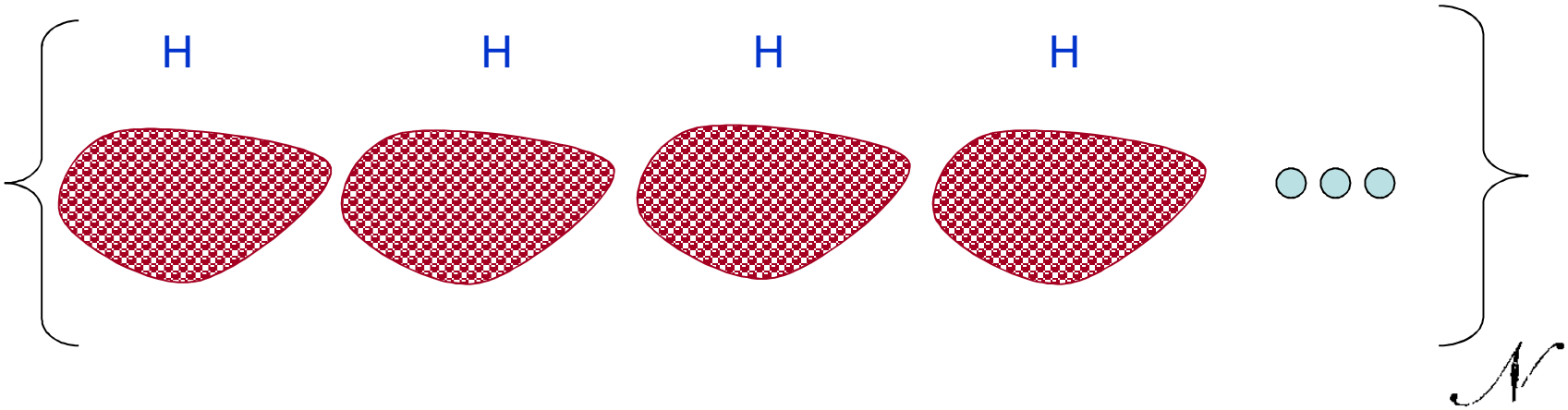
FORMULATION OF QUANTUM STATISTICS

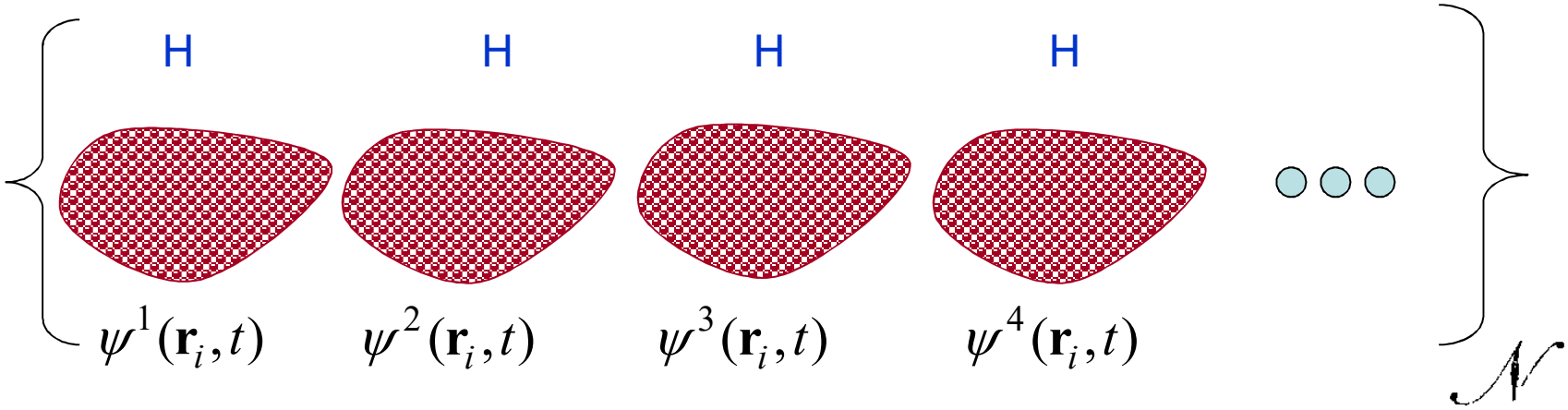
THE scope of the ensemble theory developed in Chapters 2–4 is extremely general, though the applications considered so far were confined either to classical systems or to quantum-mechanical systems composed of *distinguishable* entities. When it comes to quantum-mechanical systems composed of *indistinguishable* 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.

Quantum-mechanical ensemble theory: the density matrix

We consider an ensemble of N identical systems, where N>>1. These systems are characterized by a (common) Hamiltonian, which may be denoted by the operator H.



At time t, the physical states of the various systems in the ensemble will be characterized by the wave functions $\psi(\boldsymbol{r}_i, t)$, where r_i denote the position coordinates relevant to the system under study.



Let $\psi^k(\mathbf{r}_i,t)$ denote the (normalized) wave function characterizing the physical state in which the kth system of the ensemble happens to be at time t; naturally, k = 1, 2,..., $\mathcal{N}$.

$$H\psi^k(\mathbf{r}_i,t)=i\hbar\frac{\partial\psi^k(\mathbf{r}_i,t)}{\partial t}$$

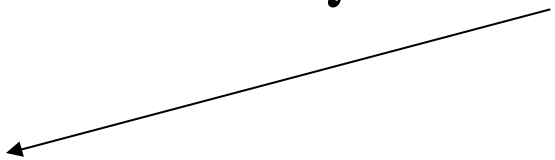
Which is identical with the Hamilton equations in classical ensemble theory

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

$$\psi^k(t)=\sum_n a_n^k(t)\varphi_n$$

$$a_n^k(t)=?$$

$$a_n^k(t)=\int\varphi_n^*\psi^k(t)d\tau$$



The volume element of the coordinate space of the given system

Obviously enough, the physical state of the kth system can be described equally well in terms of the coefficient $a_n^k(t)$

$$a_n^k(t) \equiv \psi^k(t)$$

The time variation of these coefficients will be given by

$$\dot{a}_n^k(t) = \int \varphi_n^* \dot{\psi}^k d\tau$$

$$= \frac{1}{i\hbar} \int \varphi_n^* H \psi^k(t) d\tau$$

$$= \frac{1}{i\hbar} \int \varphi_n^* H \sum_m a_m^k(t) \varphi_m d\tau$$

$$\psi^k(t) = \sum_n a_n^k(t) \varphi_n$$

$$i\hbar\dot{a}_n^k(t) = \sum_m \left\{ \left[\int \varphi_n^* H \varphi_m d\tau \right] a_m^k(t) \right\}$$

$$H_{nm} = \int \varphi_n^* H \varphi_m d\tau \qquad = \sum_m H_{nm} a_m^k(t)$$

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

$$\sum_n \left| a_n^k(t) \right|^2 = 1 \qquad \text{(for all k)}$$

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

$$\rho_{mn}(t) = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} \left\{ a_m^k(t) a_n^{k*}(t) \right\}$$

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),

$$\rho_{nn}(t) = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} \left| a_n^k(t) \right|^2 \qquad \sum_n \rho_{nn}(t) = \frac{1}{\mathcal{N}} \sum_n \sum_{k=1}^{\mathcal{N}} \left| a_n^k(t) \right|^2$$

$$\sum_n \rho_{nn}(t) = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} \sum_n \left| a_n^k(t) \right|^2 = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} 1 = \frac{1}{\mathcal{N}} \mathcal{N} = 1$$

$$\sum_n \rho_{nn}(t) = 1$$

We had stated that: $a_n^k(t) \equiv \psi^k(t)$

$$\left\{ H\psi^k(t) = i\hbar\dot{\psi}^k(t) \right\} \equiv \left\{ i\hbar\dot{a}_n^k(t) = \sum_m H_{nm} a_m^k(t) \right\}$$

Now we are going to state that:

$$\rho_{mn}(t) \equiv a_n^k(t) \equiv \psi^k(t)$$

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

$$\rho_{mn}(t) = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} \left\{ a_m^k(t) a_n^{k*}(t) \right\}$$

$$i\hbar\rho_{mn}(t) = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} i\hbar \left\{ a_m^k(t) a_n^{k*}(t) \right\}$$

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

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

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

$$i\hbar\dot{a}_n^k(t) = \sum_m H_{nm}a_m^k(t)$$

$$i\hbar\dot{\rho}_{mn}(t) = \frac{1}{\mathcal{N}}\sum_{k=1}^{\mathcal{N}}\sum_l H_{ml}a_l^k(t)\left\{a_n^{k*}(t)\right\} - \frac{1}{\mathcal{N}}\sum_{k=1}^{\mathcal{N}} a_m^k(t)\left\{\sum_l H_{nl}^* a_l^{k*}(t)\right\}$$

$$i\hbar\dot{\rho}_{mn}(t) = \frac{1}{\mathcal{N}}\sum_{k=1}^{\mathcal{N}}\sum_l H_{ml}\left\{a_l^k(t)a_n^{k*}(t)\right\} - \frac{1}{\mathcal{N}}\sum_{k=1}^{\mathcal{N}}\sum_l H_{l\,\mathrm{n}}\left\{a_m^k(t)a_l^{k*}(t)\right\}$$

$$i\hbar\dot{\rho}_{mn}(t) = \sum_l H_{ml}\left\{\frac{1}{\mathcal{N}}\sum_{k=1}^{\mathcal{N}}\left\{a_l^k(t)a_n^{k*}(t)\right\}\right\} - \sum_l H_{l\,\mathrm{n}}\left\{\frac{1}{\mathcal{N}}\sum_{k=1}^{\mathcal{N}}\left\{a_m^k(t)a_l^{k*}(t)\right\}\right\}$$

$$i\hbar\dot{\rho}_{mn}(t)=\sum_l H_{ml}\left\{\frac{1}{\mathcal{N}}\sum_{k=1}^{\mathcal{N}}\left\{a_l^k(t)a_n^{k*}(t)\right\}\right\}-\sum_l H_{l\,\mathrm{n}}\left\{\frac{1}{\mathcal{N}}\sum_{k=1}^{\mathcal{N}}\left\{a_m^k(t)a_l^{k*}(t)\right\}\right\}$$

$$\rho_{mn}(t)=\frac{1}{\mathcal{N}}\sum_{k=1}^{\mathcal{N}}\left\{a_m^k(t)a_n^{k*}(t)\right\}$$

$$i\hbar\dot{\rho}_{mn}(t)=\sum_l H_{ml}\rho_{l\,\mathrm{n}}(t)-\sum_l H_{l\,\mathrm{n}}\rho_{ml}(t)$$

$$i\hbar\dot{\rho}_{mn}(t)=\sum_l H_{ml}\rho_{l\,\mathrm{n}}(t)-\sum_l \rho_{ml}(t)H_{l\,\mathrm{n}}$$

$$i\hbar\dot{\rho}_{mn}(t)=\sum_l\left(H_{ml}\rho_{l\,\mathrm{n}}(t)-\rho_{ml}(t)H_{l\,\mathrm{n}}\right)$$

$$i\hbar\dot{\rho}_{mn}(t)=\left(H\rho-\rho H\right)_{mn}$$

$$i\hbar\dot{\rho}_{mn}(t)=\left[H,\rho\right]$$

$$i\hbar\dot{\rho}_{mn}(t) = \left[H, \rho\right]$$

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:

$$\text{i) } \rho = \rho(H) \rightarrow \quad [\rho, H] = [\rho(H), H] = 0 \quad \longrightarrow i\hbar\dot{\rho}_{mn}(t) = 0$$ ☺

$$\text{ii) } \dot{H} = 0 \rightarrow \quad H \neq H(t) \rightarrow \; V \neq V(t) \rightarrow \; \psi(t) = \varphi(r)e^{-iEt/\hbar} \rightarrow$$

$$a \neq a(t) \rightarrow \; \dot{a}_n^k = 0 \;\&\; \dot{a}_n^{k*} = 0 \rightarrow \; i\hbar\dot{\rho}_{mn}(t) = 0$$ ☺

Now, if the basis functions φ_n were the eigenfunctions of the Hamiltonian itself, then the matrices H and ρ would be diagonal:

$$H_{mn} = H_n \delta_{mn} \qquad \rho_{mn} = \rho_n \delta_{mn}$$

Why?

$$\dot{\rho} = 0 \rightarrow \ [\rho, H] = 0 \,\&\, H\varphi_n = E\varphi_n \rightarrow \ \rho\varphi_n = \rho_n \varphi_n \rightarrow$$

$$\langle \varphi_m | \rho | \varphi_n \rangle = \rho_n \langle \varphi_m | \varphi_n \rangle \rightarrow \rho_{mn} = \rho_n \delta_{mn}$$ ☺

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. This condition of *detailed balancing* is essential for the maintenance of an equilibrium 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

$$\langle G \rangle = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} \int \psi^{k*} G \psi^{k} d\tau$$

$$\langle G \rangle = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} \int \sum_{n} a_n^{k*}(t) \varphi_n^* G \sum_{m} a_m^{k}(t) \varphi_m d\tau$$

$$\langle G \rangle = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} \sum_{n,m} a_m^{k}(t) a_n^{k*}(t) \int \varphi_n^* G \varphi_m d\tau$$

$$G_{nm} = \int \varphi_n^* G \varphi_m d\tau$$

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

$$\rho_{mn}(t) = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} \left\{ a_m^{k}(t) a_n^{k*}(t) \right\}$$

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

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

$$\langle G \rangle = \sum_{n,m} \rho_{nm} G_{nm}$$

$$\langle G \rangle = \sum_{n,m} \rho_n \delta_{mn} G_{nm}$$

$$\langle G \rangle = \sum_{m} \rho_{mm} G_{mm}$$

$$\langle G \rangle = \sum_{m} (\rho G)_{mm}$$

$$\langle G \rangle = Tr(\rho G)$$

$$\langle G \rangle = Tr(\rho G)$$

$$G = I$$

$$\langle I \rangle = Tr(\rho I) = Tr(\rho)$$

$$\sum_n \rho_{nn}(t) = 1$$

$$\langle I \rangle = Tr(\rho) = 1$$

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

$$\langle G \rangle = \frac{Tr\left(\rho G\right)}{Tr\left(\rho\right)}$$

$$\langle G \rangle = \frac{Tr(\rho G)}{Tr(\rho)}$$

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.