Kinetic description of condensed media

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By means of an expansion in a parameter proportional to the small ratio of the temperature to the "binding" energy of particles in the material a kinetic equation is obtained which makes possible a rigorous description of a cold simple liquid. Problems of time irreversibility and the immediate consequences of this equation are investigated.

Systems of large numbers of interacting particles are usually so complicated that it is impossible to derive kinetic equations explicitly for them. At present the kinetic equations applicable for describing a Boltzmann gas, a weakly collisional plasma, and a number of systems which are characterized in some way by weak interactions between their component particles or quasiparticles are well known.[1–4] Many attempts have been made to go substantially beyond this category of classical systems, both some time ago[5,6] and in recent years.[7,8] These have led to a significant development in the formalism of kinetic theory (see, e.g., Ref. 9), and also to an understanding of many problems in terms of qualitatively new ideas (see, e.g., Refs. 10 and 11).

In addition, until now there has been no kinetic equation which would rigorously describe for condensed media not only the kinetics of the atomic oscillations about their equilibrium points, which in the case of, e.g., a solid body is given by the phonon description, but also substantial changes in the location of these points, i.e., in the case of a solid body would take into account the possibility of restructuring or changes in the crystal lattice. It is obvious that such an equation should also apply to the description of a cold liquid. In the present work we use an expansion in a small parameter related to the ratio of the temperature to the "binding" energy of atoms in the material, to derive such a kinetic equation. The question of the time reversibility of this equation is considered. It is shown that this kinetic equation has a family of conserved quantities associated with imperfections of the crystal lattice in the case of a solid body and with the structure of Frenkel "nuclei" and "holes" in the case of a liquid. Although the particles are assumed to obey classical mechanics in the derivation of this equation, the equation itself and its consequences differ fundamentally from the Boltzmann equation and results derived from it.

1. In what follows we will consider a system of N pairwise interacting classical particles moving in a volume V, described by the Hamiltonian

$$H=\sum_{i=1}^{N}\frac{1}{2m}\mathbf{p}_i^2+\sum_{1\le i<j\le N}U(\mathbf{r}_i-\mathbf{r}_j), \tag{1}$$

where m is the particle mass and $U(\mathbf{r}_i-\mathbf{r}_j)$ is the potential of the two-particle interaction, which we assume to be a Lennard–Jones interaction in order to be specific.

Everywhere in what follows, unless otherwise mentioned, it is assumed that the particles move in three-dimensional space.

Such a system of particles can be described systematically by an infinite hierarchy of coupled equations for the correlation functions, or equivalently, for the multiparticle distribution functions. Truncation of this system of equations is justified only in a limited number of cases, most of which reduce to the following: a) a low-density gas with a short-range repulsive interaction (the BBGKY expansion parameter is $\varepsilon=nr_0^3$, where n is the particle density and r_0 is the radius of the particle interaction); b) a weakly interacting gas (the small parameter is $\varepsilon=U/T$, where U is the typical potential energy and T is the temperature); c) a plasma with a large number N_D of particles in a Debye sphere (the small parameter is N_D^{-1}); d) a system of perfectly hard spheres (the small parameter is $\varepsilon=nR^3$, where R is the radius of a sphere and n is the number density). In all of these cases it is possible to derive a closed equation describing the function $f(t,\mathbf{r},\mathbf{v})$.

2. Unfortunately, in more complicated situations the truncation of this hierarchy of equations is not so rigorously justified. This makes it necessary to use additional physical ideas in order to look for some means of approximating the s-particle distribution functions in terms of the lower-order distributions. As examples of this we can cite the superposition approximation, the introduction of the concepts of "direct" and "indirect" correlations, etc. The possibilities of this approach have been thoroughly studied, and it is not used in the present work. Instead, we will develop a very different approach, which we now proceed to describe. The qualitative discussion in this section is necessary only to understand the motivation for the formalism derived below, and is essentially not used in the sequel.

In order to understand more complicated systems that those cited in Sec. 1, we look at the problem from a somewhat different point of view. Specifically, to study the dynamics described by the Hamiltonian (1) it is of interest to construct the one-particle trajectories $\mathbf{R}_i(t)$, and also the correlations between the trajectories of individual particles, i.e., it is necessary to find a way of describing these curves.

Of course, depending on the problem being solved it is convenient and justified to describe a set of one-particle trajectories in various "languages," ranging from attempts at solving the system of equations corresponding to the Hamil-

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tonian (1) exactly to using the Gibbs distribution. It should be noted that all of these are merely different approaches to solving an ensemble of one-particle trajectories (appropriate to a particle problem).

In other words, we must be able to answer the following questions: A) what is the probability density that in the system of particles described by Eq. (1) at time t one particle is at the point ${}^0\mathbf{r}$ with velocity ${}^1\mathbf{r}$, acceleration ${}^2\mathbf{r}$, etc., up to the kth time derivative, given by the function ${}^kF_1(t,{}^0\mathbf{r},{}^1\mathbf{r},\ldots,{}^k\mathbf{r})$?; B) how can we find the n-particle distribution functions ${}^kF_n(t,1,\ldots,n)$, where

$${}^kF_n={}^kF_n(t,{}^0\mathbf{r}_1,{}^1\mathbf{r}_1,\ldots,{}^k\mathbf{r}_1,{}^0\mathbf{r}_2,{}^k\mathbf{r}_2,\ldots,{}^0\mathbf{r}_n,{}^1\mathbf{r}_n,\ldots,{}^k\mathbf{r}_n);$$

C) how many parameters ${}^0\mathbf{r}$, ${}^1\mathbf{r},\ldots,{}^k\mathbf{r},\ldots$ must be retained in order to get a closed (in some approximation; see below) description of an ensemble of one-particle trajectories?

Let us say some additional words about questions A, B, and C. Note that if the positions and velocities of all particles are given at time t, then by using the equations of motion we can find all the higher derivatives at this time. Furthermore, the question of the probability density for a finite set of derivatives to have some set of values is well posed. The equations of motion imply that this not only characterizes the particle on a given trajectory but also its neighbors.

The number of parameters needed to provide a closed description of the ensemble of one-particle trajectories is determined (see below) by the structure of a "typical" one-particle trajectory, i.e., in the final analysis by the Hamiltonian (1), which provides an idea of the "complexity" of the molecular motion. Looking ahead we note that in the sequel it will be shown rigorously that for problems treated in the present work it is necessary to take $k=2$ [see Eqs. (20)–(25)].

As a simple example we look at the systems considered in Sec. 1 from this viewpoint. It is easy to see that the one-particle trajectories in cases a and d are accurately approximated by piecewise-linear segments, and in cases b and c are slightly curved, i.e., they can be approximated well by straight lines. This implies that to describe these systems we need only two parameters, $\mathbf{r}={}^0\mathbf{r}$ and $\mathbf{v}={}^1\mathbf{r}$.

For inhomogeneous media of the form b and c, when it is necessary to also take into account the self-consistent field, the approximate trajectories are no longer straight, but on time scales short compared with $\tau_{\text{coll}}=\omega_{\text{coll}}^{-1}$, where ω_{coll} is the collision frequency, are given by

$$\dot{\mathbf{v}}=-\frac{1}{m}\nabla_{\mathbf{r}}U(\mathbf{r},\{f\}),$$

where $U(\mathbf{r},\{f\})$ is the self-consistent potential, which is a functional of the distribution function. However, to describe an ensemble of trajectories it suffices as before to use the two parameters $\mathbf{r}$ and $\mathbf{v}$, since the next derivative (the acceleration) is given by the self-consistent field.

Note that the possibility of assigning to a particle at the point $\mathbf{r}$ an acceleration that depends on $\mathbf{r}$, the distribution function, and the interparticle potential, i.e., the possibility of introducing the usual self-consistent potential, is very exceptional. To see this it suffices to consider a simple example: a crystal in the harmonic approximation. Specifically, suppose that in a crystal with temperature T the atom at the nth site is displaced by a distance δr. In this case, as can easily be seen by expanding the motion of the atoms in normal modes, we can speak only of the probability that an atom undergoes some acceleration $\mathbf{a}$, since for δr on the order of the amplitude l_T of the thermal oscillations we have

$$\frac{\langle(\mathbf{a}-\langle\mathbf{a}\rangle)^2\rangle}{\langle\mathbf{a}\rangle^2}\sim 1. \tag{2}$$

This relation is physically transparent: the total force acting on the given atom and composed of largely canceling forces due to neighboring atoms varies rapidly as the location of a nearest neighbor changes by a quantity of order l_T, which gives rise to large fluctuations in the acceleration. Thus, the acceleration experienced by the atom in question depends not on its distribution function and those of its neighbors, but specifically on their positions at the particular time. This enables us to understand why it is impossible to derive a closed equation for the function $f(t,\mathbf{r},\mathbf{v})$ describing a crystal and why it is necessary to resort, say, to phonon language.

To conclude we note that a particle trajectory, like any smooth curve, can be approximated to arbitrarily high accuracy by a series of straight lines. However, we are interested in a certain sense in uniform approximations, i.e., those which can accurately approximate segments of one-particle trajectories corresponding to a time interval Δt. Here

$$\tau_m \ll \Delta t \ll \tau, \tag{3}$$

and τ_m and τ are some times which characterize the molecular motion, whose specific definition depends on the problem in question.

In the examples noted in Sec. 1 we have

$$\tau_m\sim\frac{r_0}{v_T},\qquad \tau\sim\frac{1}{\omega_{\text{coll}}}, \tag{4}$$

where r_0 is the range of the interparticle interaction (taking into account plasma shielding, i.e., $\tau_m\sim\omega_e^{-1}$, where ω_e is the plasma frequency), v_T is the thermal velocity, and ω_{coll} is the collision frequency.

3. We proceed to the direct derivation of the kinetic equation in question. We introduce the function

$${}^k\rho_t(\Omega)=\sum_P\prod_{q=0}^{k}\prod_{i=1}^{N}\delta({}^q\mathbf{r}_{P(i)}-\mathbf{R}_i^{(q)}(t)), \tag{5}$$

where $\mathbf{R}_i(t)$ is the trajectory of the ith particle, we have written $\mathbf{R}_i^{(q)}(t)=(d^q/dt^q)\mathbf{R}_i$, and the summation over P stands for summation over all permutations of the N elements. Here the ith element goes into $P(i)$ under the permutation P; Ω is a point in multidimensional space, i.e.,

$$\Omega=({}^0\mathbf{r}_1,{}^1\mathbf{r}_1,\ldots,{}^k\mathbf{r}_1,{}^0\mathbf{r}_2,{}^1\mathbf{r}_2,\ldots,{}^k\mathbf{r}_2,\ldots,{}^0\mathbf{r}_N,{}^1\mathbf{r}_N,\ldots,{}^k\mathbf{r}_N).$$

The evolution of the multidimensional vector $(\mathbf{R}_i^{(0)}(t),\mathbf{R}_i^{(1)}(t),\ldots,\mathbf{R}_i^{(k)}(t))$ is described by the system of equations $(k\geqslant 1)$

$$\frac{d}{dt}\mathbf{R}_i^{(0)}=\mathbf{R}_i^{(1)}, \quad \frac{d}{dt}\mathbf{R}_i^{(1)}=\mathbf{R}_i^{(2)}, \quad \ldots \quad , \frac{d}{dt}\mathbf{R}_i^{(k)}=\mathbf{U}_i^{(k+1)}, \tag{6}$$

where $\mathbf{U}_i^{(k+1)}$ is defined by induction as follows:

$$\mathbf{U}_i^{(2)}=-\frac{1}{m}\nabla_i \sum_{j=1,j\neq i}^{N} \mathbf{U}(\mathbf{R}_i^{(0)}-\mathbf{R}_j^{(0)}), \tag{7}$$

$$\mathbf{U}_i^{(p+1)}=\sum_{j=1}^{N}\sum_{q=0}^{p-2}\left(\mathbf{R}_j^{(q+1)},\frac{\partial}{\partial \mathbf{R}_j^{(q)}}\right)\mathbf{U}_i^{(p)}, \quad \text{where } p\geqslant 2. \tag{8}$$

Expressions (6)–(8) are obtained simply by successive differentiation with respect to time of the equations of motion of the system (1).

Note that Eqs. (6) yield an analog of Liouville's Theorem: the volume corresponding to the element

$$\prod_{i=1}^{N}\prod_{q=0}^{k} d\mathbf{R}_i^{(q)},$$

is conserved, where we have used the notation $d\mathbf{r}=dr_1dr_2dr_3$ for an arbitrary three-component vector $\mathbf{r}=(r_1,r_2,r_3)$.

Using (5) and (6) we find the equation describing the evolution of ${}^k\rho_t$:

$$\left[\frac{\partial}{\partial t}+\sum_{q=0}^{k-1}\sum_{i=1}^{N}\left({}^{(q+1)}\mathbf{r}_i,\frac{\partial}{\partial({}^q\mathbf{r}_i)}\right) +\sum_{i=1}^{N}\left(\mathbf{U}_i^{(k+1)},\frac{\partial}{\partial({}^k\mathbf{r}_i)}\right)\right]{}^k\rho_t=0. \tag{9}$$

Note that $\mathbf{U}_i^{(k+1)}$ does not depend on $\mathbf{R}_j^{(k)}$ for $k\geqslant 1$, where i and j are arbitrary integers such that $1\leqslant i\leqslant N$ and $1\leqslant j\leqslant N$. This means that after integrating (9) by parts, we obtain a chain of equations for the multiparticle distribution function

$${}^kF_p=\frac{1}{(N-p)!}\int {}^k\rho_t(\Omega)\prod_{i=p+1}^{N}\prod_{q=0}^{k} d({}^q\mathbf{r}_i), \tag{10}$$

specifically

$$\left(\frac{\partial}{\partial t}+\sum_{j=1}^{p}\sum_{q=0}^{k-1}\left({}^{(q+1)}\mathbf{r}_j,\frac{\partial}{\partial({}^q\mathbf{r}_j)}\right)+\sum_{j=1}^{p}\left(\mathbf{U}_j^{(k+1)}\right.\right.$$
$$\left.\left.\times(p),\frac{\partial}{\partial({}^k\mathbf{r}_j)}\right)\right){}^kF_p=-\int\sum_{j=1}^{p}\left(\mathbf{U}^{(k+1)}(j,p\right.$$
$$\left.+1),\frac{\partial}{\partial({}^k\mathbf{r}_j)}\right){}^kF_{p+1}(t,1,\ldots,p,p+1)\prod_{q=0}^{k} d({}^q\mathbf{r}_{p+1}), \tag{11}$$

where $\mathbf{U}^{(k+1)}(j,i)$ is obtained according to (7) and (8) by retaining in the right-hand side of Eq. (7) for $\mathbf{U}_j^{(2)}$ the single term $\mathbf{U}(\mathbf{R}_j^{(0)}-\mathbf{R}_i^{(0)})$ with the single change in notation $\mathbf{R}_j^{(q)}\rightarrow{}^q\mathbf{r}_j$ and $\mathbf{R}_i^{(q)}\rightarrow{}^q\mathbf{r}_i$—for $q=0$, $k-1$; in addition we have the relation

$$\mathbf{U}_j^{(k+1)}(p)=\sum_{i=1,i\neq j}^{p}\mathbf{U}^{(k+1)}(j,i),$$

which defines the notation $\mathbf{U}_j^{(k+1)}(p)$.

The linearity of (9) implies that if ${}^k\rho_t(\Omega)$ is an arbitrary function such that the expression ${}^k\rho_t(\Omega)d\Omega$ is proportional to the probability that at time t the state of the system is located in an infinitesimal volume $d\Omega$ near the point Ω and the function ${}^kF_p$ is given by expression (10), then Eq. (11) continues to hold for them. In what follows Eqs. (11) are interpreted only in this sense.

The hierarchy of equations (11) is a generalization of the well-known BBGKY hierarchy, which is obtained in the limit $k=1$. [It is true that when the BBGKY hierarchy is employed one usually uses a normalization of the multiparticle distribution function which differs from that employed in (10)].

We emphasize again that in order to investigate different systems of particles it is convenient to choose different values of the number k.

4. Before proceeding to study the low-temperature kinetics we must discuss the question of the choice of the system ensemble which we intend to describe by the multiparticle distribution functions. A simple but rather artificial example which rigorously demonstrates the need to make a reasonable choice of the ensemble is given in the appendix. There it is shown that the multiparticle distribution functions are just characteristics of the ensemble of particle systems they describe. In order that the results obtained using them describe an individual representative of the ensemble so as to make physical sense, the choice of the ensemble as a whole must be subjected to certain restrictions. The requirements imposed on the ensemble can be represented in various ways. For example, we can require that certain relations between the multiparticle distribution functions hold (here, of course, relationships which are maintained as the ensemble evolves have special significance; in this connection we recall the Boltzmann condition of molecular chaos or the principle of decay of correlations). Naturally, this question can be put in a different way: does there correspond to each set of initial data, i.e., to each representative, some ensemble of particle systems which adequately describes its dynamics? In view of these remarks we proceed to consider specific examples which will be studied in the present work.

We assume that kinetic processes in a crystal are being studied. What restrictions must be imposed on the ensemble of systems in this case? It is obvious that the ensemble must contain only systems with precisely the same position of the crystal lattice or one that differs over distances much less than the amplitude of the thermal oscillations, since then the ensemble can be interpreted as the state of a single crystal under conditions such that we do not have exact information about the position of each atom and must resort to a probabilistic description. But if we assume that the ensemble contains a system of particles with different positions of the crystal lattice, then we can construct ensembles for which the one-particle distribution function does not depend on position or has an arbitrary preassigned period. This means that we cannot interpret the results in terms of a single crystal only. To the other restrictions imposed on the ensemble we must add requirements associated with the closeness of the systems that compose it in terms of energy.

It is noteworthy that when we use phonon terminology to describe kinetic processes in a crystal, an ensemble of systems in which the crystal lattice has the same position for each representative is used from the very beginning, which is guaranteed by expanding in small displacements of an atom about its equilibrium position.

As will be shown below, when we go over to the case of a liquid the situation regarding the construction of an adequate ensemble remains essentially unchanged. That is, a liquid is uniform only when we average over times much larger than

$$\tau=\sigma/v_T, \tag{12}$$

where v_T is the thermal velocity and σ is the characteristic scale length of the interatomic interaction potential; here we have assumed $n\sigma^3\sim 1$, where n is the atomic density. On the other hand, the atoms are located in the potential produced by their immediate neighbors with a characteristic magnitude U_S. If

$$\varepsilon=\left(\frac{T}{U_S}\right)^{1/2}\ll 1 \tag{13}$$

then they undergo oscillations at the natural frequency

$$\omega_0\sim\left(\frac{U_S}{m\sigma^2}\right)^{1/2}. \tag{14}$$

It is then easy to see that

$$\tau_m=\frac{1}{\omega_0}\ll\tau=\frac{\sigma}{v_T}. \tag{15}$$

In what follows we will use the notation n, σ, U_S, v_T, ω_0, τ_m, τ, ε for the same quantities in the solid state as well unless otherwise noted. Equation (13) constitutes a simple restriction on the range of temperatures, and in the present work is always assumed to hold.

From this physical picture of the atomic motion in a liquid it follows that at times much less than τ [cf. Eqs. (12) and (15)] their motion is similar to that of atoms in a solid body. This means that ensembles of systems appropriate for describing these two different media should be constructed in a similar fashion. To construct an ensemble suitable for describing both media we take an arbitrary nonnegative function $\varphi(t)$ which increases monotonically in the interval from $-\infty$ to 0 and falls off monotonically in the interval from 0 to $+\infty$ so that

$$\int_{-\infty}^{+\infty}\varphi(t)dt=1$$

holds, and the characteristic time scale τ_φ of the function $\varphi(t)$ satisfies the inequality

$$\tau_m=\frac{1}{\omega_0}\ll\tau_\varphi\ll\tau=\frac{\sigma}{v_T}. \tag{16}$$

We introduce the quantity

$${}^k\rho_t^*(\Omega)=\int_{-\infty}^{+\infty}\varphi(t-\tau)\,{}^k\rho_\tau(\Omega)d\tau, \tag{17}$$

where ${}^k\rho_t(\Omega)$ is given by (5).

To obtain a smooth ${}^k\rho_t^*(\Omega)$ we can, e.g., perform further averaging over the initial particle velocities and positions. Then the width Δv in velocity and the width Δr in position of allowable distributions of the initial conditions satisfy the inequalities

$$\Delta v\ll v_T,\quad \Delta r\ll l_T=\tau_m v_T\ll\sigma, \tag{18}$$

where l_T is the amplitude of the thermal oscillations.

The quantity ${}^k\rho_t^*(\Omega)$ resulting from these operations specifies the ensemble which we study. It is easy to discern the close relationship between the ensembles constructed here and the quasiaverages which are widely used in thermodynamics.[4] This is of course completely natural.

From (17) it follows that this ensemble describes the motion of individual particles, in some sense averaged over a time interval of order τ_φ. On the other hand, the average over the initial conditions satisfying (18) causes the representatives of the ensemble to be close both in energy and in location of the crystal lattice or in the local density distribution (at least initially) in the liquid. In what follows it is extremely important to understand that even at times $t=+\infty$, i.e., after thermal equilibrium is established, and even when ${}^k\rho_t^*(\Omega)$ satisfies the inequalities (18), the distribution functions of the ensemble (17) can be time-dependent. This is not at all inconsistent with the Gibbs distribution: the Gibbs distribution would result if we used sufficiently large τ_φ in (17) (strictly speaking, if we took the limit $\tau_\varphi\to+\infty$), which in no way guarantees that the restriction imposed above in Eq. (16) is satisfied. Time-independent distribution functions corresponding to the Gibbs distribution can be obtained from the distribution functions of the ensemble (17) by additional averaging of the latter over a sufficiently long time interval. The time dependence of these distribution functions is studied in detail in Secs. 8 and 9.

5. Let us write down the first equation in (11) for $k=1$:

$$(\partial_t+\mathbf{v}_1\partial_{\mathbf{r}_1})^1F_1(t,1)=-\mathrm{div}_{\mathbf{v}_1}\int\partial_{\mathbf{r}_1}U(\mathbf{r}_1-\mathbf{r}_2)\times{}^1F_2(t,1,2)d\mathbf{r}_2d\mathbf{v}_2 \tag{19}$$

and the first two equations of (11) for $k=2$:

$$(\partial_t+\hat{L}_1)F_1(t,1)=-\mathrm{div}_{\mathbf{a}_1}\int\mathbf{K}_{12}F_2(t,1,2)d2, \tag{20}$$

$$(\partial_t+\hat{L}_1+\hat{L}_2+\hat{L}_{12})F_2(t,1,2)=-\mathrm{div}_{\mathbf{a}_1}\int\mathbf{K}_{13}F_3(t,1,2,3)d3-\mathrm{div}_{\mathbf{a}_2}\int\mathbf{K}_{23}F_3(t,1,2,3)d3, \tag{21}$$

where

$$F_1(t,1)={}^2F_1(t,1),\quad F_2(t,1,2)={}^2F_2(t,1,2),$$

$$F_3={}^2F_3(t,1,2,3),\quad {}^0\mathbf{r}_i=\mathbf{r}_i,\quad {}^1\mathbf{r}_i=\mathbf{v}_i,$$

$${}^2\mathbf{r}_i=\mathbf{a}_i,\quad L_i=\mathbf{v}_i\partial_{\mathbf{r}_i}+\mathbf{a}_i\partial_{\mathbf{v}_i},$$

$$\mathbf{K}_{12}=-\frac{1}{m}(\mathbf{v}_1-\mathbf{v}_2,\partial_{\mathbf{r}_1})\partial_{\mathbf{r}_1}U(\mathbf{r}_1-\mathbf{r}_2),$$

$$\hat{L}_{12}=\mathbf{K}_{12}(\partial_{\mathbf{a}_1}-\partial_{\mathbf{a}_2}).$$

When condition (13) holds, by using, say, the Gibbs distribution we can easily see that the *i*th atom is near (within a distance of order l_T) the point $\mathbf{r}_i^*$, which ensures at least a local minimum of the potential due to the neighbors of the *i*th atom, i.e.,

$$\nabla_{\mathbf{r}_i}\sum_{j=1,j\neq i}^{N}U(\mathbf{r}_i-\mathbf{r}_j)\bigg|_{\mathbf{r}_i=\mathbf{r}_i^*}=0. \tag{22}$$

Note that $\mathbf{r}_i^*$ is a function of time; moreover, we can assert that

$$\left|\frac{d\mathbf{r}_i^*}{dt}\right|\lesssim v_T.$$

The points $\mathbf{r}_i^*(t)$ move differently in liquids and solids, but this plays no part in the following discussion. The important thing is merely to note that in a sphere with center at the point $\mathbf{r}_i^*(t)$ and radius R,

$$l_T\ll v_T\tau_\varphi\ll R\ll\sigma,$$

there is necessarily one and only one particle (recall that $n\sigma^3\sim 1$).

It is easy to see that the *i*th atom experiences an acceleration of order $\omega_0 v_T$ [see Eqs. (13) and (14) and the comment following (15)], i.e., it is small at low temperatures, but is a sum of large quantities of order

$$\frac{1}{m}\frac{U_0}{\sigma}, \tag{23}$$

which largely cancel one another. Here U_0 is the typical value of the interatomic potential.

This cancellation of large quantities is a serious complication for the study of the low-temperature kinetics using Eqs. (11) with $k=1$. Specifically, in accordance with the foregoing remarks, the contributions to the integral appearing in the right-hand side of (19) from the separate parts of the integration region are not individually small, but they almost completely cancel one another, leaving only a quantity of order $\omega_0 v_T$ [see Eq. (13)]. That is, even a relatively small error in ${}^1F_2$ can lead to a considerable change in the value of this integral.

If we take $k=2$ in Eq. (11) the situation changes considerably. The derivative a_i of the acceleration of the *i*th atom is a quantity of order $\omega_0^2 v_T$,

$$\mathbf{a}_i=-\frac{1}{m}\sum_{j=1,j\neq i}^{N}(\mathbf{v}_i-\mathbf{v}_j,\partial_{\mathbf{r}_i})\partial_{\mathbf{r}_i}U(\mathbf{r}_i-\mathbf{r}_j), \tag{24}$$

i.e., this quantity is composed of terms of order

$$\frac{1}{m}\frac{U_0}{\sigma^2}v_T, \tag{25}$$

which, like their sum, decrease as the temperature is reduced.

In consequence of this, we consider below only the case $k=2$. Note that the following relations hold (see the explanation below):

$$\int_{D_j}F_2(t,1_i,2_j)d2=F_1(t,1_i);\quad \int_{D_j}F_1(t,2_j)d2=1, \tag{26}$$

$$\int_{D_j}\mathbf{v}_2F_2(t,1_i,2_j)d2=F_1(t,1_i)\int_{D_j}\mathbf{v}_2F_1(t,2_j)d2, \tag{27}$$

$$\int_{D_k}F_3(t,1_i,2_j,3_k)d3=F_2(t,1_i,2_j), \tag{28}$$

$$\int_{D_k}\mathbf{v}_3F_3(t,1_i,2_j,3_k)d3$$
$$=F_2(t,1_i,2_j)\int_{D_k}\mathbf{v}_3F_1(t,3_k)d3, \tag{29}$$

where 1_i signifies $|\mathbf{r}_1-\mathbf{r}_i^*|\ll\sigma$, while no restrictions are placed on $\mathbf{a}_1$ and $\mathbf{v}_1$; the integration over D_j means taking the integral over all $\mathbf{v}_2$ and $\mathbf{a}_2$ in Eqs. (26) and (27) [over $\mathbf{v}_3$ and $\mathbf{a}_3$ in Eqs. (28) and (29)] and with respect to $\mathbf{r}_2$ [$\mathbf{r}_3$ in Eqs. (28) and (29)] over the sphere with center $\mathbf{r}_j^*$ [$\mathbf{r}_k^*$ in Eqs. (28) and (29)] and radius R such that $v_T\tau_\varphi\ll R\ll\sigma$; in Eqs. (26)–(29) it is assumed that $i\neq j\neq k$.

Equation (26) becomes obvious if we note that the configuration-space sphere with center at the point $\mathbf{r}_j^*$ and the radius R specified above [see Eqs. (16) and (17) and the comment following (22)] contains exactly one particle (arbitrarily labeled *j*) with unit probability [to within terms which are exponentially small in ε, defined in Eq. (13)]. In the derivation of the first of Eqs. (26) it is important to use the fact that $i\neq j$.

Equation (27) is more complicated and has important physical content. Note that the function

$$\int F_2(t,1_i,2_j)d\mathbf{a}_2d\mathbf{r}_2, \tag{30}$$

where the integral is taken over all $\mathbf{a}_2$ and over $\mathbf{r}_2$ within the specified sphere, is proportional to the probability density that a single particle, arbitrarily labeled *i*, is located at the point $\mathbf{r}_1$ with velocity $\mathbf{v}_1$ and acceleration $\mathbf{a}_1$, while another particle, arbitrarily labeled *j*, has velocity $\mathbf{v}_2$. Let us ascertain the extent to which the "state" of particle *i* is "coupled" to the velocity of particle *j*. Suppose that we know the positions and velocities of all the particles at time $t=0$. Noting that the neighboring particles, separated by distances of order $n^{-1/3}\sim\sigma$, "mix" their velocities due to interactions over a time of order ω_0^{-1} we can easily see that the process by which the mixing of the particle velocities occurs propagates through space with velocity

$$v\sim\omega_0\sigma.$$

We can therefore assert that after a time of order $\Delta t \gg \omega_0^{-1}$ the velocity of the *j*th particle depends approximately equally on the initial conditions for the particles throughout a sphere of radius $r(\Delta t)$, where

$$r(\Delta t)\sim v\Delta t\sim \omega_0\sigma\Delta t,$$

i.e., the velocity $\mathbf{v}_j(\Delta t)$ of the *j*th particle at a time Δt depends on $\sim 6N(\Delta t)$ variables where

$$N(\Delta t)\sim nr^3(\Delta t)\sim(\omega_0\Delta t)^3$$

is the number of particles in a sphere of radius $r(\Delta t)$. If we change the velocity of the *j*th particle by a quantity of order v_T or its position by a quantity of order l_T at time $t=0$, then the subsequent motion of this particle will be altogether different, i.e., $\mathbf{v}_j(\Delta t)$ also changes by a quantity of order v_T. Since $\mathbf{v}_j(\Delta t)$ depends approximately equally on the initial conditions for the particles in a sphere of radius $r(\Delta t)$, it follows that changing any of the $N(\Delta t)$ velocities or $N(\Delta t)$ positions on which $\mathbf{v}_j(\Delta t)$ depends sensitively by a quantity of order v_T or l_T respectively alters $\mathbf{v}_j(\Delta t)$ by a quantity of order v_T, i.e.,

$$\frac{\partial \mathbf{v}_j(\Delta t)}{\partial \mathbf{v}_i(0)}\sim 1,\quad \frac{\partial \mathbf{v}_j(\Delta t)}{\partial \mathbf{r}_i(0)}\sim\frac{v_T}{l_T}\sim\omega_0,$$

where $v_i(0)$ and $\mathbf{r}_i(0)$ are the initial velocity and position of the *i*th particle belonging to the specified sphere. In consequence of this we find that a change in the initial velocities and positions in this sphere by amounts of order $v_T/N(\Delta t)$ and $l_T/N(\Delta t)$ significantly changes $v_j(\Delta t)$.

Consequently, it is easy to see that the effect of the *i*th particle on the velocity of the *j*th particle is of order

$$1/N(\Delta t).$$

From the definition of our ensemble [see Eqs. (16) and (17)] we find that in the present problem we must set

$$\Delta t\sim\tau_\varphi,$$

and hence

$$N(\tau_\varphi)\sim(\omega_0\tau_\varphi)^3.$$

Thus, taking, e.g.,

$$\tau_\varphi\lesssim\left(\frac{\sigma}{\omega_0 v_T}\right)^{1/2},$$

which satisfies (16), we find that the effect of the state of the *i*th particle on the velocity of the *j*th particle is determined in our ensemble by the quantity

$$\left(\frac{v_T}{\omega_0\sigma}\right)^{3/2}\sim\varepsilon^{3/2},$$

i.e., it is negligible [see Eq. (13)]. This means we can rewrite (30) in the form

$$\int F_2(t,1_i,2_j)d\mathbf{r}_2d\mathbf{a}_2=F_1(t,1_i)\int F_1(t,2_j)d\mathbf{r}_2d\mathbf{a}_2,$$

where the integral is taken over the region specified following Eq. (30); this expression immediately yields (27).

Let us add some further comments regarding (27). We express the velocity of the *i*th particle in the form of a rapidly varying part $\mathbf{v}_f$ with characteristic time scale much less than τ_φ and a slowly varying part $\mathbf{v}_s$ with characteristic time scale greater than or of order τ_φ. The "slow" part of the velocity is associated with the long-wavelength motions of the medium, which are approximately the same at nearby atoms. That is to say, the functions

$$\int F_1(t,1_i)d\mathbf{r}_1d\mathbf{a}_1\quad\text{and}\quad\int F_1(t,2_j)d\mathbf{r}_2d\mathbf{a}_2,\tag{31}$$

where the integrals are carried out as indicated in (30), are strongly coupled if the points $\mathbf{r}_i^*$ and $\mathbf{r}_j^*$ are close to one another; the quantity $\mathbf{v}_s$ is determined by all the particles in the sphere of radius $\omega_0\tau_\varphi\sigma$, i.e., the *j*th particle has little effect on it. To avoid confusion it is necessary to clearly understand the difference between the dependence of the velocity $\mathbf{v}_i$ of the *i*th particle on $\mathbf{v}_j$, i.e., the velocity of the *j*th particle, and the relationship between the functions (31).

Note that it follows from the Gibbs distribution that in a state of thermodynamic equilibrium the velocity of a particle is uncorrelated with the positions and velocities of other particles [cf. the Hamiltonian (1)]. It is easy to see that the latter is related in a certain way to the above results, but is by no means identical.

Note that (27) is valid only after the initial correlations decay, i.e., after the passage of a time long in comparison with ω_0^{-1}. It is necessary to take this into account in Eqs. (32)–(38) (see below) in estimating their range of applicability. Note that Eqs. (26) and (27) do not imply at all that

$$F_2(t,1,2)=F_1(t,1)F_1(t,2)$$

for $|\mathbf{r}_1-\mathbf{r}_2|\sim\sigma$; furthermore, it follows from the results of Sec. 8 that this is not even true.

6. Using Eqs. (26)–(29) we find closed equations for the functions F_1 and F_2. If we note that according to Eqs. (16) and (17) the spatial width of the maxima of the functions F_2 and F_3 is limited by

$$v_T\tau_\varphi\ll\sigma,$$

and using Eqs. (20), (26), and (27), we find

$$(\partial_t+\hat{L}_1)F_1(t,1)=-\operatorname{div}_{\mathbf{a}_1}\int \mathbf{K}_{12}\theta_{12}F_1(t,2)d2,\tag{32}$$

where θ_{12} is a function introduced to exclude "self-action." It can be defined, e.g., as follows:

$$\theta_{12}=\begin{cases}1, & |\mathbf{r}_1-\mathbf{r}_2|>r_0\\ 0, & |\mathbf{r}_1-\mathbf{r}_2|<r_0\end{cases},\tag{33}$$

where $v_T\tau_\varphi\ll r_0\ll\sigma$ and $U(r_0)-U_{\min}\gg T$, and $U_{\min}$ is the minimum value of the interatomic interaction potential.

Using Eqs. (21) and (26)–(29) we find an equation describing $F_2(t,1,2)$:

$$\begin{aligned}\partial_t+\hat{L}_1+\hat{L}_2+\hat{L}_{12})F_2(t,1,2)\\ =-\operatorname{div}_{\mathbf{a}_1}F_2(t,1,2)\int \theta_{123}\mathbf{K}_{13}F_1(t,3)d3\\ -\operatorname{div}_{\mathbf{a}_2}F_2(t,1,2)\int \theta_{123}\mathbf{K}_{23}F_1(t,3)d3,\end{aligned}\tag{34}$$

where θ_{123} is a function introduced to exclude self-action; it can be defined, e.g., by $\theta_{123}=\theta_{13}\theta_{23}$ [cf. Eq. (33)].

From (20) it follows that

$$F_1(t,1)=F_1\left(t_0,\mathbf{r}_1+\mathbf{v}_1(t_0-t)+\frac{\mathbf{a}_1}{2}(t_0-t)^2,\mathbf{v}_1+\mathbf{a}_1\times(t_0-t),\mathbf{a}_1\right)-\int_0^{t-t_0}e^{-\tau\hat{L}_1}\mathrm{div}_{\mathbf{a}_1}\int\mathbf{K}_{13}F_2\times(t-\tau,1,3)d3d\tau, \tag{35}$$

where t_0 is an arbitrary time. Noting that

$$\lim_{\mathbf{v}_1\to\infty}F_1(t,1)=\lim_{\mathbf{v}_1\to\infty}F_2(t,1,2)=0,$$

and hence

$$\lim_{t\to\infty}F_1\left(t_0,\mathbf{r}_1+\mathbf{v}_1t+\frac{\mathbf{a}_1}{2}t^2,\mathbf{v}_1+\mathbf{a}_1t,\mathbf{a}_1\right)=0,$$

we find for sufficiently large values of t (see below)

$$F_1(t,1)=-\int_0^{+\infty}e^{-\tau\hat{L}_1}\mathrm{div}_{\mathbf{a}_1}\int\mathbf{K}_{13}F_2(t-\tau,1,3)d3d\tau. \tag{36}$$

The limiting process which yields (36) is nonuniform. This, however, causes no problems in what follows, and we will not go into this rather delicate point in more detail.

Equation (36) has no analog in the treatment of conventional kinetic equations, i.e., those obtained from the usual BBGKY hierarchy, which corresponds in our case to $k=1$.

Taking into consideration that the acceleration is typically of order $\omega_0 v_T$ we can regard Eq. (36) as justified for

$$t-t_0\gg\omega_0^{-1}. \tag{37}$$

The time scale on which $F_1(t,1)$ and $F_2(t,1,2)$ vary, however, is at least of order τ_φ [cf. Eqs. (10) and (17)], which enables us to simplify Eq. (36) somewhat and to write

$$F_1(t,1)=-\int_0^{+\infty}e^{-\tau\hat{L}_1}\mathrm{div}_{\mathbf{a}_1}\int\mathbf{K}_{13}F_2(t,1,3)d3d\tau. \tag{38}$$

It is of interest to note that after the time interval (37) has passed the functions F_1 and F_2 evolve so as to produce (38), and consequently make the right-hand side of (38) nonnegative, i.e., the function $F_2(t,1,2)$ on the right-hand side of this expression is subject to some severe restrictions.

The action of the operator $e^{-\tau\hat{L}_1}$ is very simple and can be written as follows:

$$F_1(t,1)=-\int_0^{+\infty}d\tau\int d3(\mathbf{K}_{13},\nabla_{\mathbf{a}_1}F_2(t,1,3))\times\left|\begin{array}{l}\mathbf{r}_1\to\mathbf{r}_1-\mathbf{v}_1\tau+\dfrac{\mathbf{a}_1}{2}\tau^2,\\ \mathbf{v}_1\to\mathbf{v}_1-\mathbf{a}_1\tau\end{array}\right. \tag{39}$$

where the indicated values are substituted into the scalar product after the differentiation with respect to $\mathbf{a}_1$ is carried out.

Substitution of (38) into (34) yields a closed equation for F_2.

7. Before continuing our discussion we write down equations for the functions F_1 and F_2 for future reference:

$$(\partial_t+\hat{L}_1)F_1(t,1)=-\mathrm{div}_{\mathbf{a}_1}F_1(t,1)\int\theta_{13}\mathbf{K}_{13}F_1(t,3)d3, \tag{40}$$

$$(\partial_t+\hat{L}_1+\hat{L}_2+\hat{L}_{12})F_2(t,1,2)=P(t,1,2)+P(t,2,1), \tag{41}$$

where

$$P(t,1,2)=\mathrm{div}_{\mathbf{a}_1}F_2(t,1,2)\int\int_0^{+\infty}\int\theta_{123}\mathbf{K}_{13}e^{-\tau\hat{L}_3}\times(\mathbf{K}_{34},\nabla_{\mathbf{a}_3}F_2(t,3,4))d3d4d\tau. \tag{42}$$

In addition, Eq. (38), which expresses $F_1(t,1)$ in terms of $F_2(t,1,2)$, also holds.

Note that Eqs. (6) contain solutions which do not correspond to any real particle motions described by the Hamiltonian (1). This implies that additional conditions must be imposed on the functions ${}^kF_p$ to exclude distribution functions associated with these nonexistent motions. Using (1) we find

$$\ddot{\mathbf{r}}_i=-\frac{1}{m}\nabla_{\mathbf{r}_i}\sum_{j=1,j\neq i}^{N}U(\mathbf{r}_i-\mathbf{r}_j). \tag{43}$$

From Eqs. (5), (10), and (43) we find

$$\mathbf{a}_1F_1(t,1)+\frac{1}{m}\int\frac{\partial U(\mathbf{r}_1-\mathbf{r}_2)}{\partial\mathbf{r}_1}F_2(t,1,2)d2=0. \tag{44}$$

Taking into account Eqs. (38) and (44) we arrive at the following condition:

$$\mathbf{a}_1\int_0^{+\infty}d\tau\int e^{-\tau\hat{L}_1}(\mathbf{K}_{12},\nabla_{\mathbf{a}_1}F_2(t,1,2))d2=\frac{1}{m}\int\frac{\partial U(\mathbf{r}_1-\mathbf{r}_2)}{\partial\mathbf{r}_1}F_2(t,1,2)d2. \tag{45}$$

Condition (45) always holds if it holds initially, i.e., (45) is actually a restriction on the choice of initial conditions for Eq. (41).

Turning to Eq. (10), the comments following Eq. (38), and Eq. (45), we find that in order to obtain a physically meaningful Cauchy problem for Eq. (41) we must impose the following conditions on the choice of the initial data, i.e., on the function $F_2(t=0,1,2)$:

$$F_2(t=0,1,2)=F_2(t=0,2,1)\geqslant 0, \tag{46}$$

$$\frac{1}{N}\int F_2(t=0,1,2)d2=-\int_0^{+\infty}\int e^{-\tau\hat{L}_1}$$

$$\times(\mathbf{K}_{12},\nabla_{\mathbf{a}_1}F_2(t=0,1,2))d2d\tau, \qquad (47)$$

$$\mathbf{a}_1\int_0^{+\infty}d\tau\int e^{-\tau\hat{L}_1}(\mathbf{K}_{12},\nabla_{\mathbf{a}_1}F_2(t=0,1,2))d2$$

$$=\frac{1}{m}\int\frac{\partial U(\mathbf{r}_1-\mathbf{r}_2)}{\partial\mathbf{r}_1}F_2(t,1,2)d2, \qquad (48)$$

$$\int F_2(t=0,1,2)d1d2=N^2, \qquad (49)$$

where N is the number of particles in the system [cf. Eq. (1)].

The Cauchy problem for Eq. (40) is physically meaningful only when the function $F_1(t=0,1)$ chosen as the initial condition corresponds to a function $F_2(t=0,1,2)$ which satisfied (46)–(49), for which

$$F_1(t=0,1)=\frac{1}{N}\int F_2(t=0,1,2)d2. \qquad (50)$$

If Eqs. (46)–(50) hold initially they remain valid thereafter.

We point out once more why the restrictions (46)–(50) arise: Eqs. (46), (49), and (50) follow from (10); Eq. (47) is a consequence of "discarding" the initial time interval (37) during which F_1 and F_2 change so as to satisfy (38) when we study the evolution of the system; Eq. (48) was introduced to exclude the nonexistent motions contained in Eq. (6).

8. The reversibility of Eqs. (40) and (41) in this situation can be interpreted in different ways. The first is the answer to the question, do the functions F_1 and F_2 satisfying (40) and (41) respectively go over to functions which again satisfy (40) and (41) under time inversion, i.e., under the transformation

$$\begin{aligned}&t\rightarrow -t,\\ &\mathbf{r}\rightarrow\mathbf{r},\\ &\mathbf{v}\rightarrow-\mathbf{v},\\ &\mathbf{a}\rightarrow\mathbf{a}.\end{aligned} \qquad (51)$$

The second meaning of reversibility is the answer to the following question: suppose that the initial conditions $F_1(t=0,\mathbf{r}_1,\mathbf{v}_1,\mathbf{a}_1)$ [or $F_2(t=0,\mathbf{r}_1,\mathbf{v}_1,\mathbf{a}_1,\mathbf{r}_2,\mathbf{v}_2,\mathbf{a}_2)$] correspond to a physically meaningful Cauchy problem [cf. Eqs. (46)–(50)]. Then do the functions $F_1(t=0,\mathbf{r}_1,-\mathbf{v}_1,\mathbf{a}_1)$ [or $F_2(t=0,\mathbf{r}_1,-\mathbf{v}_1,\mathbf{a}_1,\mathbf{r}_2,-\mathbf{v}_2,\mathbf{a}_2)$] correspond to a similar Cauchy problem? For simplicity in what follows we will use the following notation:

$$\hat{T}F_1(t,1)=F_1(-t,\mathbf{r}_1,-\mathbf{v}_1,\mathbf{a}_1),$$

$$\hat{T}F_1(t=0,1)=F_1(t=0,\mathbf{r}_1,-\mathbf{v}_1,\mathbf{a}_1),$$

and similar notations for the function F_2.

We recall that the Boltzmann equation is irreversible in time in the first sense because the collisional term is even under the transformation (51).

Admissible initial data for the Boltzmann equation need only satisfy the relation

$$\int f(t=0,\mathbf{r}_1,\mathbf{v}_1)d\mathbf{r}_1 d\mathbf{v}_1=N, \qquad (52)$$

i.e., in the second sense the Boltzmann equation is trivially reversible. Equation (52) is so simple that the question of reversibility of the Boltzmann equation in the second sense is usually not even raised.

It is easy to see that if the function $F_1(t,1)$ satisfies Eq. (40), then the function $\hat{T}F_1(t,1)$ must also satisfy (40), i.e., Eq. (40) is reversible in the first sense. But the fact that $F_2(t,1,2)$ satisfies (41) does not imply that $\hat{T}F_2(t,1,2)$ satisfies (41) also, i.e., Eq. (41) is time-irreversible in the first sense. The formal reason for this irreversibility is quite obvious: the derivation of Eq. (38) from (35) involved a limiting process. Furthermore, the reversibility of (40) and the irreversibility of (41) necessiate a much more careful analysis.

We will now clarify the physical content of these results, which appear somewhat strange at first glance. Irreversibility is closely connected to the way the system "forgets" initial correlations, i.e., the way initial conditions are "forgotten" in the approach to thermal equilibrium. Moreover, in this case by no means all the initial conditions (correlations) are forgotten. In fact, it is easy to see that, say, in a crystal the correlations in velocity and displacement from the initial positions of the different atoms are quickly forgotten, but information about the position of the crystal lattice is retained in its entirety through the function

$$\int F_1(t,1)d\mathbf{v}_1 d\mathbf{a}_1.$$

In the case of a liquid the quantity $\int F(t,1)d\mathbf{V}_1 d\mathbf{a}_1$ gives the local density and is also closely related to the local density at the initial time. Note that this picture corresponds to the results derived on the behavior of the solutions of Eqs. (40) and (41) under time reversal: the reversibility of Eq. (40) retains information, e.g., about the initial position of the crystal lattice, while the irreversible evolution of F_2 is associated with the forgetting of correlations, e.g., in velocity or deviation of the particles from their equilibrium position. Note that if ${}^kF_p$ evolves irreversibly, it follows from [see Eq. (10)]

$${}^kF_p=\frac{1}{N-p}\int {}^kF_{p+1}(t,1,\ldots,p,p+1)d(p+1),$$

that ${}^kF_{p+1}$ evolves more irreversibly. The converse is in general false, since the contribution of the irreversible correlations ${}^kF_{p+1}$ to the right-hand side of this identity can vanish.

The way certain correlations are "remembered" can of course be expressed as a conservation law. Consider the function

$$W(z,t)=\frac{1}{V}\int w(z,t,\mathbf{r})d\mathbf{r}, \qquad (53)$$

where

$$w(z,t,\mathbf{r})=\int \theta(\ln F_1(t,\mathbf{r},\mathbf{v},\mathbf{a})-z)d\mathbf{v}d\mathbf{a}, \tag{54}$$

with

$$\theta(x)=\begin{cases}1, & x\geqslant 0\\ 0, & x<0\end{cases}.$$

Using Eq. (40) we find

$$\partial_t w(z,t,\mathbf{r})+\mathrm{div}_{\mathbf{r}}\mathbf{j}(z,t,\mathbf{r})=0, \tag{55}$$

where

$$\mathbf{j}(z,t,\mathbf{r})=\int \mathbf{v}\theta(\ln F_1(t,\mathbf{r},\mathbf{v},\mathbf{a})-z)d\mathbf{v}d\mathbf{a}. \tag{56}$$

From (53)–(56) we find

$$\partial_t W(z,t)=-\frac{1}{V}\int \mathbf{j}d\mathbf{S}, \tag{57}$$

where the right-hand side of (57) contains a surface integral restricted to the medium we are analyzing, i.e., the right-hand side is of order $V^{-1/3}$.

Thus, for sufficiently large V, i.e., in the limit $V\rightarrow+\infty$ and $N\rightarrow+\infty$ with $n=N/V=$const we have

$$\partial_t W(z,t)=0, \tag{58}$$

i.e., the function $W(z,t)$ is actually time-independent.

From (58) it follows that

$$\frac{d}{dt}\frac{1}{V}\int g(F_1(t,1))d1=0, \tag{59}$$

where $g(x)$ is an arbitrary function such that this integral converges. It is obvious that (59) holds if we take into account the following identity:

$$\frac{1}{V}\int g(F_1(t,1))d1=-\int_{-\infty}^{+\infty} g(e^z)\frac{dW(z,t)}{dz}dz. \tag{60}$$

We can consider a function analogous to $W(z,t)$ defined in terms of $F_2(t,1,2)$:

$$W_1(z,t)=\frac{1}{V^2}\int \theta(\ln F_2(t,1,2)-z)d1d2. \tag{61}$$

However, using the relation

$$F_2(t,1,2)=F_1(t,1)F_1(t,2)$$

for $|\mathbf{r}_1-\mathbf{r}_2|\gg\sigma$, we find [see the comment preceding Eq. (58)]

$$W_1(z,t)=-\int_{-\infty}^{+\infty} W(z-z',t)\frac{dW(z',t)}{dz'}dz'. \tag{62}$$

Note that relations (53), (59), (61), and (62) admit a natural probabilistic interpretation.

A number of important consequences follow from Eqs. (58) and (59). Consider the ensemble (17), (18) under conditions such that the latter describes a liquid at time $t=0$. It is easy to see that under these conditions the function $F_1(t=0,1)$, regarded as a function of $\mathbf{r}$, consists of a set of maxima whose width is δr [cf. Eqs. (16) and (17)]:

$$l_T\lesssim\delta r\lesssim v_T\tau_\varphi.$$

In this case, taking $g(x)=x^2$, we find

$$G=\int F_1^2 d1\gtrsim N\frac{1}{(\omega_0\tau_\varphi)^3 V_T^9}. \tag{63}$$

But if the maxima of the one-particle distribution function are smeared out in the course of evolution, then after the passage of a sufficiently long time t the quantity G would assume the value

$$G=\int F_1^2 d1\sim N\frac{n}{\omega_0^3 v_T^6}. \tag{64}$$

However, the latter cannot occur in view of the incompatibility of the inequalities

$$N\frac{n}{\omega_0^3 v_T^6}\ll N\frac{1}{(\omega_0\tau_\varphi)^3 v_T^9} \tag{65}$$

[cf. Eqs. (63) and (64)] and the requirement that G not vary in time.

Thus, we can conclude that as the function F_1 evolves it is not smeared out, i.e., F_1 continues to consist of a set of maxima. For a liquid these are displaced, of course, in space so as to maintain homogeneity under averaging over sufficiently long times [cf. Eq. (12)]. Note that even after thermal equilibrium is established in the liquid the quantity $\int F_1(t,\mathbf{r},\mathbf{v},\mathbf{a})d\mathbf{a}$, is not identically equal to $\int F_1(t,\mathbf{r},-\mathbf{v},\mathbf{a})d\mathbf{a}$, since if these expressions were identical we would have

$$\frac{\partial}{\partial t}\int F_1(t,\mathbf{r},\mathbf{v},\mathbf{a})d\mathbf{v}d\mathbf{a}=0, \tag{66}$$

which contradicts the results found above. To be sure, averaging $\int F_1(t,\mathbf{r},\mathbf{v},\mathbf{a})d\mathbf{a}$ over a sufficiently long time [cf. Eq. (12)] should yield a Maxwellian distribution.

In the next section we will clarify the physical meaning of the result that $W(z,t)$ is independent of time in a solid.

We proceed now to the consideration of irreversibility in the second sense. Note that just because Eqs. (47) and (48) hold for the function $F_2(t=0,1,2)$, it does not follow that they hold for $\hat{T}F_2(t=0,1,2)$. Hence the problem is irreversible in the second sense.

It is not hard to see that if the functions $F_1(t=0,1)$ and $F_2(t=0,1,2)$ are related by Eq. (44) then the functions $\hat{T}F_1(t=0,1)$ and $\hat{T}F_2(t=0,1,2)$ also satisfy this relation. At the same time, if the original functions satisfy Eq. (38), this does not imply that functions obtained by time reversal also satisfy (38). This means that the functions $\hat{T}F_1(t=0,1)$ and $\hat{T}F_2(t=0,1,2)$ are no longer one- and two-particle distribution functions of any physically meaningful ensemble.

9. We now explore the physical meaning of the time independence of $W(z,t)$ [cf. Eq. (53)]. In this section we will employ a gedanken experiment, which makes the exposition more compact and clearer.

In the solid phase, when the temperature satisfies $T\ll U_S$ [cf. Eq. (13)], i.e., the atoms oscillate about their respective equilibrium positions with a characteristic velocity V_T and frequency ω_0, the quantity

$$G=\int F_1^2 d1 \sim N\left(\frac{m}{T}\right)^{9/2} \tag{67}$$

increases relatively rapidly as the temperature is decreased.

Consider the following initial state: the entire solid body is broken up into tubes of length L and divided up in checkerboard fashion so that their temperatures are equal to T_h and T_l with

$$T_l \ll T_h \ll U_S, \tag{68}$$

and the volumes occupied by the high- and low-temperature phases are equal. We also assume

$$\sigma \ll L, \quad 1 \ll VL^{-3}. \tag{69}$$

This justifies the use of the temperatures T_h and T_l, so that we need not concern ourselves with the small quantity of material which separates these tubes and which of course cannot be assigned any temperature, since it is not in an equilibrium state.

We pose the question, what temperature T_0 will be established in the system after it reaches thermal equilibrium?

The use of the standard model of a weakly anharmonic crystal yields

$$T_0 \sim \frac{1}{2} T_h, \tag{70}$$

which follows simply from energy conservation. But in actuality, the correct answer is quite different: using (67) we find

$$G=\int F_1^2 d1 \sim N\left(\frac{m}{T_l}\right)^{9/2}, \tag{71}$$

from which it follows that

$$T_0 \sim T_l. \tag{71}$$

The value T_0 given by (70) is considerably greater than that determined by (71). To the natural question regarding where the "excess" energy went there is an obvious answer: the usual model of a weakly anharmonic crystal does not take into account the possibility that the crystal lattice itself can change in the approach to equilibrium, i.e., defects, "frozen" internal stresses, and other imperfections can develop which entail the expenditure of energy. It is these processes which consume the supposedly excess energy.

Thus, the quantity G [Eq. (67)] characterizes processes in a solid associated with changes in the crystal lattice when thermal equilibrium is being established: if G is sufficiently large [cf. Eqs. (67) and (71)], then most of the energy is expended in the formation of various imperfections in the crystal lattice.

In a liquid different values of W correspond to the somewhat different probabilities of encountering a "nucleus" or "hole" of the various structures when these are studied using the Frenkel theory.

Note that real liquids and solids are of course not collections of particles described by classical mechanics and interacting through spherically symmetric two-particle potentials. In actuality, the directional nature of chemical bonds, quantum-mechanical effects, and three- and four-particle interactions often play a decisive role. They should all be taken into account when the present results are applied to real media.

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APPENDIX

Let D be a bounded region in the phase space of the system (1), and consider a set S:

$$S=\bigcup_{n=-\infty}^{n=+\infty} \hat{U}_{n\tau_0} D,$$

where $\hat{U}_{n\tau_0}$ is the evolution operator and τ_0 is some nonzero time interval. We prescribe an ensemble of systems as follows: the probability that the state of a system is in the infinitesimal volume $d\Omega$ in the neighborhood of a point Ω of phase space is equal to

$$\frac{1}{V_S} d\Omega,$$

if the point Ω belongs to the set S and is zero otherwise; here V_S is the phase volume of the set S.

It is easy to see that in this case all many-particle distribution functions will be periodic in time with period τ_0. Note that the quantity τ_0 is completely unrelated to the particle dynamics, but rather is determined solely by the choice of ensemble.

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