geometrical interpretation is as follows. If we follow the motion of a representative point in Γ space, we find that the density of representative points in its neighborhood is constant. Hence the distribution of representative points moves in Γ space like an incompressible fluid.

The observed value of a dynamical quantity O of the system, which is generally a function of the coordinates and conjugate momenta, is supposed to be its averaged value taken over a suitably chosen ensemble:

$$\langle O \rangle = \frac{\int d^{3N}p\, d^{3N}q\, O(p,q)\rho(p,q,t)}{\int d^{3N}p\, d^{3N}q\, \rho(p,q,t)} \tag{3.42}$$

This is called the ensemble average of O. Its time dependence comes from that of ρ, which is governed by Liouville's theorem. In principle, then, this tells us how a quantity approaches equilibrium—the central question of kinetic theory. In the next section we shall derive the Boltzmann transport equation using this approach.

Under certain conditions one can prove an *ergodic theorem*, which says that if one waits a sufficiently long time, the locus of the representative point of a system will cover the entire accessible phase space. More precisely, it says that the representative point comes arbitrarily close to any point in the accessible phase space. This would indicate that the ensemble corresponding to thermodynamic equilibrium is one for which ρ is constant over the accessible phase space. This is actually what we shall assume.*

3.5 THE BBGKY HIERARCHY

One can define correlation functions f_s, which give the probability of finding s particles having specified positions and momenta, in the systems forming an ensemble. The function f_1 is the familiar distribution function. The exact equations of motion for f_s in classical mechanics can be written down. They show that to find f_1 we need to know f_2, which in turns depends on a knowledge of f_3, and so on till we come the full N-body correlation function f_N. This system of equations is known as the BBGKY† hierarchy. We shall derive it and show how the chain of equations can be truncated to yield the Boltzmann transport equation. The "derivation" will not be any more rigorous than the one already given, but it will give new insight into the nature of the approximations.

Consider an ensemble of systems, each being a gas of N molecules enclosed in volume V, with Hamiltonian $\mathscr{H}$. Instead of the general notation $\{p_i, q_i\}$

---

*See the remarks about the relevance of the ergodic theorem in Section 4.5.

†BBGKY stands for Bogoliubov-Born-Green-Kirkwood-Yvon. For a detailed discussion and references see N. N. Bogoliubov in *Studies in Statistical Mechanics*, J. de Boer and G. E. Uhlenbeck, Eds., Vol. I (North-Holland, Amsterdam, 1962).

($i = 1, \dots, 3N$), we shall denote the coordinates by the Cartesian vectors $\{\mathbf{p}_i, \mathbf{r}_i\}$ ($i = 1, \dots, N$), for which we use the abbreviation

$$z_i = (\mathbf{p}_i, \mathbf{r}_i), \qquad \int dz_i = \int d^3p_i\, d^3r_i \tag{3.43}$$

The density function characterizing the ensemble is denoted by $\rho(1, \dots, N, t)$, and assumed to be symmetric in $z_1, \dots, z_N$. Its integral over all phase space is a constant by Liouville's theorem; hence we can normalized it to unity:

$$\int dz_1 \cdots dz_N\, \rho(1, \dots, N, t) = 1 \tag{3.44}$$

Thus the ensemble average of any function $O(1, \dots, N)$ of molecular coordinates can be written as

$$\langle O \rangle \equiv \int dz_1 \cdots dz_N\, \rho(1, \dots, N, t) O(1, \dots, N) \tag{3.45}$$

Using the Hamiltonian equations of motion (3.38), we rewrite Liouville's theorem in the form

$$\frac{\partial \rho}{\partial t} = \sum_{i=1}^{N} \left(\nabla_{p_i} \rho \cdot \nabla_{r_i} \mathscr{H} - \nabla_{r_i} \rho \cdot \nabla_{p_i} \mathscr{H} \right) \tag{3.46}$$

Assume that the Hamiltonian is of the form

$$\begin{aligned} \mathscr{H} &= \sum_{i=1}^{N} \frac{\mathbf{p}^2}{2m} + \sum_{i=1}^{N} U_i + \sum_{i<j} v_{ij} \\ U_i &= U(\mathbf{r}_i) \\ v_{ij} &= v_{ji} = v(|\mathbf{r}_i - \mathbf{r}_j|) \end{aligned} \tag{3.47}$$

Then

$$\begin{aligned} \nabla_{p_i} \mathscr{H} &= \frac{\mathbf{p}_i}{m} \\ \nabla_{r_i} \mathscr{H} &= -\mathbf{F}_i - \sum_{\substack{j=1 \\ (j \neq i)}}^{N} \mathbf{K}_{ij} \end{aligned} \tag{3.48}$$

where

$$\begin{aligned} \mathbf{F}_i &= -\nabla_{r_i} U(\mathbf{r}_i) \\ \mathbf{K}_{ij} &= -\nabla_{r_i} v(|\mathbf{r}_i - \mathbf{r}_j|) \end{aligned} \tag{3.49}$$

Liouville's theorem can now be cast in the form

$$\left[\frac{\partial}{\partial t} + h_N(1, \dots, N) \right] \rho(1, \dots, N) = 0 \tag{3.50}$$

where

$$h_N(1,\ldots,N) = \sum_{i=1}^{N} S_i + \frac{1}{2}\sum_{\substack{i,j=1\\(i\neq j)}}^{N} P_{ij}$$

$$S_i \equiv \frac{\mathbf{p}_i}{m}\cdot\nabla_{r_i} + \mathbf{F}_i\cdot\nabla_{p_i} \tag{3.51}$$

$$P_{ij} \equiv \mathbf{K}_{ij}\cdot\nabla_{p_i} + \mathbf{K}_{ji}\cdot\nabla_{p_j} = \mathbf{K}_{ij}\cdot\left(\nabla_{p_i} - \nabla_{p_j}\right)$$

The single-particle distribution function is defined by

$$f_1(\mathbf{p},\mathbf{r},t) \equiv \left\langle \sum_{i=1}^{N} \delta^3(\mathbf{p}-\mathbf{p}_i)\delta^3(\mathbf{r}-\mathbf{r}_i)\right\rangle = N\int dz_2 \cdots dz_N\, \rho(1,\ldots,N,t) \tag{3.52}$$

The factor N in the last form comes from the fact that all terms in the sum in the preceding term have the same value, owing to the fact that ρ is symmetric in $z_1,\ldots,z_N$. Integrating f_1 over z_1 yields the correct normalization N, by virtue of (3.44).

The general s-particle distribution function, or correlation function, is defined by

$$f_s(1,\ldots,z,t) \equiv \frac{N!}{(N-s)!}\int dz_{s+1} \cdots dz_N\, \rho(1,\ldots,N,t) \qquad (s=1,\ldots,N) \tag{3.53}$$

The combinatorial factor in front comes from the fact that we do not care which particle is at z_1, which is at z_2, etc. The equation of motion is

$$\frac{\partial}{\partial t}f_s = \frac{N!}{(N-s)!}\int dz_{s+1} \cdots dz_N \frac{\partial}{\partial t}\rho = -\frac{N!}{(N-s)!}\int dz_{s+1} \cdots dz_N\, h_N\rho \tag{3.54}$$

We isolate those terms in h_N involving only the coordinates $z_1,\ldots,z_s$:

$$\begin{aligned} h_N(1,\ldots,N) &= \sum_{i=1}^{s} S_i + \sum_{s+1}^{N} S_i + \frac{1}{2}\sum_{\substack{i,j=1\\(i\neq j)}}^{s} P_{ij} + \frac{1}{2}\sum_{\substack{i,j=s+1\\(i\neq j)}}^{N} P_{ij} + \sum_{i=1}^{s}\sum_{j=s+1}^{N} P_{ij} \\ &= h_s(1,\ldots,s) + h_{N-s}(s+1,\ldots,N) + \sum_{i=1}^{s}\sum_{j=s+1}^{N} P_{ij} \end{aligned} \tag{3.55}$$

Note that

$$\int dz_{s+1} \cdots dz_N\, h_{N-s}(s+1,\ldots,N)\rho(1,\ldots,N) = 0 \tag{3.56}$$

because h_{N-s} consists of gradient terms in **p** with **p**-independent coefficients, and a gradient term in **r** with an **r**-independent coefficient. Thus the integral evaluates ρ on the boundary of phase space, where we assume ρ to vanish. Substituting (3.55) into (3.54), we obtain

$$\begin{aligned}\left(\frac{\partial}{\partial t}+h_s\right)f_s &= -\frac{N!}{(N-s)!}\int dz_{s+1}\cdots dz_N \sum_{i=1}^{s}\sum_{j=s+1}^{N} P_{ij}\rho(1,\dots,N)\\ &= -\sum_{i=1}^{s}\int dz_{s+1}P_{i,s+1}\frac{N!}{(N-s+1)!}\int dz_{s+2}\cdots dz_N\,\rho(1,\dots,N)\\ &= -\sum_{i=1}^{s}\int dz_{s+1}P_{i,s+1}f_{s+1}(1,\dots,s+1) \qquad (3.57)\end{aligned}$$

In passing from the first to the second equation we have used the fact that the sum over j gives $N-s$ identical terms. Now substitute P_{ij} from (3.51), and note that the second term there does not contribute, because it leads to a vanishing surface term. We then arrive at

$$\left(\frac{\partial}{\partial t}+h_s\right)f_s(1,\dots,s) = -\sum_{i=1}^{s}\int dz_{s+1}\mathbf{K}_{i,s+1}\cdot\nabla_{p_i}f_{s+1}(1,\dots,s+1)$$
$$(s=1,\dots,N) \qquad (3.58)$$

which is the BBGKY hierarchy. The left side of each of the equations above is a "streaming term," involving only the s particles under consideration. For $s>1$ it includes the effect of intermolecular scattering among the s particles. The right-hand side is the "collision integral," which describes the effect of scattering between the particles under consideration with an "outsider," thus coupling f_s to f_{s+1}.

The first two equations in the hierarchy read

$$\left(\frac{\partial}{\partial t}+\frac{\mathbf{p}_1}{m}\cdot\nabla_{r_1}+\mathbf{F}_1\cdot\nabla_{p_1}\right)f_1(z_1,t) = -\int dz_2\,\mathbf{K}_{12}\cdot\nabla_{p_1}f_2(z_1,z_2,t) \qquad (3.59)$$

$$\begin{aligned}&\left[\frac{\partial}{\partial t}+\frac{\mathbf{p}_1}{m}\cdot\nabla_{r_1}+\frac{\mathbf{p}_2}{m}\cdot\nabla_{r_2}+\mathbf{F}_1\cdot\nabla_{p_1}+\mathbf{F}_2\cdot\nabla_{p_2}+\tfrac{1}{2}\mathbf{K}_{12}\cdot\left(\nabla_{p_1}-\nabla_{p_2}\right)\right]\\ &\quad\times f_2(z_1,z_2,t)\\ &\quad= -\int dz_3\left(\mathbf{K}_{13}\cdot\nabla_{p_1}+\mathbf{K}_{23}\cdot\nabla_{p_2}\right)f_3(z_1,z_2,z_3,t) \qquad (3.60)\end{aligned}$$

The terms in the equations above have dimensions f_s/time, and different time scales are involved:

$$\begin{aligned}\mathbf{K}\cdot\nabla_p &\sim \frac{1}{\tau_c}\\ \mathbf{F}\cdot\nabla_p &\sim \frac{1}{\tau_e} \qquad (3.61)\\ \frac{\mathbf{p}}{m}\cdot\nabla_r &\sim \frac{1}{\tau_s}\end{aligned}$$

where τ_c is the duration of a collision, τ_e is the time for a molecule to traverse a characteristic distance over which the external potential varies significantly, and τ_s is the time for a molecule to traverse a characteristic distance over which the correlation function varies significantly. The time τ_c is the shortest, and τ_e the longest.

The equation for f_1 is unique in the hierarchy, in that "streaming" sets a rather slow time scale, for it does not involve intermolecular scattering, (there being only one particle present.) The collision integral, which has more rapid variations, sets the time scale of f_1. This is why the equilibrium condition is determined by the vanishing of the collision integral.

In contrast, the equation for f_2 (and higher ones as well) contains a collision term of the order $1/\tau_c$ on the left side. The collision integral on the right side is smaller by a factor of the order nr_0^3 (where n is the density, and r_0 the range of the intermolecular potential) because the integration of $\mathbf{r}_3$ extends only over a volume of radius r_0. Now $r_0 \approx 10^{-8}$ cm and $n \approx 10^{19}$ cm^{-3} under standard conditions. Hence $nr_0^3 \approx 10^{-5}$. Thus for f_2 (and higher equations too) the time scale is set by the streaming terms instead of the collision integral, which we shall neglect.

With neglect of the right side of (3.60), the hierarchy is truncated at f_2, and we have only two coupled equations for f_1 and f_2:

$$\left(\frac{\partial}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \nabla_{r_1}\right) f_1(z_1, t) = -\int_{r_0} dz_2 \, \mathbf{K}_{12} \cdot \nabla_{p_1} f_2(z_1, z_2, t) \equiv \left(\frac{\partial f_1}{\partial t}\right)_{\text{coll}} \tag{3.62}$$

$$\left[\frac{\partial}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \nabla_{r_1} + \frac{\mathbf{p}_2}{m} \cdot \nabla_{r_2} + \tfrac{1}{2}\mathbf{K}_{12} \cdot \left(\nabla_{p_1} - \nabla_{p_2}\right)\right] f_2(z_1, z_2, t) = 0 \tag{3.63}$$

where we have set all external forces to zero, for simplicity. We shall also assume for simplicity that the force $\mathbf{K}$ vanishes outside a range r_0. To remind us of this fact, we put the subscript r_0 on the integral in the first equation, indicating that the spatial part of the integral is subject to $|\mathbf{r}_1 - \mathbf{r}_2| < r_0$.

The salient qualitative features of (3.62) and (3.63) are that f_2 varies in time with characteristic period τ_c, and in space with characteristic distance r_0, while f_1 varies much less rapidly, by a factor nr_0^3. Thus f_1 measures space and time with much coarser scales than f_2.

The correlations in f_2 are produced by collisions between particles 1 and 2. When their positions are so far separated as to be out of molecular interaction range, we expect that there will be no correlation between 1 and 2, and f_2 will assume a product form (neglecting, of course, possible correlations produced by collisions with a third particle):

$$f_2(z_1, z_2, t) \xrightarrow[|\mathbf{r}_1 - \mathbf{r}_2| \gg r_0]{} f_1(z, t) f_1(z_2, t) \tag{3.64}$$

To evaluate $(\partial f_1/\partial t)_{\text{coll}}$, however, we need f_2 not in the uncorrelated region, but in the region where the two particles are colliding. To look at this

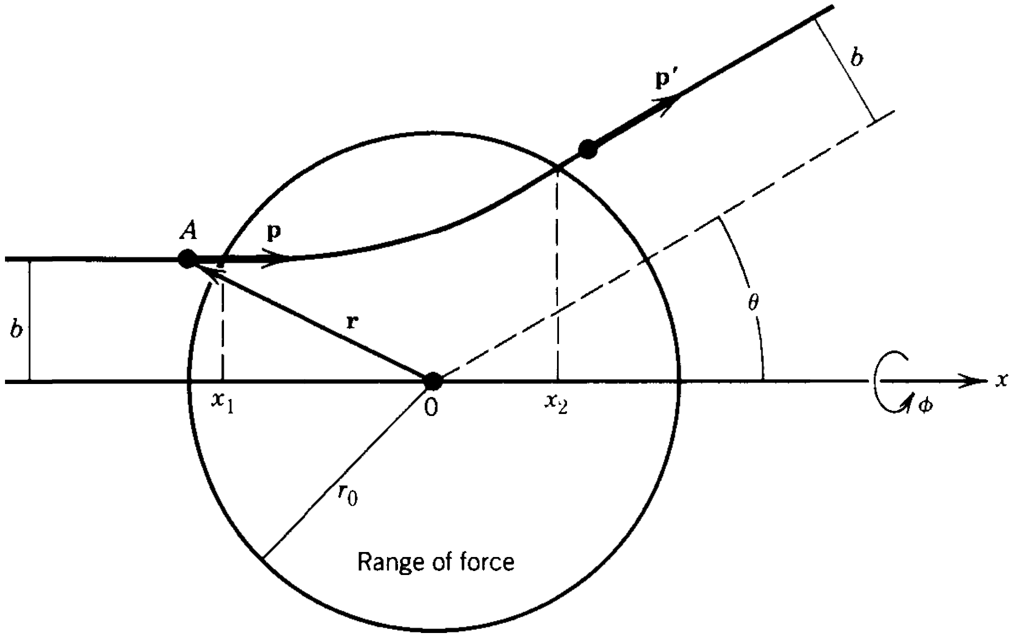

Fig. 3.8 Illustration of behavior of two-particle correlation function. The separation between the two particles is $\mathbf{r}$, and the relative momentum $\mathbf{p}$. The two particles are correlated only inside the range of the intermolecular force, indicated by the sphere of radius r_0. Outside the sphere, the correlation function is a product of two one-particle distribution functions. In equilibrium there is a steady scattering of beams of particles of all momenta, from all directions, at all impact parameters.

region it is convenient to use total and relative coordinates, defined as follows:

$$\begin{aligned} \mathbf{P} &= \mathbf{p}_2 + \mathbf{p}_1 \qquad & \mathbf{p} &= \frac{\mathbf{p}_2 - \mathbf{p}_1}{2} \\ \mathbf{R} &= \frac{\mathbf{r}_2 + \mathbf{r}_1}{2} \qquad & \mathbf{r} &= \mathbf{r}_2 - \mathbf{r}_1 \end{aligned} \tag{3.65}$$

Then (3.63) becomes

$$\begin{gathered} \left(\frac{\partial}{\partial t} + \frac{\mathbf{p}}{m}\cdot\nabla_R + \frac{\mathbf{p}}{m}\cdot\nabla_r + \mathbf{K}(\mathbf{r})\cdot\nabla_p\right) f_2(\mathbf{P},\mathbf{R},\mathbf{p},\mathbf{r},t) = 0 \\ \mathbf{K}(\mathbf{r}) \equiv -\nabla_r v(r) \end{gathered} \tag{3.66}$$

Transform to the center-of-mass system by putting $\mathbf{P} = 0$. The above can then be rewritten, to first order in dt, as the streaming condition (with $\mathbf{P}$ and $\mathbf{R}$ suppressed for clarity):

$$f_2\left(\mathbf{p} + \mathbf{K}(\mathbf{r})\,dt, \mathbf{r} + \frac{\mathbf{p}}{m}\,dt, t + dt\right) = f_2(\mathbf{p},\mathbf{r},t) \tag{3.67}$$

It traces the classical trajectories in the force field $\mathbf{K}$ centered at O, as illustrated in Fig. 3.8. If f_2 were peaked at point A initially, then (3.67) says that as time goes on the peak will move along the trajectory for that particular initial condition.

The equilibrium situation, for which $\partial f_2/\partial t = 0$, is a steady-state scattering, by the force field **K**, of a beam of particles consisting of all momenta, at all impact parameters. Referring to Fig. 3.8, we may describe the steady state as follows: Outside the sphere of interaction the uncorrelated factorized form (3.64) holds. However, boundary values of the momenta are correlated through the fact that momenta entering the sphere at a specific impact parameter must leave the sphere at the correct scattering angle, and vice versa.

To "derive" the Boltzmann transport equation, we assume that, since f_2 has a shorter time scale than f_1, it reaches equilibrium earlier than f_1. Thus we set $\partial f_2/\partial t = 0$, and assume f_2 has attained the equilibrium form described earlier. Similarly, we assume that the range of force r_0 is essentially zero from the point of view of f_1. Thus in the factorized form of f_2 just before and after a collision, we can put $\mathbf{r}_2$ and $\mathbf{r}_1$ both equal to the same value.

With this in mind, we substitute (3.63) into (3.62) to obtain

$$\begin{aligned}\left(\frac{\partial f_1}{\partial t}\right)_{\text{coll}} &\equiv -\int_{r_0} dz_2\, \mathbf{K}_{12} \cdot \nabla_{p_1} f_2(z_1, z_2, t)\\ &= -\int_{r_0} dz_2\, \mathbf{K}_{12} \cdot (\nabla_{p_1} - \nabla_{p_2}) f_2(z_1, z_2, t)\\ &= \frac{1}{m}\int_{r_0} dz_2\, (\mathbf{p}_1 \cdot \nabla_{r_1} + \mathbf{p}_2 \cdot \nabla_{r_2}) f_2(z_1, z_2, t) \qquad (3.68)\end{aligned}$$

Using the coordinates defined in (3.66), and neglecting the gradient with respect to **R**, we have

$$\begin{aligned}\left(\frac{\partial f_1}{\partial t}\right)_{\text{coll}} &= -\frac{1}{m}\int d^3p_2 \int_{r<r_0} d^3r\, (\mathbf{p}_1 - \mathbf{p}_2) \cdot \nabla_r f_2\\ &= \frac{1}{m}\int d^3p_2\, |\mathbf{p}_1 - \mathbf{p}_2| \int d\phi\, b\, db \int_{x_1}^{x_2} dx\, \frac{\partial}{\partial x} f_2 \qquad (3.69)\end{aligned}$$

where the notation is indicated in Fig. 3.8. Now we set

$$\begin{aligned} f_2(x_1) &= f_1(\mathbf{p}_1) f_1(\mathbf{p}_2)\\ f_2(x_2) &= f_1(\mathbf{p}_1') f_1(\mathbf{p}_2')\end{aligned}$$

where $\mathbf{p}_1', \mathbf{p}_2'$ are the final momenta in the scattering process, when the initial momenta are $\mathbf{p}_1$, $\mathbf{p}_2$ and the impact parameter is b. Using the definition (3.21) of the classical cross section, we finally have

$$\left(\frac{\partial f_1}{\partial t}\right)_{\text{coll}} = \int d^3p_2\, d\Omega\, |\mathbf{v}_1 - \mathbf{v}_2| (d\sigma/d\Omega)(f_1' f_2' - f_1 f_2) \qquad (3.70)$$

which is the same as (3.34).

PROBLEMS

3.1 Give a few numerical examples to show that the condition (3.1) is fulfilled for physical gases at room temperatures.

3.2 Explain qualitatively why all molecular interactions are electromagnetic in origin.

3.3 For the collision between perfectly elastic spheres of diameter a,

(*a*) calculate the differential cross section with classical mechanics in the coordinate system in which one of the spheres is initially at rest;

(*b*) compare your answer with the quantum mechanical result. Consider both the low-energy and the high-energy limit. (See, e.g., L. I. Schiff, *Quantum Mechanics*, 2nd ed. (McGraw-Hill, New York, 1955), p. 110).

3.4 Consider a mixture of two gases whose molecules have masses m and M, respectively, and which are subjected to external forces $\mathbf{F}$ and $\mathbf{Q}$, respectively. Denote the respective distribution functions by f and g. Assuming that only binary collisions between molecules are important, derive the Boltzmann transport equation for the system.

3.5 This problem illustrates in a trivial case how the ensemble density tends to a uniform density over the accessible phase space. Consider an ensemble of systems, each of which consists of a single free particle in one dimension with momentum p and coordinate q. The particle is confined to a one-dimensional box with perfectly reflecting walls located at $q = -1$ and $q = 1$ (in arbitrary units.) Draw a square box of unit sides in the pq plane (the phase space). Draw a square of sides 1/2 in the upper left corner of this box. Let the initial ensemble correspond to filling this corner box uniformly with representative points.

(*a*) What is the accessible part of the phase space? (i.e., the region that the representative points can reach through dynamical evolution from the initial condition.)

(*b*) Consider how the shape of the distribution of representative point changes at regular successive time intervals. How does the distribution look after a long time?

Suggestion: When a particle is being reflected at a wall, its momentum changes sign. Represent what happens in phase space by continuing the locus of the representative point to a fictitious adjacent box in pq space, as if the wall were absent. "Fold" the adjacent box onto the original box properly to get the actual trajectory of the representative point. After a long time, you need many such adjacent boxes. The "folding back" will then give you a picture of the distribution.