponding columns of the determinant), the wave function ψ_A merely changes its sign, as it indeed should. However, if two or more particles happen to be in the same single-particle state, then the corresponding rows of the determinant become identical and the wave function vanishes.[7] Such a state is physically impossible to realize. We therefore conclude that if a system composed of indistinguishable particles is characterized by an antisymmetric wave function, then the particles of the system must all be in different single-particle states—a result equivalent to *Pauli's exclusion principle* for electrons. Conversely, a statistical system composed of particles obeying an exclusion principle must be described by a wave function which is antisymmetric in its arguments. The statistics governing the behavior of such particles is called *Fermi–Dirac*, or simply *Fermi*, statistics and the constituent particles themsel   are referred to as *fermions*. The statistical weight factor $W_{F.D.}\{n_i\}$ for such a sy⌐   ⌐ is unity so long as the n_i in the distribution set are either 0 or 1; otherwise, it is zero:

$$W_{\text{F D.}}\{n_i\} = \begin{cases} 1 & \text{if} \quad \sum_i n_i^2 = N, \\[2mm] 0 & \text{if} \quad \sum_i n_i^2 > N. \end{cases} \tag{19}^8$$

No such problems arise for systems characterized by symmetric wave functions; particular, we have no restriction whatsoever on the values of the numbers n_i. The statistics governing the behavior of such systems is called *Bose-Einstein*, or simply *Bose*, statistics and the constituent particles themselves are referred to as *sons*. The weight factor $W_{\text{B.E.}}\{n_i\}$ is identically equal to 1, whatever the values the numbers n_i:

$$W_{\text{B.E.}}\{n_i\} = 1; \quad n_i = 0.1, 2, \ldots \tag{20}$$

It should be pointed out here that there exists an intimate connection between e statistics governing a particular species of particles and the intrinsic spin of particles. For instance, particles with an integral spin (in units of $\hbar$, of course) ey Bose-Einstein statistics, while particles with a half-odd integral spin obey Fermi-Dirac statistics. Examples in the first category are photons, phonons, π-mesons, gravitons, He^4-atoms, etc., while those in the second category are electrons, nucleons (protons and neutrons), μ-mesons, neutrinos, He^3-atoms, etc.

Finally, it must be emphasized that, although we have derived our conclusions re on the basis of a study of non-interacting systems, the basic results hold for teracting systems as well. In general, the desired wave function $\psi(q)$ will not expressible in terms of the single-particle wave functions $u_i(q_m)$: nonetheless, will have to be either of the kind $\psi_S(q)$, satisfying eqn. (14), or of the kind $_A(q)$, satisfying eqn. (15).

5.5. The density matrix and the partition function of a system of free particles[9]

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

$$\langle r_1, \ldots, r_N | \hat{\rho} | r_1', \ldots r_N' \rangle = \frac{1}{Q_N(\beta)} \langle r_1, \ldots r_N | e^{-\beta \hat{H}} | r_1', \ldots, r_N' \rangle, \tag{1}$$

where $Q_N(\beta)$ is the *partition function* of the system:

$$Q_N(\beta) = \text{Tr}\,(e^{-\beta \hat{H}}) = \int \langle r_1, \ldots, r_N | e^{-\beta \hat{H}} | r_1, \ldots, r_N \rangle \, d^{3N} r. \tag{2}$$

For brevity, we denote the vector r_i by the letter i and the primed vector r_i' by i'. Further, let $\psi_E(1, \ldots, N)$ denote the eigenfunctions of the Hamiltonian, the suffix E representing the corresponding eigenvalues. We then have

$$\langle 1, \ldots, N | e^{-\beta \hat{H}} | 1', \ldots, N' \rangle = \sum_E e^{-\beta E} \left[\psi_E(1, \ldots, N) \psi_E^*(1', \ldots, N') \right], \tag{3}$$

here the summation goes over all possible values of E; cf. eqn. (5.3.11).

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 k_i rather than the energies ε_i; so we write

$$E = \frac{\hbar^2 K^2}{2m} = \frac{\hbar^2}{2m}(k_1^2 + k_2^2 + \cdots + k_N^2), \tag{4}$$

where the k_i on the right-hand side are the wave vectors of the individual particles. Imposing periodic boundary conditions, the *normalized* single-particle wave functions are

$$u_k(r) = V^{-1/2} \exp\{i(k \cdot r)\}, \tag{5}$$

with

$$k = 2\pi V^{-1/3} n; \tag{6}$$

here, n stands for a three-dimensional vector whose components can have values $0, \pm 1, \pm 2, \ldots$. The wave function ψ of the total system would then be, see eqns (5.4.16) and (5.4.17),

$$\psi_K(1, \ldots, N) = (N!)^{-1/2} \sum_P \delta_P P \left\{u_{k_1}(1) \ldots u_{k_N}(N)\right\}, \tag{7}$$

where the magnitudes of the individual k_i are such that

$$(k_1^2 + \cdots + k_N^2) = K^2. \tag{8}$$

The number δ_P in the expression for ψ_K is identically equal to $+1$ if the particles are bosons. For fermions, it is $+1$ or -1 according as the permutation P is even or odd. Thus, quite generally, we may write

$$\delta_P = (\pm 1)^{[P]}, \tag{9}$$

where $[P]$ denotes the order of the permutation; note that the upper sign in this expression holds for bosons while the lower sign holds for fermions. The factor $(N!)^{-1/2}$ has been introduced here to secure the normalization of the total wave function.

Now, it makes no difference to the wave function (7) whether the permutations P are carried out on the coordinates $1, \ldots, N$ or on the wave vectors $k_1, \ldots, k_N$, because after all we are going to sum over *all* the $N!$ permutations. Denoting the permuted coordinates by $P1, \ldots, PN$ and the permuted wave vectors by $Pk_1, \ldots, Pk_N$, eqn. (7) may be written as

$$\psi_K(1, \ldots, N) = (N!)^{-1/2} \sum_P \delta_P \left\{u_{k_1}(P1) \ldots u_{k_N}(PN)\right\} \tag{10a}$$

$$= (N!)^{-1/2} \sum_P \delta_P \left\{u_{Pk_1}(1) \ldots u_{Pk_N}(N)\right\}. \tag{10b}$$

Equations (10) may now be substituted into (3), with the result

$$\langle 1, \ldots, N | e^{-\beta \hat{H}} | 1', \ldots, N' \rangle = (N!)^{-1} \sum_K e^{-\beta \hbar^2 K^2 / 2m} \times$$

$$\times \left[\sum_P \delta_P \left\{ u_{k_1}(P1)\ldots u_{k_N}(PN) \right\} \sum_{\tilde{P}} \delta_{\tilde{P}} \left\{ u^*_{\tilde{P}k_1}(1')\ldots u^*_{\tilde{P}k_N}(N') \right\} \right], \quad (11)$$

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 K is, therefore, equivalent to $(1/N!)$ times a summation over all the vectors $k_1, \ldots, k_N$ *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 $\tilde{P}k_1 = k_1, \ldots, \tilde{P}k_N = k_N$ (and hence $\delta_{\tilde{p}} = 1$ for both kinds of statistics), and include a factor of $(N!)$ along. The net result is

$$\langle 1, \ldots, N | e^{-\beta \hat{H}} | 1', \ldots, N' \rangle = (N!)^{-1} \sum_{k_1,\ldots,k_N}$$

$$e^{-\beta \hbar^2 (k_1^2 + \cdots + k_N^2)/2m} \left[\sum_P \delta_P \left\{ u_{k_1}(P1)u^*_{k_1}(1') \right\} \ldots \left\{ u_{k_N}(PN)u^*_{k_N}(N') \right\} \right]. \quad (12)$$

Substituting from (5) and noting that, in view of the largeness of V, the summations over the k_i may be replaced by integrations, eqn. (12) becomes

$$\langle 1, \ldots, N | e^{-\beta \hat{H}} | 1', \ldots, N' \rangle$$

$$= \frac{1}{N!(2\pi)^{3N}} \sum_P \delta_P \left[\int e^{-\beta \hbar^2 k_1^2 /2m - ik_1 \cdot (P1-1')} d^3 k_1 \ldots \right.$$

$$\left. \int e^{-\beta \hbar^2 k_N^2 /2m + ik_N \cdot (PN-N')} d^3 k_N \right] \quad (13)$$

$$= \frac{1}{N!} \left(\frac{m}{2\pi\beta\hbar^2} \right)^{3N/2} \sum_P \delta_P [f(P1 - 1')\ldots f(PN - N')], \quad (14)$$

where

$$f(\xi) = \exp\left(-\frac{m}{2\beta\hbar^2} \xi^2 \right). \quad (15)$$

Here, use has been made of the mathematical result (5.3.12), which is clearly a special case of the present formula.

Introducing the *mean thermal wavelength*

$$\lambda = \frac{h}{(2\pi mkT)^{1/2}} = \hbar \left(\frac{2\pi\beta}{m} \right)^{1/2} \quad (16)$$

and rewriting our coordinates as $r_1, \ldots, r_N$, the diagonal elements among (14) take the form

$$\langle r_1, \ldots, r_N | e^{-\beta \hat{H}} | r_1, \ldots, r_N \rangle = \frac{1}{N!\lambda^{3N}} \sum_P \delta_P [f(Pr_1 - r_1)\ldots f(Pr_N - r_N)],$$

$$(17)$$

where

$$f(r) = \exp(-\pi r^2/\lambda^2).$$ (18

To obtain the partition function of the system, we have to integrate (17) over all the coordinates involved. However, before we do that, we would like to make some observations on the summation $\sum_P$. First of all, we note that the leading term in this summation, namely the one for which $Pr_i = r_i$, is identically equal to unity (because $f(0) = 1$). This is followed by a group of terms in which *only one* pair interchange (among the coordinates) has taken place; a typical term in this group will be $f(r_j - r_i)f(r_i - r_j)$ where $i \neq j$. This group of terms is followed by other groups of terms in which *more than one* pair interchanges have taken place. Thus, we may write

$$\sum_P = 1 \pm \sum_{i<j} f_{ij}f_{ji} + \sum_{i<j<k} f_{ij}f_{jk}f_{ki} \pm \cdots.$$ (19

where $f_{ij} \equiv f(r_i - r_j)$; 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

$$\frac{nh^3}{(2\pi mkT)^{3/2}} \ll 1.$$ (20

where n is the particle density in the system, then the sum $\sum_P$ in (19) may be approximated by unity. Accordingly, the partition function of the system becomes see eqn. (17).

$$Q_N(V.T) \equiv \text{Tr}(e^{-\beta\hat{H}}) \approx \frac{1}{N!\lambda^{3N}} \int 1 (d^{3N}r) = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N.$$ (21

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 treatme the precise classical limit for the partition function $Q_N(V,T)$. Incidentally, w have achieved something more. Firstly, we have automatically recovered here the Gibbs correction factor $(1/N!)$ which was introduced into the classical treatmen on an *ad hoc*, semi-empirical basis. We, of course, tried to understand its origi in terms of the inherent in ''−·' guishability of the particles. Here, on the oth 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 relate to the indistinguishability of the particles); cf. Problem 5.4. Secondly, we fin here a formal justification for computing the number of microstates of a syste— corresponding to a given region of its phase space by dividing the volume that region into cells of a "suitable" size and then counting instead the number these cells. This correspondence becomes all the more transparent by noting th formula (21) is exactly equivalent to the classical expression

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

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 condition (20). Now, in statistical mechanical studies, a system which cannot be treated classically is said to be *degenerate*; the quantity $(n\lambda^3)$ is, therefore, referred to as the *degeneracy discriminant*. Accordingly, the condition that classical considerations may be applicable to a given physical system is that "the value of the degeneracy discriminant of the system be much less than unity".

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

$$\langle r_1, \ldots, r_N | \hat{\rho} | r_1, \ldots, r_N \rangle \approx \left(\frac{1}{V}\right)^N, \tag{23}$$

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, $\langle r | \hat{\rho} | r \rangle = (1/V)$, 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,

$$\langle r_1, r_2 | e^{-\beta \hat{H}} | r_1, r_2 \rangle = \frac{1}{2\lambda^6}[1 \pm \exp(-2\pi r_{12}^2/\lambda^2)] \tag{24}$$

and hence

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

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

$$= \frac{1}{2}\left(\frac{V}{\lambda^3}\right)^2 \left[1 \pm \frac{1}{2^{3/2}}\left(\frac{\lambda^3}{V}\right)\right] \tag{25}$$

$$\approx \frac{1}{2}\left(\frac{V}{\lambda^3}\right)^2. \tag{26}$$

Combining (24) and (26), we obtain

$$\langle r_1, r_2 | \hat{\rho} | r_1, r_2 \rangle \approx \frac{1}{V^2}[1 \pm \exp(-2\pi r_{12}^2/\lambda^2)]. \tag{27}$$

Thus, if r_{12} is comparable to λ, the probability density (27) may differ considerably from the classical value $(1/V)^2$. In particular, the probability density for a pair of *bosons* to be a distance r apart is larger than the classical, r-independent value by a factor of $[1 + \exp(-2\pi r^2/\lambda^2)]$ which becomes as high as 2 as $r \to 0$. The corresponding result for a pair of *fermions* is smaller than the classical value by

a factor of $[1 - \exp(-2\pi r^2/\lambda^2)]$ which becomes ₁ow as 0 as $r \to 0$. Thus, we obtain a *positive* spatial correlation among particles obeying Bose statistics and a *negative* spatial correlation among particles obeying Fermi statistics; see also Sec. 6.3.
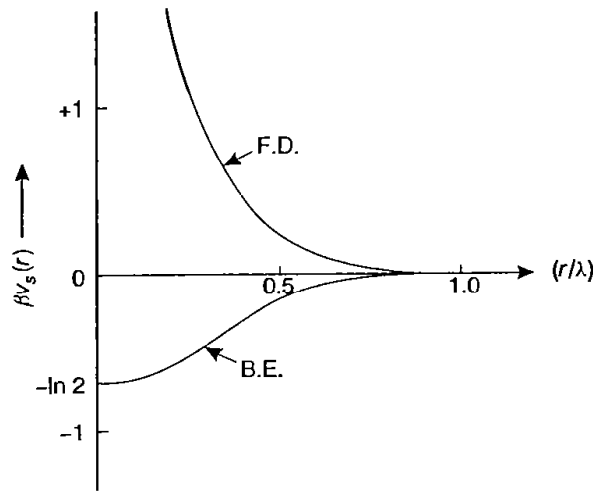

FIG. 5.1. The statistical potential $v_s(r)$ between a pair of particles obeying Bose–Einstein statistics or Fermi–Dirac statistics.

Another way of expressing correlations (among otherwise non-interacting particles) is by introducing a *statistical* interparticle potential $v_s(r)$ and then treating the particles classically (Uhlenbeck and Gropper, 1932). The potential $v_s(r)$ must be such that the Boltzmann factor $\exp(-\beta v_s)$ is precisely equal to the pair distribution function [...] in (27), i.e.,

$$v_s(r) = -kT \ln[1 \pm \exp(-2\pi r^2/\lambda^2)]. \tag{28}$$

Figure 5.1 shows a plot of the statistical potential $v_s(r)$ for a pair of bosons or fermions. In the Bose case, the potential is throughout attractive, thus giving rise to a "statistical attraction" among bosons; in the Fermi case, it is throughout repulsive, giving rise to a "statistical repulsion" among fermions. In either case, the potential vanishes rapidly as r becomes larger than λ; accordingly, its influence becomes less important as the temperature of the system rises.

Problems

5.1. Evaluate the density matrix ρ_{mn} of an electron spin in the representation which makes $\hat{\sigma}_x$ diagonal. Next, show that the value of $\langle \sigma_z \rangle$, resulting from this representation, is precisely the same as the one obtained in Sec. 5.3.

Hint: The representation needed here follows from the one used in Sec. 5.3 by carrying out a transformation with the help of the unitary operator

$$\hat{U} = \begin{pmatrix} 1/\sqrt{2} & 1/\sqrt{2} \\ -1/\sqrt{2} & 1/\sqrt{2} \end{pmatrix}.$$

5.2. Prove that

$$\langle q|e^{-\beta\hat{H}}|q'\rangle \equiv \exp\left[-\beta\hat{H}\left(-i\hbar\frac{\partial}{\partial q}, q\right)\right]\delta(q - q').$$

where $\hat{H}(-i\hbar\,\partial/\partial q, q)$ is the Hamiltonian of the system, in the q-representation, which formally operates upon the Dirac delta function $\delta(q - q')$. Writing the δ-function in a suitable form. apply this result to (i) a free particle and (ii) a linear harmonic oscillator.

5.3. Derive the density matrix ρ for (i) a free particle and (ii) a linear harmonic oscillator in the *momentum* representation and study its main properties along the lines of Sec. 5.3.

5.4. Study the density matrix and the partition function of a system of free particles, using the *unsymmetrized* wave function (5.4.3) instead of the *symmetrized* wave function (5.5.7). Show that, following this procedure, one obtains neither the Gibbs' correction factor $(1/N!)$ nor a spatial correlation among the particles.

5.5. Show that in the *first* approximation the partition function of a system of N non-interacting, indistinguishable particles is given by

$$Q_N(V, T) = \frac{1}{N!\,\lambda^{3N}} Z_N(V, T),$$

where

$$Z_N(V, T) = \int \exp\left\{-\beta \sum_{i<j} v_s(r_{ij})\right\} d^{3N}r.$$

$v_s(r)$ being the statistical potential (5.5.28). Hence evaluate the *first-order* correction to the equation of state of this system.

5.6. Determine the values of the degeneracy discriminant $(n\lambda^3)$ for hydrogen, helium and oxygen at N.T.P. Make an estimate of the respective temperature ranges where the magnitude of this quantity becomes comparable to unity and hence quantum effects become important.

5.7. Show that the quantum-mechanical partition function of a system of N *interacting* particles approaches the classical form

$$Q_N(V, T) = \frac{1}{N!\,h^{3N}} \int e^{-\beta E(q,p)} (d^{3N}q\, d^{3N}p)$$

as the mean thermal wavelength λ becomes much smaller than (i) the mean interparticle distance $(V/N)^{1/3}$ and (ii) a characteristic length r_0 of the interparticle potential.[10]

5.8. Prove the following theorem due to Peierls.[11]

"If $\hat{H}$ is the hermitian Hamiltonian operator of a given physical system and $\{\phi_n\}$ an arbitrary orthonormal set of wave functions satisfying the symmetry requirements and the boundary conditions of the problem, then the partition function of the system satisfies the following inequality:

$$Q(\beta) \geq \sum_n \exp\left\{-\beta\langle\phi_n|\hat{H}|\phi_n\rangle\right\};$$

the equality holds when $\{\phi_n\}$ is a complete orthonormal set of eigenfunctions of the Hamiltonian itself."

Notes

[1] For simplicity of notation, we suppress the coordinates r_i in the argument of the wave function ψ^k.

[2] It may be noted that in this (so-called energy) representation the density operator $\hat{\rho}$ may be written as

$$\hat{\rho} = \sum_n |\phi_n\rangle \rho_n \langle\phi_n|, \tag{12}$$

for then

$$\rho_{kl} = \sum_n \langle\phi_k|\phi_n\rangle \rho_n \langle\phi_n|\phi_l\rangle = \sum_n \delta_{kn}\rho_n\delta_{nl} = \rho_k\delta_{kl}.$$

[3] The mathematical details of this derivation can be found in Knbo (1965), pp. 175-7.

[4] We are studying here a single-component system composed of "spinless" particles. Generalization to a system composed of particles with spin and to a system composed of two or more components is quite straightforward.

[5] It may be mentioned here that as early as in 1905 Ehrenfest pointed out that to obtain Planck's formula for the black-body radiation one must assign equal *a priori* probabilities to the various states $\{n_i\}$.

[6] An even (odd) permutation is one which can be arrived at from the original order by an even (odd) number of "pair interchanges" among the arguments. For example, of the six permutations

$$(1,2,3), \quad (2,3,1), \quad (3,1,2), \quad (1,3,2), \quad (3,2,1) \quad \text{and} \quad (2,1,3),$$

of the arguments 1, 2 and 3, the first three are *even* permutations while the last three are *odd*. A single interchange, among any two arguments, is clearly an *odd* permutation.

[7] This is directly related to the fact that if we effect an interchange of two particles in the *same* single-particle state, then $P\psi_A$ will obviously be identical with ψ_A. At the same time, if we also have: $P\psi_A = -\psi_A$, then ψ_A must be identically zero.

[8] Note that the condition $\sum_i n_i^2 = N$ necessarily implies that all n_i are either 0 or 1. On the other hand, if any of the n_i are greater than 1, the sum $\sum_i n_i^2$ is necessarily greater than N.

[9] For a general survey of the density matrix and its applications, see ter Haar (1961).

[10] See Huang (1963), Sec. 10.2.

[11] R. E. Peierls (1938), *Phys. Rev.* 54, 918. See also Huang (1963), Sec. 10.3.