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Statistical physics of liquids

A liquid in thermodynamic equilibrium is described at the macroscopic level in terms of a few characteristic variables such as temperature T , pressure P , volume V , the (average) number of particles \bar{N} , mass density ρ_0 , etc. (Fermi, 1956). The thermodynamic properties listed above are not all independent and are related through a relation termed the equation of state. The equilibrium liquid transforms into a crystalline solid when its temperature T falls below a characteristic value T_m . The latter is termed the freezing point of the liquid at the corresponding pressure. The liquid state involves random motion of the constituent particles, each of which represents a basic microscopic unit for the system. The normal liquid is isotropic in a time-averaged sense. At freezing this isotropic symmetry of the normal liquid state is spontaneously broken. The crystalline state has a characteristic long-range order of the individual microscopic units. The transformation of the liquid into a crystalline solid involves the absorption of latent heat. This transformation is somewhat distinct from the condensation of the gaseous state into the liquid state. In the latter case both the states are disordered. In Fig. 1.1 we display schematically a phase diagram showing the different equilibrium states for the corresponding values of the thermodynamic properties T and P . For example, the horizontal arrow in Fig. 1.1 indicates that as we cross the line separating the phases a transition from the liquid to the crystalline state occurs. This is accompanied by a discontinuous change of the thermodynamic properties (such as the volume V) and is called a first-order transition. The coexistence line of the liquid and gaseous states terminates at the critical point. Beyond this point the transformation from one state to another occurs through a continuous, or second-order, phase transition. For the solid and the liquid states no such termination of the phase line occurs. The corresponding diagram showing the existence of the phases in the P - T plane is presented in Fig. 1.2. The part of the P - T plane which is not physically accessible to a single phase is marked as the coexistence region. Transformation from one state to another occurs here. The phase diagrams describe the equilibrium states as a function of the thermodynamic parameters. However, almost all liquids can, with varying degrees of ease, be supercooled below T_m without developing long-range order of the crystalline state. The supercooled liquid develops very slow dynamics. This slowing down is far more drastic than the decrease in the average speed of the liquid particles for the cooling to lower temperatures. The time taken for a characteristic fluctuation to relax to equilibrium increases by orders of magnitude as

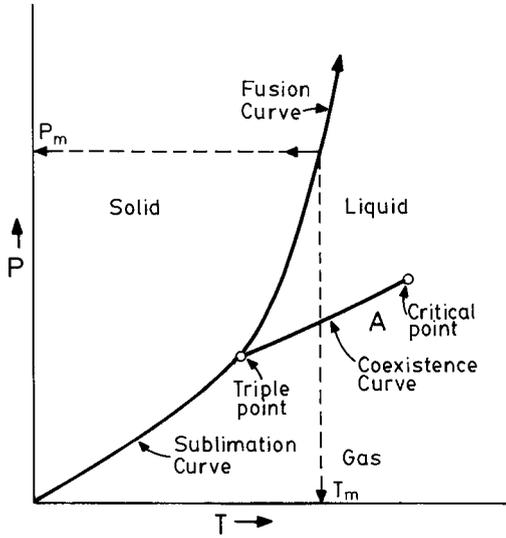


Fig. 1.1 The equilibrium phase diagram (schematic) of a simple fluid in the pressure (P) and temperature (T) plane.

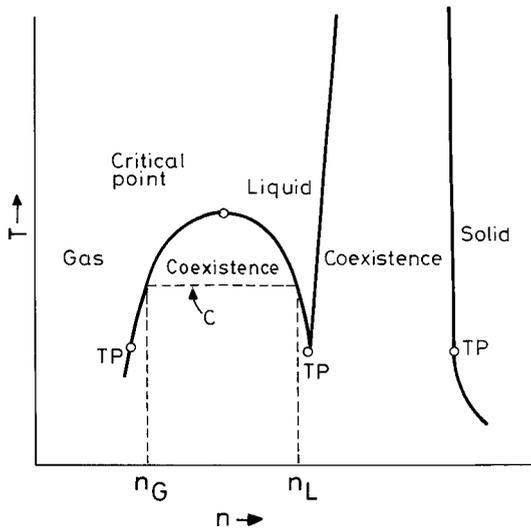


Fig. 1.2 The equilibrium phase diagram (schematic) of a simple fluid in the density n (equivalent to n_0 in the text) and temperature (T) plane. The regions marked for coexistence are unavailable for a single phase and represent transformation.

the liquid is increasingly supercooled. The viscosity of the liquid increases below T_m until a situation in which the liquid stops flowing and transforms into an amorphous solid is reached. We will study in this book models for understanding the behavior of the liquid at the freezing point T_m and beyond. Our treatment involves primarily a coarse-grained picture of the microscopic-level description of the liquid.

1.1 Basic statistical mechanics

The microscopic description of the liquid is formulated here by treating the individual microscopic units in terms of the laws of classical physics. The justification of the classical approximation depends on the value of the thermal de Broglie wavelength $\Lambda_0 = h/\sqrt{2\pi mk_B T}$ corresponding to the average momentum of the liquid particles (of mass m) at a temperature T . $k_B = 1.38 \times 10^{-16}$ erg/K is the Boltzmann constant. If the mean nearest-neighbor separation of the liquid particles $l_0 \simeq \rho_0^{-1/3}$ is such that the ratio $\xi_{Tr} = \Lambda_0/l_0 \ll 1$ then the classical description is justified. For most liquids (Hansen and McDonald, 1986; Barrat and Hansen, 2003) barring hydrogen and neon, this ratio is small near the triple point. For molecular liquids another characteristic quantity, namely the ratio $\xi_R = \Theta_{Rot}/T$ between the characteristic rotational temperature $\Theta_{Rot} = \hbar^2/(2Ik_B)$ (I is the molecular moment of inertia of the molecule) and temperature T should also be small. However, as the temperature T falls and density ρ_0 increases, ξ_{Tr} increases. In the classical approximation the contributions to the thermodynamic properties from the kinetic and interaction parts of the Hamiltonian can be obtained separately. If \mathcal{R}_e represents the absolute value of the ratio of the kinetic and potential parts of the total energy of the system of particles then $\mathcal{R}_e \sim 1$ corresponds to the liquid state. On the other hand, for the gaseous and solid states we have $\mathcal{R}_e \gg 1$ and $\mathcal{R}_e \ll 1$, respectively. The liquid state thus represents an intermediate between two extremes. Alternatively, this characterization of the liquid state can be done in terms of the interaction potential. Let a pair of particles in the system interact via a potential of depth $\sim \epsilon$ and range $\sim \sigma$. The liquid state will correspond to the particles being cohesive, which requires that the total volume $V \sim N\sigma^3$ and the average kinetic energy $k_B T \sim \epsilon$. Indeed, the intermediate nature of the liquid state makes it particularly difficult to develop a quantitatively accurate model for its thermodynamic or dynamic properties at high densities. Both for dilute gases and for low-density solids the corresponding idealized model, namely the perfect gas and the harmonic solid, can be treated exactly. Such a reference state is lacking for a high-density liquid. In this book we will describe how the methods of classical statistical mechanics have been used to develop models for strongly interacting liquids and further extended to gain an understanding of the properties of deeply supercooled states.

1.1.1 Thermodynamic functions

The first law of thermodynamics provides us with a definition of the internal energy U as a property of the equilibrium thermodynamic state. The second law of thermodynamics defines another state function S representing the thermodynamic entropy of the system. The first two laws are expressed in terms of the basic equation treating the variations of U and S as exact differentials,

$$T dS = dU + P dV - \mu d\bar{N}, \quad (1.1.1)$$

where V is the volume and \bar{N} is the number of particles N in the system. Note that the number of particles \bar{N} is used here as a macroscopic (extensive) thermodynamic property

of the system (similar to the volume V). In order to distinguish it from the number of particles N in the system in a microscopic picture (to be used later) we denote it with a bar. μ is the chemical potential. The internal energy U can be treated as a function of T and V , giving the differential,

$$dU = c_v dT + \left(\frac{\partial U}{\partial V} \right)_T dV, \quad (1.1.2)$$

where $c_v = (\partial U / \partial T)_V$ is the specific heat at constant volume. Using eqn. (1.1.2) in eqn. (1.1.1) and the fact that dS is an exact differential, we obtain the thermodynamic relation

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P. \quad (1.1.3)$$

From the second law of thermodynamics follows the entropy function S of the thermodynamic state. As a direct consequence of the second law it follows that for an *isolated* system the entropy S never decreases. Equivalently, for a change from a state A to another state B (Fermi, 1936)

$$S(\text{B}) - S(\text{A}) \leq \int_{\text{A}}^{\text{B}} \frac{dQ}{T}, \quad (1.1.4)$$

where the equality holds for a reversible change. Thus for an isolated system going through an infinitesimal change the heat supplied $\Delta Q \leq T \Delta S$. Using the first law, this inequality leads to

$$\Delta U + P \Delta V - T \Delta S \leq 0. \quad (1.1.5)$$

For a constant-temperature and constant-volume process therefore we have $\Delta(U - TS) \leq 0$. Hence for an isolated system the function $F = U - TS$ always decreases and equilibrium is reached when the function F reaches a minimum. On the other hand, if the temperature T and pressure P remain constant, the inequality (1.1.5) tells us that $\Delta(U - TS + PV) \leq 0$. Therefore in constant-temperature, constant-pressure processes the thermodynamic function $G = U - TS + PV \leq 0$ is minimized. F and G are called the Helmholtz and Gibbs free energies, respectively. Using the result (1.1.1), the differentials of F and G are obtained as

$$\begin{aligned} dF &= dU - T dS - S dT \\ &= -P dV + \mu d\bar{N} - S dT \end{aligned} \quad (1.1.6)$$

$$\begin{aligned} dG &= dU - T dS - S dT + P dV + V dP \\ &= \mu d\bar{N} + V dP - S dT. \end{aligned} \quad (1.1.7)$$

From the above equations it follows that the thermodynamic potentials F and G can be treated as functions of the corresponding sets of thermodynamic variables, $F \equiv F(T, V, \bar{N})$

and $G \equiv G(T, P, \bar{N})$. For the Gibbs free energy the situation is somewhat special since, apart from \bar{N} , the other two thermodynamic variables on which it depends are both intensive properties, i.e., independent of the size of the system. We can write the Gibbs free energy per particle as $G(T, P, \bar{N}) = \bar{N}g(T, P)$. We obtain, from eqn. (1.1.7), the chemical potential μ as

$$\mu = \left(\frac{\partial G}{\partial \bar{N}} \right)_{P,T} = g(T, P) = \frac{G}{\bar{N}}, \quad (1.1.8)$$

which is the Gibbs free energy per particle. Using the relation $G = \mu\bar{N}$ in eqn. (1.1.7), we obtain the very useful Gibbs–Duhem relation,

$$\bar{N} d\mu - V dP + S dT = 0. \quad (1.1.9)$$

The above relation implies that, at the transition for the coexisting phases at equal temperature and pressure ($dP = dT = 0$), the chemical potentials of the two phases are also equal,

$$\mu_1 = \mu_2. \quad (1.1.10)$$

The Gibbs free energy per particle is continuous through the phase transition. However, from eqn. (1.1.9) it follows that

$$-\left(\frac{\partial \mu}{\partial P} \right)_T = \frac{V}{\bar{N}} = v, \quad (1.1.11)$$

$$\left(\frac{\partial \mu}{\partial T} \right)_P = \frac{S}{\bar{N}} = s. \quad (1.1.12)$$

Thus the first derivative of the Gibbs free energy is discontinuous at the transition (hence the name first-order transition). The respective amounts of discontinuity are equal to the changes in specific volume and entropy for the two phases across the transition. We therefore obtain

$$-\left(\frac{\partial \Delta \mu}{\partial T} \right)_P \bigg/ \left(\frac{\partial \Delta \mu}{\partial P} \right)_T = \frac{\Delta s}{\Delta v}. \quad (1.1.13)$$

Since the change in Gibbs free energy (per particle) $\Delta \mu$ is a function of the intensive variables P and T , we can use the chain rule to write the LHS of eqn. (1.1.13) as $(\partial P / \partial T)_{\Delta \mu}$. At the transition $\Delta \mu$ is zero and hence the corresponding derivative is obtained as

$$\frac{dP(T)}{dT} = \left(\frac{\partial P}{\partial T} \right)_{\Delta \mu=0} = \frac{\Delta s}{\Delta v}. \quad (1.1.14)$$

Using the fact that at the transition the temperature T remains constant, the difference between the specific entropies is $\Delta s = L/T$, where L is the latent heat of the transition. Hence, denoting the change of specific volume between the two phases as $\Delta v = v_2 - v_1$,

the above equation for the rate of change of pressure P at coexistence with temperature T is obtained as

$$\boxed{\frac{dP(T)}{dT} = \frac{L}{T(v_2 - v_1)}} \quad (1.1.15)$$

The above equation is termed the Clapeyron equation.

1.1.2 The classical N -particle system

We begin with a review of a few basic results concerning a fluid as a classical statistical mechanical system. We consider a fluid as a system of volume V containing N particles of mass m and following Newton's laws of motion. The Hamiltonian for the system is given by the sum of a kinetic part $K(\mathbf{p}_1, \dots, \mathbf{p}_N)$ and a potential part $U(\mathbf{r}_1, \dots, \mathbf{r}_N)$,

$$\begin{aligned} H &= \sum_{\alpha=1}^N \frac{p_{\alpha}^2}{2m} + U(\mathbf{r}_1, \dots, \mathbf{r}_N) \\ &= \sum_{\alpha=1}^N \frac{p_{\alpha}^2}{2m} + \frac{1}{2} \sum'_{\alpha, \beta} u(r_{\alpha\beta}), \end{aligned} \quad (1.1.16)$$

where \mathbf{r}_{α} and \mathbf{p}_{α} , respectively, denote the position and momentum of the α th particle and $r_{\alpha\beta} = |\mathbf{r}_{\alpha} - \mathbf{r}_{\beta}|$. We assume that the particles of the fluid interact through a two-body potential $u(\mathbf{r}_{\alpha\beta})$ dependent on the vector $\mathbf{r}_{\alpha\beta}$ connecting the two interacting particles. In an isotropic system u is a function of only $r_{\alpha\beta}$. We treat here the simplified case in which there is no external potential. The prime in the summation in the second term on the RHS of (1.1.16) indicates that the $\alpha = \beta$ term is excluded. The equations of motion of the particles are given by

$$\dot{\mathbf{r}}_{\alpha} \equiv \frac{d\mathbf{r}_{\alpha}}{dt} = \frac{\partial H}{\partial \mathbf{p}_{\alpha}}, \quad \dot{\mathbf{p}}_{\alpha} \equiv \frac{d\mathbf{p}_{\alpha}}{dt} = -\frac{\partial H}{\partial \mathbf{r}_{\alpha}}, \quad (1.1.17)$$

for $\alpha = 1, \dots, N$. These equations with appropriate initial conditions determine the classical dynamics of the N -particle system. In the phase-space description the system is described in terms of a single phase point in the $6N$ -dimensional phase space involving the variables $\{\mathbf{r}_{\alpha}, \mathbf{p}_{\alpha}\}$ for the N particles. The dynamics of the system is then represented by the trajectory of a single phase point in the phase space. The physically measured value of a dynamic variable is then given by an average on the phase-space trajectory. In equilibrium such an average is replaced, using the ergodic hypothesis (Dorfman, 1999), by an average over an appropriate ensemble representative of the system. Each member of the ensemble is an identical copy of the system evolving independently under the above equations of motion. The "fluid" constituted by these points in the phase space has a characteristic density termed the phase-space density $f^{(N)}(\mathbf{r}^N, \mathbf{p}^N, t)$. This is the density of representative points corresponding to the members of the ensemble in any particular part of the phase space. Thus $f^{(N)} d\mathbf{r}_1 d\mathbf{p}_1 \dots d\mathbf{r}_N d\mathbf{p}_N$ is the number of phase points in an

elementary volume $d\mathbf{r}^N d\mathbf{p}^N$ at time t . It also represents the probability that a particular member of the ensemble will be in a state in which the position and momentum coordinates of the i th particle (for $i = 1, \dots, N$) lie in the ranges \mathbf{r}_i to $\mathbf{r}_i + d\mathbf{r}_i$ and \mathbf{p}_i to $\mathbf{p}_i + d\mathbf{p}_i$, respectively. Since the total number of ensemble members is fixed, we can maintain the normalization

$$\int d\mathbf{r}^N d\mathbf{p}^N f^{(N)}(\mathbf{r}^N, \mathbf{p}^N, t) = 1, \tag{1.1.18}$$

where we have used the notation $d\mathbf{r}_1 d\mathbf{p}_1 \cdots d\mathbf{r}_N d\mathbf{p}_N \equiv d\mathbf{r}^N d\mathbf{p}^N$.

1.1.3 The BBGKY hierarchy equations

The time evolution of $f^{(N)}$ is given by the Liouville equation, which is obtained by applying the continuity equation for the “incompressible fluid” formed by the phase points of the ensemble. Therefore

$$\frac{\partial f^{(N)}}{\partial t} + \sum_{\alpha=1}^N \left[\frac{\partial f^{(N)}}{\partial \mathbf{r}_\alpha} \cdot \dot{\mathbf{r}}_\alpha + \frac{\partial f^{(N)}}{\partial \mathbf{p}_\alpha} \cdot \dot{\mathbf{p}}_\alpha \right] = 0. \tag{1.1.19}$$

Using the equation of motion eqn. (1.1.17), we obtain from (1.1.19)

$$\frac{\partial f^{(N)}}{\partial t} + \{H, f^{(N)}\} = 0, \tag{1.1.20}$$

with the Poisson bracket between variables A and B being defined as

$$\{A, B\} = \sum_{\alpha=1}^N \left[\frac{\partial A}{\partial \mathbf{r}_\alpha} \cdot \frac{\partial B}{\partial \mathbf{p}_\alpha} - \frac{\partial A}{\partial \mathbf{p}_\alpha} \cdot \frac{\partial B}{\partial \mathbf{r}_\alpha} \right]. \tag{1.1.21}$$

The above equation for the time evolution of $f^{(n)}$ is often written as

$$\left[\frac{\partial}{\partial t} + i\mathcal{L} \right] f^{(N)} = 0 \tag{1.1.22}$$

in terms of the Liouville operator \mathcal{L} :

$$\mathcal{L} \equiv i\{H, \}. \tag{1.1.23}$$

The formal solution of the above equation for the N -particle distribution function is obtained as

$$f^{(N)}(t) = \exp[-i\mathcal{L}t]f^{(N)}(0). \tag{1.1.24}$$

It is useful to compare the above result for the time evolution of $f^{(N)}(t)$ with the time evolution of an operator $A(\mathbf{r}^N, \mathbf{p}^N)$. Since A is not explicitly dependent on t its change with time is controlled by that of $\{\mathbf{r}^N, \mathbf{p}^N\}$. Therefore the equation of motion for A is obtained as

$$\frac{\partial A}{\partial t} = \sum_{\alpha=1}^N \left[\frac{\partial A}{\partial \mathbf{r}_\alpha} \cdot \dot{\mathbf{r}}_\alpha + \frac{\partial A}{\partial \mathbf{p}_\alpha} \cdot \dot{\mathbf{p}}_\alpha \right] \equiv i\mathcal{L}A. \tag{1.1.25}$$

The solution of the above equation gives for the time dependence of $A(t)$ the result

$$A(t) = \exp[+i\mathcal{L}t]A(0). \tag{1.1.26}$$

The time dependence of $f^{(N)}$ is therefore different from that of a dynamic variable. It represents the motion of the phase points in the phase space. The Liouville equation obtained for eqns. (1.1.17) makes this dynamics similar to that of an incompressible fluid.

Let us consider the number of representative points present in a small elementary volume at $t = 0$. With the progress of time this elementary volume stretches out, changing its shape, but its total volume remains unchanged. In mathematical terms, in the Hamiltonian dynamics, the Jacobian of the corresponding transformation of the phase-space variables is unity,

$$J[\mathbf{r}^N(0), \mathbf{p}^N(0) \rightarrow \mathbf{r}^N(t), \mathbf{p}^N(t)] = 1. \tag{1.1.27}$$

This is termed the Liouville theorem. The phase-space trajectories of the different points never cross each other since the dynamics at this level is completely deterministic. Starting from an initial configuration the evolution is always unique.

The Liouville equation describes the dynamics at the level of N particles. Using the definition (1.1.16) of the Hamiltonian for the N -particle system interacting through the two-body potential, the operator \mathcal{L} in eqn. (1.1.23) is further simplified. The derivative of H with respect to the particle coordinates is given by

$$\frac{\partial H}{\partial \mathbf{r}_\alpha} = \sum'_\beta \frac{\partial u(r_{\alpha\beta})}{\partial \mathbf{r}_\alpha} \equiv -\mathbf{F}_{\alpha\beta}, \tag{1.1.28}$$

$\mathbf{F}_{\alpha\beta}$ being the force on the α th particle due to interaction with the β th particle. The prime in the sum indicates that the $\alpha = \beta$ term is absent. Note that in the definition (1.1.16) for H we have dropped for simplicity the presence of any possible external potential and hence there is no external force on the particles here. This operator \mathcal{L} is expressed as a sum of one-body and two-body terms:

$$\mathcal{L} = \sum_{\alpha=1}^N S_\alpha + \frac{1}{2} \sum'_{\alpha,\beta=1}^N \theta_{\alpha,\beta}, \tag{1.1.29}$$

$$S_\alpha \equiv \frac{\mathbf{p}_\alpha}{m} \cdot \nabla_{\mathbf{r}_\alpha}, \tag{1.1.30}$$

$$\theta_{\alpha,\beta} = \mathbf{F}_{\alpha\beta} \cdot (\nabla_{\mathbf{p}_\alpha} - \nabla_{\mathbf{p}_\beta}), \tag{1.1.31}$$

where the prime in the sum indicates that the terms for $\alpha = \beta$ are omitted. The above form of the Liouville operator is conveniently used to obtain a description of the dynamics at a reduced level. Starting from the level of N particles, the reduced distribution function giving the conditional probability of finding a reduced number of particles is defined. Thus the s -particle ($s < N$) reduced distribution function $f^{(s)}$ is defined as

$$f^{(s)}(\mathbf{x}^s, t) = \frac{N!}{(N-s)!} \int f^{(N)}(\mathbf{x}^N, t) d\mathbf{x}_{s+1} \dots d\mathbf{x}_N, \tag{1.1.32}$$

where the position \mathbf{r}_α and momentum \mathbf{p}_α for the α th particle are jointly denoted by the single variable \mathbf{x}_α . The notation $\mathbf{x}^n \equiv \{\mathbf{x}_1, \dots, \mathbf{x}_s\}$ is used as the argument in eqn. (1.1.32). Starting from the Liouville equation (1.1.22) and integrating out the positions and momenta for the $(N - s)$ particles, the dynamical equation for the reduced function $f^{(s)}$ is obtained as

$$\left\{ \frac{\partial}{\partial t} + \sum_{i=1}^s \frac{\mathbf{p}_i}{m} \cdot \nabla_{\mathbf{r}_i} + \frac{1}{2} \sum_{i,j=1}^{s'} \theta_{i,j} \right\} f^{(s)}(\mathbf{x}^s, t) = - \sum_{i=1}^s \int d\mathbf{x}_{s+1} \theta_{i,s+1} f^{(s+1)}(\mathbf{x}^{(s+1)}, t), \quad (1.1.33)$$

where the prime in the double sum indicates the absence of the $i = j$ term. The distribution function $f^{(N)}$ vanishes when the coordinate \mathbf{x}_α is at the limits of the integration, i.e., when \mathbf{r}_α is outside the volume of the system or $\mathbf{p}_\alpha \rightarrow \infty$. Hence the terms in which the integrand is a total derivative with respect to the integrated variable of position and momentum have been set equal to zero in deriving eqn. (1.1.33). With some further simplifications eqn. (1.1.33) for $f^{(s)}$ also reduces to the following form in terms of the force \mathbf{F}_{ij} between the i th and j th particles:

$$\left\{ \frac{\partial}{\partial t} + \sum_{i=1}^s \left[\frac{\mathbf{p}_i}{m} \cdot \nabla_{\mathbf{r}_i} + \left(\sum_{j=1}^{s'} \mathbf{F}_{ij} \right) \cdot \nabla_{\mathbf{p}_i} \right] \right\} f^{(s)}(\mathbf{x}^s, t) = - \sum_{i=1}^s \int d\mathbf{x}_{s+1} \mathbf{F}_{i,s+1} \cdot \nabla_{\mathbf{p}_i} f^{(s+1)}(\mathbf{x}^{(s+1)}, t). \quad (1.1.34)$$

Equations (1.1.33) and (1.1.34) relate the distribution function $f^{(s)}$ to its counterpart at the next level, i.e., $f^{(s+1)}$, and thus for $s = 1, \dots, N$ eqn. (1.1.33) gives rise to a hierarchy of N equations for the reduced distribution functions. This is known as the BBGKY hierarchy of equations for classical dynamics. At the simplest level, an approximate solution for the one-particle distribution function $f^{(1)}(\mathbf{r}, \mathbf{p}, t)$ is obtained from the first equation of the BBGKY hierarchy:

$$\left(\frac{\partial}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \nabla_{\mathbf{r}_1} \right) f^{(1)}(\mathbf{x}_1, t) = - \int d\mathbf{r}_2 \int d\mathbf{p}_2 \mathbf{F}_{12} \cdot \nabla_{\mathbf{p}_1} f^{(2)}(\mathbf{x}_1, \mathbf{x}_2, t). \quad (1.1.35)$$

1.1.4 The Boltzmann equation

In order to reach a closed equation for the one-particle distribution function $f^{(1)}(\mathbf{x}_1, t)$ from the above equation a relation linking the two-point function $f^{(2)}(\mathbf{x}_1, \mathbf{x}_2, t)$ to $f^{(1)}$ is needed. The simplest approximation in this regard is to ignore all correlation between the particles and use, in the mean-field approximation,

$$f^{(2)}(\mathbf{x}_1, \mathbf{x}_2, t) \approx f^{(1)}(\mathbf{x}_1, t) f^{(1)}(\mathbf{x}_2, t). \quad (1.1.36)$$

Using this closure relation in eqn. (1.1.35), we obtain what is termed the Vlasov equation,

$$\left(\frac{\partial}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \nabla_{\mathbf{r}_1} + \bar{\mathbf{F}}_1(\mathbf{r}_1, \mathbf{p}_1, t) \cdot \nabla_{\mathbf{p}_1} \right) f^{(1)}(\mathbf{r}_1, \mathbf{p}_1, t) = 0, \quad (1.1.37)$$

where we have defined the average force exerted on particle 1 by other particles as

$$\bar{\mathbf{F}}_1(\mathbf{r}_1, \mathbf{p}_1, t) = \int d\mathbf{r}_2 \int d\mathbf{p}_2 \bar{\mathbf{F}}_{12} f^{(1)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2, t). \quad (1.1.38)$$

The term involving $\bar{\mathbf{F}}_{12}$ in eqn. (1.1.38) is similar to the contribution which would appear in the presence of an external potential. Hence the Vlasov equation represents a collisionless approximation in the presence of an effective mean field. The above description of the dynamics is useful in plasma physics, in which long-range Coulomb forces are present. However, this is not a good approximation for studying a liquid with short-range interactions. In general, the RHS of eqn. (1.1.35) represents the contribution from the two-body interaction term to the dynamic evolution of $f^{(1)}(\mathbf{x}_1, t)$ and is termed the collision contribution. The above equation is therefore written in the schematic form

$$\left[\frac{\partial}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \nabla_{\mathbf{r}_1} \right] f^{(1)}(\mathbf{r}_1, \mathbf{p}_1, t) = \left(\frac{\partial f^{(1)}}{\partial t} \right)_{\text{coll}}. \quad (1.1.39)$$

The RHS of the equation involving interaction of two particles is approximated through different schemes with a proper closing relation for the hierarchy in terms of the one-particle function. The most studied among the various approximations is the case of the Boltzmann equation in which the RHS $(\partial f^{(1)}/\partial t)_{\text{coll}}$ is approximated in terms of binary-collision contributions only. At low densities only two particles are likely to collide at a given point. The evaluation of the two-point functions before collision is done with the approximation of molecular chaos. Thus the factorization of eqn. (1.1.36) is applied. This again remains valid at low densities when successive binary collisions are completely uncorrelated. The collision of two particles at a point \mathbf{r} is governed by the laws of classical mechanics. The momenta of the particles before and that after collisions are denoted by $\{\mathbf{p}_1, \mathbf{p}_2\}$ and $\{\mathbf{p}'_1, \mathbf{p}'_2\}$, respectively. The RHS of eqn. (1.1.39) is approximated as (Dorfman, 1999)

$$\begin{aligned} \left(\frac{\partial f^{(1)}}{\partial t} \right)_{\text{coll}} &= \frac{1}{m} \int d\mathbf{p}_2 d\Omega \left(\frac{d\sigma}{d\Omega} \right) |\mathbf{p}_1 - \mathbf{p}_2| \\ &\times \left[f^{(1)}(\mathbf{r}, \mathbf{p}'_1, t) f^{(1)}(\mathbf{r}, \mathbf{p}'_2, t) - f^{(1)}(\mathbf{r}, \mathbf{p}_1, t) f^{(1)}(\mathbf{r}, \mathbf{p}_2, t) \right]. \end{aligned} \quad (1.1.40)$$

where $d\sigma/d\Omega$ denotes the differential scattering cross section in solid angle $d\Omega$ defined around the $(\mathbf{p}_1 - \mathbf{p}_2)$ vector of relative motion between the two particles before the collision.

The approximation (1.1.40) gives rise to the Boltzmann H theorem which implies that the many-particle system evolves irreversibly to an equilibrium state. The time evolution