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CHAPTER 2

Statistical Mechanics and Molecular Distribution Functions

This chapter is devoted to a brief summary of the principles of classical statistical mechanics, to a discussion of the link between statistical mechanics and thermodynamics, and to the definitions of a variety of equilibrium and time-dependent distribution functions. It also establishes much of the notation that is used in later parts of the book.

2.1 THE LIOUVILLE EQUATION AND THE BBGKY HIERARCHY

Consider an isolated, macroscopic system consisting of N identical particles, each of which has three, translational degrees of freedom. The dynamical state of the system at a given time is completely specified by the $3N$ coordinates $\mathbf{r}^N \equiv \{\mathbf{r}_1, \dots, \mathbf{r}_N\}$ and $3N$ momenta $\mathbf{p}^N \equiv \{\mathbf{p}_1, \dots, \mathbf{p}_N\}$ of the particles. The values of these variables define a *phase point* in a $6N$ -dimensional *phase space*. Let $\mathcal{H}_N(\mathbf{r}^N, \mathbf{p}^N)$ be the hamiltonian of the system, which we write in the form

$$\mathcal{H}_N(\mathbf{r}^N, \mathbf{p}^N) = \frac{1}{2m} \sum_{i=1}^N |\mathbf{p}_i|^2 + V_N(\mathbf{r}^N) \quad (2.1.1)$$

where m is the particle mass and $V_N(\mathbf{r}^N)$ is the total potential energy. Then the motion of the phase point along its *phase trajectory* is determined by Hamilton's equations:

$$\dot{\mathbf{r}}_i = \frac{\partial \mathcal{H}_N}{\partial \mathbf{p}_i} \quad (2.1.2)$$

$$\dot{\mathbf{p}}_i = -\frac{\partial \mathcal{H}_N}{\partial \mathbf{r}_i} \quad (2.1.3)$$

where $i = 1, \dots, N$. These equations are to be solved subject to $6N$ initial conditions on the coordinates and momenta.

The aim of equilibrium statistical mechanics is to calculate observable properties of the system either as averages over a phase-space trajectory (the method of Boltzmann) or as averages over an ensemble of systems, each of which is a replica of the system of interest (the method of Gibbs). The main features of the two methods are discussed in later sections of this chapter. For the present, it is sufficient to recall that in Gibbs' formulation of statistical mechanics the distribution of phase points of the ensemble is described by a phase-space probability density $f^{(N)}(\mathbf{r}^N, \mathbf{p}^N; t)$; the quantity $f^{(N)} d\mathbf{r}^N d\mathbf{p}^N$ is the probability that at time t the physical system is in a microscopic state represented by a phase point lying in the infinitesimal, $6N$ -dimensional phase-space element $d\mathbf{r}^N d\mathbf{p}^N$. Given a complete knowledge of the probability density, it would be possible to calculate the average value of any function of the coordinates and momenta.

The time evolution of the phase-space probability density is governed by the Liouville equation. The latter is the $6N$ -dimensional analogue of the equation of continuity of an incompressible fluid; it describes the fact that phase points of the ensemble are neither created nor destroyed as time evolves. The Liouville equation can be written in compact form as

$$\frac{\partial f^{(N)}}{\partial t} = \{\mathcal{H}_N, f^{(N)}\} \quad (2.1.4)$$

where $\{A, B\}$ denotes the Poisson bracket:

$$\{A, B\} \equiv \sum_{i=1}^N \left(\frac{\partial A}{\partial \mathbf{r}_i} \cdot \frac{\partial B}{\partial \mathbf{p}_i} - \frac{\partial A}{\partial \mathbf{p}_i} \cdot \frac{\partial B}{\partial \mathbf{r}_i} \right) \quad (2.1.5)$$

Another convenient form is obtained by introducing the Liouville operator \mathcal{L} , defined as

$$\mathcal{L} = i\{\mathcal{H}_N, \quad \} \quad (2.1.6)$$

Equation (2.1.4) then becomes

$$\frac{\partial f^{(N)}}{\partial t} = -i\mathcal{L}f^{(N)} \quad (2.1.7)$$

the formal solution to which is

$$f^{(N)}(\mathbf{r}^N, \mathbf{p}^N; t) = \exp(-i\mathcal{L}t)f^{(N)}(\mathbf{r}^N, \mathbf{p}^N; 0) \quad (2.1.8)$$

The time dependence of an arbitrary dynamical variable, A say, can be represented in a manner similar to (2.1.7). Any such variable is a function of the phase-space coordinates $\mathbf{r}^N, \mathbf{p}^N$ and changes in A are associated solely with changes in the independent variables. Thus

$$\frac{dA}{dt} = \sum_{i=1}^N \left(\frac{\partial A}{\partial \mathbf{r}_i} \cdot \frac{d\mathbf{r}_i}{dt} + \frac{\partial A}{\partial \mathbf{p}_i} \cdot \frac{d\mathbf{p}_i}{dt} \right) \quad (2.1.9)$$

If we substitute from Hamilton's equations (2.1.2) and (2.1.3) and use the definition (2.1.6), Eqn (2.1.9) becomes

$$\frac{dA}{dt} = i\mathcal{L}A \tag{2.1.10}$$

This has the formal solution

$$A(t) = \exp(i\mathcal{L}t)A(0) \tag{2.1.11}$$

The description of the system that is provided by the full phase-space probability density is for many purposes unnecessarily detailed. If we are interested only in the behaviour of a subset of particles of size n , say, the unwanted information can be eliminated by integrating $f^{(N)}$ over the coordinates and momenta of the remaining $(N-n)$ particles. We therefore define a reduced phase-space distribution function $f^{(n)}(\mathbf{r}^n, \mathbf{p}^n; t)$ for $n < N$ by

$$f^{(n)}(\mathbf{r}^n, \mathbf{p}^n; t) = \frac{N!}{(N-n)!} \iint f^{(N)}(\mathbf{r}^N, \mathbf{p}^N; t) d\mathbf{r}^{(N-n)} d\mathbf{p}^{(N-n)}, \quad n < N \tag{2.1.12}$$

where we use the notation $\mathbf{r}^n \equiv \{\mathbf{r}_1, \dots, \mathbf{r}_n\}$, $\mathbf{r}^{(N-n)} \equiv \{\mathbf{r}_{n+1}, \dots, \mathbf{r}_N\}$, etc. The meaning of $f^{(n)}(\mathbf{r}^n, \mathbf{p}^n; t)$ is that $f^{(n)} d\mathbf{r}^n d\mathbf{p}^n$ is $N!/(N-n)!$ times the probability of finding *any* subset of n particles in the reduced phase-space element $d\mathbf{r}^n d\mathbf{p}^n$ at time t , irrespective of the coordinates and momenta of the remaining particles; the factor $N!/(N-n)!$ is the number of ways of choosing n particles from N .

The equations of motion of the reduced distribution functions are much more complicated in form than the Liouville equation. Let us suppose that the total force acting on particle i is the sum of an external force \mathbf{X}_i and of pair forces \mathbf{F}_{ij} due to other particles j , with $\mathbf{F}_{ii} = 0$. Then the Liouville equation can be written as

$$\frac{\partial f^{(N)}}{\partial t} + \frac{1}{m} \sum_{i=1}^N \mathbf{p}_i \cdot \frac{\partial f^{(N)}}{\partial \mathbf{r}_i} + \sum_{i=1}^N \mathbf{X}_i \cdot \frac{\partial f^{(N)}}{\partial \mathbf{p}_i} = - \sum_{i,j} \mathbf{F}_{ij} \cdot \frac{\partial f^{(N)}}{\partial \mathbf{p}_i} \tag{2.1.13}$$

We now multiply through by $N!/(N-n)!$ and integrate over $3(N-n)$ coordinates and momenta. By employing the definition (2.1.12), and exploiting the symmetry of $f^{(N)}$ with respect to interchange of particle labels and the fact that $f^{(N)}$ vanishes as $\mathbf{p}_i \rightarrow \pm\infty$ or when \mathbf{r}_i lies outside the volume occupied by the system, we find that

$$\begin{aligned}
 \frac{\partial f^{(n)}}{\partial t} + \frac{1}{m} \sum_{i=1}^{(n)} \mathbf{p}_i \cdot \frac{\partial f^{(n)}}{\partial \mathbf{r}_i} + \sum_{i=1}^{(n)} \mathbf{X}_i \cdot \frac{\partial f^{(n)}}{\partial \mathbf{p}_i} \\
 = - \frac{N!}{(N-n)!} \sum_i \sum_j \int \int \mathbf{F}_{ij} \cdot \frac{\partial f^{(N)}}{\partial \mathbf{p}_i} d\mathbf{r}^{(N-n)} d\mathbf{p}^{(N-n)} \\
 = - \sum_i \sum_j \mathbf{F}_{ij} \cdot \frac{\partial f^{(n)}}{\partial \mathbf{p}_i} - \frac{N!}{(N-n)!} \sum_{i=1}^n \sum_{j=n+1}^N \int \int \mathbf{F}_{ij} \cdot \frac{\partial f^{(N)}}{\partial \mathbf{p}_i} d\mathbf{r}^{(N-n)} d\mathbf{p}^{(N-n)} \\
 \stackrel{(*)}{=} - \sum_i \sum_j \mathbf{F}_{ij} \cdot \frac{\partial f^{(n)}}{\partial \mathbf{p}_i} - \sum_{i=1}^n \int \int \mathbf{F}_{i,n+1} \cdot \frac{\partial f^{(n+1)}}{\partial \mathbf{p}_i} d\mathbf{r}_{n+1} d\mathbf{p}_{n+1} \quad (2.1.14)
 \end{aligned}$$

Thus the behaviour of $f^{(n)}$ is linked to that of $f^{(n+1)}$ by the formula

$$\left\{ \frac{\partial}{\partial t} + \sum_{i=1}^n \left[\frac{1}{m} \mathbf{p}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} + \left(\mathbf{X}_i + \sum_{j=1}^n \mathbf{F}_{ij} \right) \cdot \frac{\partial}{\partial \mathbf{p}_i} \right] \right\} f^{(n)}(\mathbf{r}^n, \mathbf{p}^n; t) \\
 = - \sum_{i=1}^n \int \int \mathbf{F}_{i,n+1} \cdot \frac{\partial}{\partial \mathbf{p}_i} f^{(n+1)}(\mathbf{r}^{n+1}, \mathbf{p}^{n+1}; t) d\mathbf{r}_{n+1} d\mathbf{p}_{n+1} \quad (2.1.15)$$

The set of equations for $n = 1, \dots, N-1$ was first derived by Yvon (1935) and is known as the BBGKY hierarchy (Kirkwood, 1935; Bogolyubov, 1946; Born and Green, 1949).

Equation (2.1.15) is not immediately useful, because it expresses one unknown function, $f^{(n)}$, in terms of another, $f^{(n+1)}$: at some stage an approximation must be made that closes the system of equations. The most important case in practice is that obtained by setting $n = 1$, i.e.

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$$\left(\frac{\partial}{\partial t} + \frac{1}{m} \mathbf{p}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} + \mathbf{X}_1 \cdot \frac{\partial}{\partial \mathbf{p}_1} \right) f^{(1)}(\mathbf{r}_1, \mathbf{p}_1; t) \\
 = - \int \int \mathbf{F}_{12} \cdot \frac{\partial}{\partial \mathbf{p}_1} f^{(2)}(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2; t) d\mathbf{r}_2 d\mathbf{p}_2 \quad (2.1.16)$$

The quantity $f^{(1)} d\mathbf{r}_1 d\mathbf{p}_1$ is N times the probability of finding a particle of the system in the six-dimensional phase element $d\mathbf{r}_1 d\mathbf{p}_1$ at time t ; $f^{(2)} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{p}_1 d\mathbf{p}_2$ is $N(N-1)$ times the probability of finding a particle in the phase element $d\mathbf{r}_1 d\mathbf{p}_1$ and, simultaneously, another particle in the phase element $d\mathbf{r}_2 d\mathbf{p}_2$.

Much effort has been devoted to finding approximate solutions to the BBGKY hierarchy on the basis of expressions that relate $f^{(2)}$ to $f^{(1)}$. The resulting kinetic equations are rarely appropriate for the study of liquids, since they mostly treat the pair correlations in a very crude way. The simplest approximation is to ignore the pair correlations altogether by writing

$$f^{(2)}(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}'; t) = f^{(1)}(\mathbf{r}, \mathbf{p}; t) f^{(1)}(\mathbf{r}', \mathbf{p}'; t) \quad (2.1.17)$$