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Self-Diffusion in Fluids with Weak Long-Range Forces

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Diffusion of a test particle in a homogeneous classical fluid with weak long-range forces is studied. The dominant mean-field effect (Vlasov's theory) vanishes for symmetry reasons. Dynamical phenomena follow then from fluctuations of the effective potential energy felt by the propagating particle. The kinetic equation corresponding to this mechanism is derived with the use of the multiple-time-scale method. Its structure resembles very much that of the (linearized) Balescu–Lenard equation of hot plasma theory. It is shown that the kinetic equation holds only if no phase transition occurs in the system. The thermalization of the diffusing particle and the high-temperature and Lorentz gas limits are discussed.

KEY WORDS: Self-diffusion (motion of a tagged particle); reduced distributions; BBGKY hierarchy; mean-field limit; van der Waals fluid; multiple-time-scale method; correlation functions; kinetic equation; Lorentz gas.

1. INTRODUCTION

The study of the motion of a selected particle in a classical fluid at thermal equilibrium is a problem of nonequilibrium statistical mechanics which has played an important role in the analysis of the foundations of kinetic theory.[2],(2) One of the basic questions studied is that of the mechanism of thermalization. Suppose that the momentum of the nonequilibrium tagged particle is known exactly at some initial time. As the microscopic states of the fluid are distributed according to the Gibbs ensemble density the momentum variable will follow, during the further motion, a complicated stochastic process. One expects that this process will eventually transform

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[2] Self-diffusion is discussed in a number of monographs on kinetic theory. See, for example, Ref. 1.

the momentum distribution of the tagged particle into an equilibrium Maxwell one. The mechanism of the thermalization process (if it occurs) yields information about the dynamical properties of the fluid. In general it is extremely hard to study this kind of question as the momentum variable evolves according to a non-Markovian process. However, in a number of asymptotic cases the problem can be reduced to solving an appropriate kinetic equation, which is local in time. The rigorous results obtained in this field have been recently reviewed by Spohn[2] (important progress is to be noted during the last decade).

The aim of the present work is to discuss a new case where it turns out to be possible to describe the evolution of the momentum distribution under the influence of the fluid in terms of a kinetic equation. From the physical point of view the problem can be stated as follows. Suppose that the fluid particles interact via weak long-range forces giving rise to the mean-field effect. The mean-field limit has been studied extensively and is known to lead to the Vlasov equation (see Ref. 2 and references given therein). However, when the fluid is initially at thermal equilibrium, the effective mean force felt by the selected particle vanishes for symmetry reasons. In order to describe the diffusion process one has thus to go in this case beyond the usual mean-field approximation and consider higher-order effects which are those of fluctuations of the potential energy. The derivation of the corresponding kinetic equation and the discussion of conditions under which it describes the thermalization process are the basic content of this paper.

In Section 2 I define precisely the system and its dynamics. The microscopic formulation of the mean-field limit and its connection with the theory of van der Waals fluids are discussed in Section 3. Section 4 is entirely devoted to the derivation of the evolution equation for the momentum distribution of the tagged particle (application of the multiple-time-scale method). In Section 5 the conditions under which a kinetic equation is obtained are derived and interpreted from the physical point of view. Section 6 contains the discussion of the kinetic equation satisfied by the momentum distribution. Its analogy with the generalized Landau equation of hot plasma theory (Balescu–Lenard equation) is stressed. The high-temperature (low-density) limit is analyzed in detail. The Lorentz gas case is then studied (Section 7), and the paper is closed with final remarks (Section 8). The mean-field limit for equilibrium pair correlations is calculated in the Appendix.

2. THE SYSTEM AND ITS DYNAMICS

I consider here a fluid composed of an infinite number of identical particles moving in R^d. The phase of particle j will be denoted by

$x_j = (q_j, p_j)$, where $q_j \in R^d$, $p_j \in R^d$ are the position and momentum vectors, respectively. All the particles are supposed to have unit masses. They interact via a spherically symmetric pair potential V. The force exerted by particle j on particle i equals

$$F(q_{ij}) = -\frac{\partial V(q_{ij})}{\partial q_i} \tag{1}$$

where $q_{ij} = q_i - q_j$.

Initially (at time $t = 0$) particle 1 is known to have momentum $p_1 = p$. The remaining degrees of freedom of the fluid are distributed according to the laws of thermal equilibrium. One can describe this situation by a set of reduced distributions of the form

$$f_s(x_1, \ldots, x_s; 0) = \delta(p_1 - p) f_s^{\text{eq}}(x_1, \ldots, x_s)/\varphi^{\text{eq}}(p_1), \qquad s = 1, 2, \ldots \tag{2}$$

Here $f_s^{\text{eq}}(x_1, \ldots, x_s)$ represents the equilibrium number density of s-tuples of particles with phases $(x_1, \ldots, x_s)$. The deviation of f_s from f_s^{eq} consists in replacing the Maxwell momentum probability density for particle 1

$$\varphi^{\text{eq}}(p_1) = (\beta/2\pi)^{d/2} \exp(-\beta p_1^2/2) \tag{3}$$

(β is the inverse temperature) by the Dirac distribution $\delta(p_1 - p)$. Functions f_s can be looked upon as obtained from the formula

$$f_s(x_1, \ldots, x_s; 0) = \lim_{\infty} N^s \int dx_{s+1} \cdots \int dx_N \rho(x_1, \ldots, x_N; 0) \tag{4}$$

where $\lim_{\infty} = \lim_{N\to\infty, n=\text{const}}$ denotes the thermodynamic limit (n is the fluid number density), and the initial ensemble density ρ is related to the equilibrium N-particle Gibbs distribution ρ^{eq} by

$$\rho(x_1, \ldots, x_N; 0) = \delta(p_1 - p)\rho^{\text{eq}}(x_1, \ldots, x_N)/\varphi^{\text{eq}}(p_1) \tag{5}$$

It is important to realize that the reduced distributions which do not depend on the phase of particle 1 have equilibrium values. For example,

$$\lim_{\infty} N^2 \int dx_1 \int dx_4 \cdots \int dx_N \, \rho(x_1, \ldots, x_N; 0) = f_2^{\text{eq}}(x_2, x_3) \tag{6}$$

This means that the influence of a single particle on correlations between other particles vanishes in the thermodynamic limit.

The time evolution of the state of the fluid will be supposed to be governed by the BBGKY hierarchy equations [see, e.g., Ref. 1(a), p. 192]:

$$\left\{ \frac{\partial}{\partial t} + \sum_{i=1}^{s} \left[p_i \cdot \frac{\partial}{\partial q_i} + \sum_{\substack{j=1 \\ (j \neq i)}}^{s} F(q_{ij}) \cdot \frac{\partial}{\partial p_i} \right] \right\} f_s(x_1, \ldots, x_s; t)$$

$$= -\int dx_{s+1} \left[\sum_{i=1}^{s} F(q_{is+1}) \cdot \frac{\partial}{\partial p_i} \right] f_{s+1}(x_1, \ldots, x_{s+1}; t) \tag{7}$$

The initial state, characterized by distributions (2), is translationally invariant (in the position space). This property is propagated in time by hierarchy (7). It follows that the one-particle distribution $f_1(x_1; t)$, which will be the main object of the present study, does not depend on variable q_1 and has the form

$$f_1(x_1; t) = n\varphi(p_1; t) \tag{8}$$

where n is the equilibrium number density.

Let me also remark that all the reduced distributions which do not depend on the phase of particle 1 [see, e.g., Eq. (6)] remain unchanged in the course of time, preserving their equilibrium values (they yield a stationary solution of the corresponding BBGKY hierarchy).

3. THE MEAN-FIELD LIMIT AND THE CONCEPT OF A VAN DER WAALS FLUID

The evolution of the momentum distribution of nonequilibrium particle 1 (self-diffusion in momentum space) corresponds in general to a complex non-Markovian process. I shall consider here an asymptotic regime where the description of this process greatly simplifies and can be given in terms of a kinetic equation. From the physical point of view the motion of the tagged particle will be studied in the mean-field limit.

A convenient analytical formulation of this limit at the microscopic level is by now well known.[2] One associates with the original system [with pair potential $V(q)$] a new one in which particles interact via a scaled potential

$$V_\epsilon(q) = \epsilon V(\epsilon^{1/d} q) \tag{9}$$

When the dimensionless positive parameter ϵ tends to zero V_ϵ becomes very weak and long range. The density of the fluid being fixed, the propagating particle feels essentially an effective mean potential field. Although the interaction V_ϵ between any given pair of particles vanishes when $\epsilon \to 0$, the total effect of the fluid medium on particle 1 shifts (in average) its energy by a finite amount. Indeed, the measure of this shift is given by an ϵ-independent integral

$$\frac{n}{2} \int dq\, \epsilon V(\epsilon^{1/d} q) = \frac{n}{2} \int dr\, V(r) \tag{10}$$

Clearly, such a constant shift has no dynamical effect, as no force results from it. This is so because mean density n stays constant all over the system whose state preserves at any time translational invariance. In this situation the changes in the momentum distribution are conditioned by fluctuations of the potential energy.

Let me remark that scaling (9) has been successfully applied to the description of the effect of long-range attractive forces in the microscopic formulation of the van der Waals theory of the liquid–vapor phase transition[3] (transport properties of fluids have been also examined along these lines[4]). The success of this approach justified calling model fluids, whose long-range pair interaction is represented by a scaled potential V_ϵ, van der Waals fluids. The physical content of the mean-field and van der Waals asymptotics is the same, the only difference being in the order of magnitude of various effects. The origin of the difference is that the scaling of the potential is accompanied in the mean-field approach by a simultaneous scaling of space and time variables ($q \to \epsilon^{1/d} q, t \to \epsilon^{1/d} t$), whereas in the theory of van der Waals fluids it is not. Thus, for example, the microscopic force between a pair of particles in a van der Waals fluid is given by

$$-\partial V_\epsilon(q)/\partial q = \epsilon^{1+1/d} F(\epsilon^{1/d} q) \tag{11}$$

[see Eq. (1)], and in the mean-field theory it equals

$$-\partial V_\epsilon(q)/\partial(\epsilon^{1/d} q) = \epsilon F(\epsilon^{1/d} q) \tag{12}$$

It follows, that the average force felt by the tagged particle in a van der Waals fluid is an effect of the order $\epsilon^{1/d}$, whereas in the mean-field limit it is a zero-order quantity leading (when the fluid is not uniform) to Vlasov's theory. From the qualitative point of view this difference in the orders of magnitude is of course irrelevant.

As has been already mentioned, in the case under consideration, there is no dynamical effect on the time scale corresponding to Vlasov's theory. The relevant time region is the one in which fluctuations in the potential energy become significant. I shall now proceed to the derivation of the corresponding evolution equation for the momentum distribution $\varphi(p_1; t)$, considering the system with the scaled interaction (9) in the limit $\epsilon \to 0$.

4. EVOLUTION OF THE MOMENTUM DISTRIBUTION OF THE TAGGED PARTICLE

It is natural to associate with the scaled potential V_ϵ the transformation of the space and time variables

$$\begin{aligned} q &\to r = \epsilon^{1/d} q \\ t &\to \tau = \epsilon^{1/d} t \end{aligned} \tag{13}$$

Fixing r and τ is equivalent to considering space and time intervals of the order $\epsilon^{-1/d}$. When the potential V is replaced by V_ϵ and variables (13) are introduced one finds that the two first equations of the hierarchy (7) take the form

$$\frac{\partial}{\partial\tau} f_1^\epsilon(p_1;\tau) = -\int dr_2 \int dp_2 F(r_{12}) \cdot \frac{\partial}{\partial p_1} f_2^\epsilon(r_{12}, p_1, p_2; \tau)$$

$$\left[\frac{\partial}{\partial\tau} + p_1 \cdot \frac{\partial}{\partial r_1} + p_2 \cdot \frac{\partial}{\partial r_2} + \epsilon F(r_{12}) \cdot \left(\frac{\partial}{\partial p_1} - \frac{\partial}{\partial p_2} \right) \right] f_2^\epsilon(r_{12}, p_1, p_2; \tau)$$

$$= -\int dr_3 \int dp_3 \left[\sum_{i=1}^{2} F(r_{i3}) \cdot \frac{\partial}{\partial p_i} \right] f_3^\epsilon(r_{12}, r_{13}, r_{23}, p_1, p_2, p_3; \tau) \tag{14}$$

The translational invariance of distributions f_s^ϵ has been made explicit in writing Eq. (14).

In order to determine the evolution of the one-particle distribution f_1^ϵ in the $\epsilon \to 0$ limit I shall apply here the multiple-time-scale method, well known in the theory of plasma.[3] In the case under consideration two time scales will suffice. The method then consists in associating with the hierarchy equations (14) a new set of equations of the form

$$\left(\frac{\partial}{\partial\tau_0} + \epsilon \frac{\partial}{\partial\tau_1} \right) \tilde{f}_1^\epsilon(p_1; \tau_0, \tau_1) = -\int dr_2 \int dp_2 F(r_{12}) \cdot \frac{\partial}{\partial p_1} \tilde{f}_2^\epsilon(r_{12}, p_1, p_2; \tau_0, \tau_1) \tag{15}$$

$$\left[\frac{\partial}{\partial\tau_0} + \epsilon \frac{\partial}{\partial\tau_1} + p_1 \cdot \frac{\partial}{\partial r_1} + p_2 \cdot \frac{\partial}{\partial r_2} + \epsilon F(r_{12}) \cdot \left(\frac{\partial}{\partial p_1} - \frac{\partial}{\partial p_2} \right) \right] \times \tilde{f}_2^\epsilon(r_{12}, p_1, p_2; \tau_0, \tau_1)$$

$$= -\int dr_3 \int dp_3 \left[\sum_{i=1}^{2} F(r_{i3}) \cdot \frac{\partial}{\partial p_i} \right] \tilde{f}_3^\epsilon(r_{12}, r_{13}, r_{23}, p_1, p_2, p_3; \tau_0, \tau_1) \tag{16}$$

Functions $\tilde{f}_s^\epsilon$ are defined over a two-dimensional time space (variables τ_0, τ_1 are independent), and the role of the derivative $\partial/\partial\tau$ is played by the operator

$$\frac{\partial}{\partial\tau_0} + \epsilon \frac{\partial}{\partial\tau_1} \tag{17}$$

[3] A particularly clear presentation of the multiple-time-scale method is given in Ref. 5 and other references therein.

It is readily checked that solutions of the new hierarchy yield solutions of the original one when restricted to the line

$$\tau_0 = \tau, \qquad \tau_1 = \epsilon\tau \tag{18}$$

Hence, the time evolution of distributions f_s^ϵ for $\tau > 0$ can be deduced from any solution of hierarchy (15), (16) satisfying the condition

$$\tilde{f}_s^\epsilon\big|_{\tau_0=\tau_1=0} = f_s^\epsilon\big|_{\tau=0}, \qquad s = 1, 2, \ldots \tag{19}$$

The interest of the method comes from the fact that outside line (18) one is free to impose additional boundary conditions. This is usually done in such a way as to guarantee the proper long-time behavior of reduced distributions in any of the time scales involved. The best clarification of this point will be provided by the application of the method presented below.

In the van der Waals (mean-field) limit correlations between particles disappear. Consequently, the reduced distributions can be asymptotically written as

$$\tilde{f}_s^\epsilon = \tilde{f}_s^0 + \epsilon\tilde{f}_s^1 + O(\epsilon^2) \tag{20}$$

where

$$\tilde{f}_s^0(y_1, \ldots, y_s; \tau_0, \tau_1) = \prod_{i=1}^{s} \tilde{f}_1^0(y_i; \tau_0, \tau_1)$$

and

$$\tilde{f}_s^1(y_1, \ldots, y_s; \tau_0, \tau_1) = \sum_{j=1}^{s} \tilde{f}_1^1(y_j; \tau_0, \tau_1) \prod_{i(\neq j)}^{s} \tilde{f}_1^0(y_i; \tau_0, \tau_1)$$

$$+ \sum_{j}^{s} \sum_{<k}^{s} g^1(r_{jk}, p_j, p_k; \tau_0, \tau_1) \prod_{i\neq(j,k)}^{s} \tilde{f}_1^0(y_i; \tau_0, \tau_1)$$

$$s = 1, 2, \ldots, \qquad y_j \equiv (r_j, p_j) \tag{21}$$

The above asymptotic representation is in full accordance with rigorous results concerning the behavior of equilibrium correlations in the van der Waals limit.[6] When put into hierarchy equations (15), (16) it leads to a consistent scheme of equations which can be (in principle) consecutively solved. The first of them [terms of the order $\epsilon^0 = 1$ in Eqs. (15) and (16)] reads

$$\frac{\partial}{\partial\tau_0} \tilde{f}_1^0(p_1; \tau_0, \tau_1) = 0 \tag{22}$$

The one-particle distribution (at least to the dominant order) does not change in the $\epsilon \to 0$ limit on the time scale corresponding to variable τ_0

[times $t \sim \epsilon^{-1/d}$; see Eqs. (13) and (18)], which is the time scale of Vlasov's theory. In order to observe its evolution variable τ_1 must be used which corresponds [on the line (18)] to physical times $t \sim \epsilon^{-1-1/d}$.

The term of the order ϵ^1 in Eq. (15) leads to the equation

$$\frac{\partial}{\partial \tau_0} \tilde{f}_1^1(p_1; \tau_0, \tau_1) + \frac{\partial}{\partial \tau_1} \tilde{f}_1^0(p_1; \tau_1) = -\int dr_2 \int dp_2 F(r_{12}) \cdot \frac{\partial}{\partial p_1} g^1(r_{12}, p_1, p_2; \tau_0, \tau_1) \quad (23)$$

Requiring that $\tilde{f}_1^1(p_1; \tau_0, \tau_1)$ is well behaved in the $\tau_0 \to \infty$ limit determines the τ_1 dependence of $\tilde{f}_1^0$ through the boundary condition

$$\lim_{\tau_0 \to \infty} \int dr_2 \int dp_2 F(r_{12}) \cdot \frac{\partial}{\partial p_1} g^1(r_{12}, p_1, p_2; \tau_0, \tau_1) = -\frac{\partial}{\partial \tau_1} \tilde{f}_1^0(p_1; \tau_1) \quad (24)$$

In order to transform Eq. (24) into an evolution equation for $\tilde{f}_1^0$ the second equation of the hierarchy is needed. The terms of the order ϵ^1 in Eq. (16), after using Eq. (23), yield the relation

$$\begin{aligned}
&\left(\frac{\partial}{\partial \tau_0} + p_1 \cdot \frac{\partial}{\partial r_1} + p_2 \cdot \frac{\partial}{\partial r_2} \right) g^1(r_{12}, p_1, p_2; \tau_0, \tau_1) \\
&\quad + F(r_{12}) \cdot \left(\frac{\partial}{\partial p_1} - \frac{\partial}{\partial p_2} \right) \tilde{f}_1^0(p_1; \tau_1) \tilde{f}_1^0(p_2; \tau_1) \\
&= -\int dr_3 \int dp_3 \left[F(r_{23}) \cdot \frac{\partial}{\partial p_2} g^1(r_{13}, p_1, p_3; \tau_0, \tau_1) \tilde{f}_1^0(p_2; \tau_1) \right. \\
&\quad \left. + F(r_{13}) \cdot \frac{\partial}{\partial p_1} g^1(r_{23}, p_2, p_3; \tau_0, \tau_1) \tilde{f}_1^0(p_1; \tau_1) \right] \quad (25)
\end{aligned}$$

Distributions which do not depend on $y_1 = (r_1, p_1)$ have equilibrium values

$$\begin{aligned}
\tilde{f}_1^0(p_2; \tau_1) &= n\varphi^{\mathrm{eq}}(p_2) \\
g^1(r_{23}, p_2, p_3; \tau_0, \tau_1) &= g^{1,\mathrm{eq}}(r_{23}) \varphi^{\mathrm{eq}}(p_2) \varphi^{\mathrm{eq}}(p_3)
\end{aligned} \quad (26)$$

Hence, with the aid of the linearized Vlasov operator $\hat{H}(2)$, which acts on a function $h(y_1, y_2)$ according to the formula

$$\hat{H}(2) h(y_1, y_2) = p_2 \cdot \frac{\partial}{\partial r_2} h(y_1, y_2) + n \int dr_3 \int dp_3 F(r_{23}) \cdot \frac{\partial}{\partial p_2} \varphi^{\mathrm{eq}}(p_2) h(y_1, y_3) \quad (27)$$

Eq. (25) can be rewritten as

$$\left[\frac{\partial}{\partial\tau_0}+p_1\cdot\frac{\partial}{\partial r_1}+\hat{H}(2)\right]g^1(r_{12},p_1,p_2;\tau_0,\tau_1)$$
$$=-nF(r_{12})\cdot\left(\frac{\partial}{\partial p_1}-\frac{\partial}{\partial p_2}\right)\tilde{f}_1^0(p_1;\tau_1)\varphi^{\text{eq}}(p_2)$$
$$-\int dr_3 F(r_{13})\cdot\frac{\partial}{\partial p_1}\tilde{f}_1^0(p_1;\tau_1)\,g^{1,\text{eq}}(r_{23})\varphi^{\text{eq}}(p_2) \tag{28}$$

Its solution may be obtained by standard techniques (the details can be found in Ref. 5). In order to write it let me introduce the notation $\hat{f}$ for the Fourier transform of function f:

$$\hat{f}(k)=(2\pi)^{-d}\int dr\,e^{-ik\cdot r}f(r) \tag{29}$$

Using the short-hand notation $\hat{R}(k,p_1,p_2;\tau_1)$ for the Fourier transform of the right-hand side of Eq. (28) (with respect to variable $r=r_{12}$),

$$\hat{R}(k,p_1,p_2;\tau_1)\equiv i\hat{V}(k)\left\{\left[n+(2\pi)^d\hat{g}^{1,\text{eq}}(k)\right]k\cdot\frac{\partial}{\partial p_1}-nk\cdot\frac{\partial}{\partial p_2}\right\}$$
$$\times\tilde{f}_1^0(p_1;\tau_1)\varphi^{\text{eq}}(p_2) \tag{30}$$

one can write the solution of Eq. (28) as

$$\hat{g}(k,p_1,p_2;\tau_0,\tau_1)$$
$$=\int_{\sigma-i\infty}^{\sigma+i\infty}\frac{dz}{2\pi i}e^{z\tau_0}\left[\frac{1}{z+ik\cdot p_{12}}\hat{g}^1(k,p_1,p_2;0,\tau_1)\right.$$
$$-\frac{i(2\pi)^d n\hat{V}(k)k\cdot\partial\varphi^{\text{eq}}(p_2)/\partial p_2}{(z+ik\cdot p_{12})D(-k;z+ik\cdot p_1)}$$
$$\left.\times\int dp_2'\frac{\hat{g}^1(k,p_1,p_2';0,\tau_1)}{z+ik\cdot(p_1-p_2')}\right]+\int_0^{\tau_0}d\mu\int_{\sigma-i\infty}^{\sigma+i\infty}\frac{dz}{2\pi i}e^{z\mu}$$
$$\times\left[\frac{\hat{R}(k,p_1,p_2;\tau_1)}{z+ik\cdot p_{12}}-\frac{i(2\pi)^d n\hat{V}(k)k\cdot\partial\varphi^{\text{eq}}(p_2)/\partial p_2}{(z+ik\cdot p_{12})D(-k;z+ik\cdot p_1)}\right.$$
$$\left.\times\int dp_2'\frac{\hat{R}(k,p_1,p_2';\tau_1)}{z+ik\cdot(p_1-p_2')}\right] \tag{31}$$

where

$$D(-k;z)\equiv 1+in(2\pi)^d\hat{V}(k)\int dp_2\frac{1}{z-ik\cdot p_2}k\cdot\frac{\partial\varphi^{\text{eq}}(p_2)}{\partial p_2} \tag{32}$$

and the complex integration (over variable z) corresponds to taking the inverse Laplace transform. The function $D(-k;z)$ is here the analog of the so-called Landau denominator (plasma dielectric function).[5] (For a detailed discussion see, e.g., Ref. 7.)

The solution (31) can be directly used to transform Eq. (24) as the latter can be written in the form

$$\frac{\partial}{\partial \tau_1} \tilde{f}_1^0(p_1;\tau_1) = \lim_{\tau_0\to\infty} \left[-i(2\pi)^d \int dp_2 \int dk\, \hat{V}(k) k \cdot \frac{\partial}{\partial p_1} \hat{g}^1(k, p_1, p_2; \tau_0, \tau_1) \right] \tag{33}$$

Taking into account Eq. (32) one finds the following evolution equation:

$$\frac{\partial}{\partial \tau_1} \tilde{f}_1^0(p_1;\tau_1) = \lim_{\tau_0\to\infty} \Lambda^{\mathrm{corr}}(p_1;\tau_0,\tau_1) + \lim_{\eta\to 0^+} \Lambda_\eta^{\mathrm{coll}}(p_1;\tau_1) \tag{34}$$

The term Λ^{corr} depends on correlations at time $\tau_0 = 0$ and is given by

$$\Lambda^{\mathrm{corr}}(p_1;\tau_0,\tau_1) = -i(2\pi)^d \int dk \int dp_2 \int_{\sigma - i\infty}^{\sigma + i\infty} \frac{dz}{2\pi i} e^{\tau_0 z} \hat{V}(k) k \cdot \frac{\partial}{\partial p_1} \frac{\hat{g}^1(k, p_1, p_2; 0, \tau_1)}{(z + ik\cdot p_{12}) D(-k; z + ik\cdot p_1)} \tag{35}$$

The collision term $\Lambda_\eta^{\mathrm{coll}}$ reads

$$\Lambda_\eta^{\mathrm{coll}}(p_1;\tau_1) = -i(2\pi)^d \int dk \int dp_2 \hat{V}(k) k \cdot \frac{\partial}{\partial p_1} \frac{\hat{R}(k, p_1, p_2; \tau_1)}{(\eta + ik\cdot p_{12}) D(-k; \eta + ik\cdot p_1)} \tag{36}$$

The integration over p_2 can be performed in $\Lambda_\eta^{\mathrm{coll}}$ owing to the relations

$$\begin{aligned} \int dp_2 \frac{1}{z + ik\cdot p_{12}} k \cdot \frac{\partial}{\partial p_2} \varphi^{\mathrm{eq}}(p_2) &= \frac{D(-k; z + ik\cdot p_1) - 1}{i(2\pi)^d n \hat{V}(k)} \\ \int dp_2 \frac{1}{z + ik\cdot p_{12}} \varphi^{\mathrm{eq}}(p_2) &= \frac{1}{z + ik\cdot p_1} \left[1 - \frac{D(-k; z + ik\cdot p_1) - 1}{(2\pi)^d n\beta \hat{V}(k)} \right] \end{aligned} \tag{37}$$

Moreover, one can easily calculate the equilibrium correlation function $\hat{g}^{1,\mathrm{eq}}(k)$ appearing in $\hat{R}(k, p_1, p_2; \tau_1)$ [see Eq. (31): the calculation is given in the Appendix]. It has the form

$$\hat{g}^{1,\mathrm{eq}}(k) = -\frac{n^2\beta\hat{V}(k)}{1+(2\pi)^d n\beta\hat{V}(k)} \tag{38}$$

With the use of Eqs. (37) and (38) the collision term can be rewritten as

$$\begin{aligned}\Lambda_\eta^{\mathrm{coll}}(p_1;\tau_1) = i\int dk\,\hat{V}(k)k\cdot\frac{\partial}{\partial p_1}\\ \times\Bigg\{-\frac{1}{D(-k;\eta+ik\cdot p_1)}+\frac{1}{\beta(k\cdot p_1-i\eta)}\\ \times\left[\frac{1}{1+(2\pi)^d n\beta\hat{V}(k)}-\frac{1}{D(-k;\eta+ik\cdot p_1)}\right]\\ \times k\cdot\frac{\partial}{\partial p_1}\Bigg\}\tilde{f}_1^0(p_1;\tau_1)\end{aligned} \tag{39}$$

The calculation of the limit $\lim_{\eta\to 0^+}\Lambda_\eta^{\mathrm{coll}} = \Lambda^{\mathrm{coll}}$ is greatly facilitated by the relation

$$\begin{aligned}\lim_{\eta\to 0^+} D(-k;\eta+ik\cdot p_1) &\equiv D(-k;ik\cdot p_1)\\ &= 1+n\beta\hat{V}(k)(2\pi)^d\Bigg\{1-\beta(\hat{k}\cdot p_1)^2\\ &\qquad\times\exp\left[-\beta(\hat{k}\cdot p_1)^2/2\right]\\ &\qquad\times\int_0^1 dw\,\exp\left[\beta(\hat{k}\cdot p_1)^2 w^2/2\right]\\ &\qquad-i\left(\frac{\beta\pi}{2}\right)^{1/2}(\hat{k}\cdot p_1)\\ &\qquad\times\exp\left[-\beta(\hat{k}\cdot p_1)^2/2\right]\Bigg\}\end{aligned} \tag{40}$$

where $\hat{k}$ is a unit vector in the direction of k ($k = |k|\hat{k}$). Indeed, Eq. (40) implies that

$$\left\{D(-k;\eta+ik\cdot p_1)-\left[1+(2\pi)^d n\beta\hat{V}(k)\right]\right\}\sim(\hat{k}\cdot p_1) \tag{41}$$

which makes the passage to the limit $\eta\to 0^+$ in the denominator $(k\cdot p_1 - i\eta)^{-1}$ in Eq. (39) very simple. Taking additionally the symmetry properties of various terms in the integrand into account one obtains the following final representation of the collision term:

$$\Lambda^{\text{coll}}(p_1;\tau_1) = (2\pi)^d n\left(\frac{\pi\beta}{2}\right)^{1/2} \int dk\,|k|[\hat{V}(k)]^2\left(\hat{k}\cdot\frac{\partial}{\partial p_1}\right) \times\left\{\frac{\exp[-\beta(\hat{k}\cdot p_1)^2/2]}{|D(-k;ik\cdot p_1)|^2}\left[\beta(\hat{k}\cdot p_1)+\left(\hat{k}\cdot\frac{\partial}{\partial p_1}\right)\right]\right\}\tilde{f}_1^0(p_1;\tau_1) \tag{42}$$

In the next section the correlation term given by Eq. (35) will be examined in the limit $\tau_0 \to \infty$ [see Eq. (34)].

5. INFLUENCE OF INITIAL CORRELATIONS

In order to establish the kinetic equation for distribution $\tilde{f}_1^0$ with the collision term (42) one must prove that

$$\lim_{\tau_0\to\infty} \Lambda^{\text{corr}}(p_1;\tau_0,\tau_1) = 0 \tag{43}$$

Clearly, Eq. (43) does not hold for an arbitrary interaction $\hat{V}(k)$. A restricting condition is imposed by the requirement that function $D(-k; z + ik\cdot p_1)$ have no zeros in the half-plane $\operatorname{Re} z > 0$ [see Eq. (35)]. As has already been shown $D(-k; z + ik\cdot p_1)$ has the structure of the plasma dielectric function. The condition for the absence of zeros of $D(-k; z + ik\cdot p_1)$ in the half-plane $\operatorname{Re} z > 0$ can be obtained on the basis of the same reasoning that leads to the Nyquist–Penrose criterion for the stability of plasma (see Ref. 7, pp. 95–101, where references to the original literature can be found).

Using Eq. (32) one finds

$$D(-k;z+ik\cdot p) = 1 + i(2\pi)^d n\hat{V}(k)\int dp_2\,\frac{1}{z+ik\cdot p_{12}}\,k\cdot\frac{\partial\varphi^{\text{eq}}(p_2)}{\partial p_2} \tag{44}$$

When $\operatorname{Re} z > 0$ the formula

$$(z+ik\cdot p_{12})^{-1} = \int_0^\infty dv\,\exp[-v(z+ik\cdot p_{12})] \tag{45}$$

holds. Inserting it into Eq. (44) one gets

$$D(-k;z+ik\cdot p_1) = 1 + (2\pi)^d n\beta\hat{V}(k) \times\int_0^\infty dv\,v\exp\left[-\frac{v^2}{2}-\frac{v\sqrt{\beta}\,(z+ik\cdot p_1)}{|k|}\right] \tag{46}$$

Formula (46) yields the analytic continuation of D to the region $\mathrm{Re}\, z \leqslant 0$. Clearly, the singularities of this function appear only at infinity ($\mathrm{Re}\, z < 0$). At the imaginary axis ($z = i\omega$, $\omega \in R^1$) Eq. (46) takes the form

$$D(-k; i(\omega + k \cdot p_1))$$
$$= 1 + (2\pi)^d n\beta\hat{V}(k)\int_0^\infty dv\, v \exp\left(-\frac{v^2}{2}\right)\cos\left[\frac{v\sqrt{\beta}\,(\omega + k \cdot p_1)}{|k|}\right]$$
$$-i\left(\frac{\beta\pi}{2}\right)^{1/2}\frac{(\omega + k \cdot p_1)}{|k|}(2\pi)^d n\beta\hat{V}(k)\exp\left[-\frac{\beta}{2}\left(\frac{\omega + k \cdot p_1}{|k|}\right)^2\right] \tag{47}$$

One can now argue as follows.

Consider function D on the contour G shown in Fig. 1, in the limit where the radius R of the semicircle tends to infinity. To all points of the semicircle there corresponds a real value of D equal to 1, as

$$\lim_{z \to \infty, \mathrm{Re}\, z \geqslant 0} D(-k; z + ik \cdot p_1) = 1 \tag{48}$$

Moreover, when z varies along the imaginary axis there is only one point ($z = -ik \cdot p_1$) where the imaginary part of $D(-k; z + ik \cdot p_1)$ vanishes [the case $z = \pm i\infty$ has been included in Eq. (48)]. At this point the real part equals

$$\mathrm{Re}\, D(-k; z + ik \cdot p_1)\big|_{z = -ik \cdot p_1} = 1 + (2\pi)^d n\beta\hat{V}(k) \tag{49}$$

Therefore, the graph on the ($\mathrm{Re}\, D$, $\mathrm{Im}\, D$) plane, corresponding to contour G of Fig. 1, crosses the axis $\mathrm{Im}\, D = 0$ at exactly two points: $\mathrm{Re}\, D = 1$ and $\mathrm{Re}\, D = 1 + (2\pi)^d n\beta\hat{V}(k)$. Imposing the condition

$$\min_{0 \leqslant |k| \leqslant \infty}\left[1 + (2\pi)^d n\beta\hat{V}(k)\right] > 0 \tag{50}$$

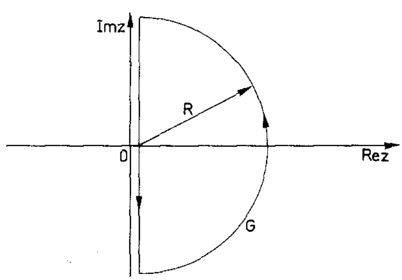

Fig. 1. Contour G in the complex z-plane used for the integration of the logarithmic derivative of function D.

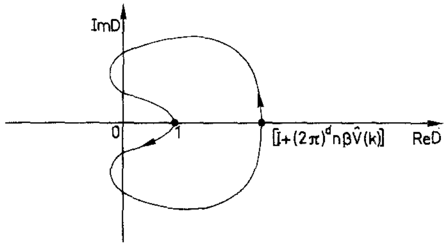

Fig. 2. Variation of the real and imaginary parts of function D along the contour G of Fig. 1.

guarantees that it does not encircle the point $z = 0$, and has the form represented schematically in Fig. 2.

But this implies that

$$\int_G \frac{dz}{D(-k; z + ik \cdot p_1)} \frac{\partial}{\partial z} D(-k; z + ik \cdot p_1) = 0 \tag{51}$$

As function D has no singularities in the half-plane $\text{Re}\, z \geqslant 0$ the vanishing of the integral in Eq. (51) means that it has no zeros in that region.

For any interaction $\hat{V}(k)$ bounded from below inequality (50) is satisfied provided the product $(n\beta)$ is sufficiently small [it is of course automatically satisfied at points k where $\hat{V}(k) \geqslant 0$]. Hence, at sufficiently high temperatures (low densities) one can expect the limit $\tau_0 \to \infty$ of $\Lambda^{\text{corr}}(p_1; \tau_0, \tau_1)$ to be well defined for a very large class of potentials. It is however to be noted that for a given interaction, for which there exist wave vectors k such that $\hat{V}(k) < 0$, the inequality (50) is violated at low temperatures (high densities), leading to divergencies in the correlation term.

From the physical point of view condition (50) excludes the possibility of a phase transition in the fluid (in the region of temperatures and densities where it is valid). Let me explain this point in a particularly simple case where the absolute minimum of $\hat{V}(k)$ is attained at point $k = 0$. Suppose that $\hat{V}(0) < 0$. [This occurs, for example, when $V(q) \leqslant 0$, $0 \leqslant |q| \leqslant \infty$.] For a fixed density n and sufficiently high temperatures inequality (50) is satisfied. Let β_c denote the inverse temperature at which the function $[1 + (2\pi)^d n\beta_c \hat{V}(k)]$ attains zero at $k = 0$, corresponding to the minimum of $\hat{V}(k)$,

$$\hat{V}'(0) = \left. \frac{d\hat{V}(|k|)}{d|k|} \right|_{k=0} = 0 \tag{52}$$

From Eq. (38) the equilibrium pair correlation function to the dominant order can written as

$$g^{\text{eq}}(q; n, \beta) = -\epsilon \int dk \exp(iq \cdot k\epsilon^{1/d}) \frac{n^2\beta\hat{V}(k)}{1 + (2\pi)^d n\beta\hat{V}(k)} \tag{53}$$

When $\beta \nearrow \beta_c$, the contribution to g^{eq} coming from wave vectors k close to $k = 0$ becomes important, as $[1 + (2\pi)^d n\beta_c \hat{V}(0)] = 0$. The asymptotic form of the integrand in this region is given by

$$\frac{n\beta_c \hat{V}(0)}{(2\pi)^d\left[(\beta - \beta_c)\hat{V}(0) + \frac{1}{2}\beta_c \hat{V}''(0)k^2\right]} \tag{54}$$

where

$$\hat{V}''(0) = \left.\frac{d^2\hat{V}(|k|)}{d|k|^2}\right|_{k=0} > 0$$

A straightforward calculation of the inverse Fourier transform of expression (54) in three dimensions yields the contribution to g^{eq} of the Ornstein–Zernicke form

$$\frac{n\epsilon}{2\pi}\left|\frac{\hat{V}(0)}{\hat{V}''(0)}\right|\frac{\exp\left\{-|q|\epsilon^{1/3}\left[2(\beta_c - \beta)|\hat{V}(0)|/\beta_c\hat{V}''(0)\right]^{1/2}\right\}}{|q|\epsilon^{1/3}} \tag{55}$$

When $\beta \nearrow \beta_c$ the range of g^{eq} tends to infinity as $(\beta_c - \beta)^{-1/2}$, which is characteristic of the mean-field behavior at the critical point of the liquid–vapor phase transition. Hence, if $\hat{V}(0) < 0$ [violation of condition (50) at sufficiently low temperatures], the system undergoes a phase transition. Inequality (50), when valid for all temperatures and densities, excludes such a possibility [a similar discussion can be presented in the case where the minimum of $\hat{V}(k)$ occurs at a point $k \neq 0$].

In the rest of this paper I shall assume that the system fulfils condition (50). It seems then highly probable that Eq. (43) is satisfied. Indeed, (i) contributions to Λ^{corr} from zeros of $D(-k; z + ik \cdot p_1)$ lying in the half-plane $\mathrm{Re}\, z < -\eta$, $\eta > 0$, vanish exponentially in the $\tau_0 \to \infty$ limit; (ii) for a given value of vector k zeros of $D(-k; z + ik \cdot p_1)$ are located in the half-plane $\mathrm{Re}\, z < -\eta(k)$, $\eta(k) > 0$ (D is an entire function of variable z with no zeros in the region $\mathrm{Re}\, z \geqslant 0$); (iii) the contribution to Λ^{corr} corresponding to the pole at $z = -ik \cdot p_{12}$ [see Eq. (35)] reads

$$-i(2\pi)^d \int dp_2 \int dk \frac{\partial}{\partial p_1} \cdot k\hat{V}(k) \frac{\hat{g}^1(k, p_1, p_2; 0, \tau_1)}{D(-k; ik \cdot p_2)} \exp(-i\tau_0 k \cdot p_{12}) \tag{56}$$

The integral over k yields the Fourier transform at point $(\tau_0 p_{12})$. So it vanishes when $\tau_0 \to \infty$, provided one can apply to the integrand the Riemann–Lebesgue theorem.

The above remarks may be of interest for an actual proof of Eq. (43). Such a proof will not be given here. In view of all these plausibility arguments I shall just assume that the correlation term vanishes when τ_0 tends to infinity and condition (50) is satisfied.

6. THE KINETIC EQUATION

Assuming that Eq. (43) holds and going back to the original time and space variables [see Eqs. (13) and (18)] one finds, with the use of Eqs. (8), (34), (42) the following kinetic equation for the momentum distribution $\varphi(p;t)$ of particle 1:

$$\frac{\partial\varphi(p;t)}{\partial t} = \epsilon^{1+1/d}(2\pi)^d n(\pi\beta/2)^{1/2}\int dk\,|k|\left[\hat{V}(k)\right]^2 \times\left(\hat{k}\cdot\frac{\partial}{\partial p}\right)\left\{\frac{\exp\left[-\beta(\hat{k}\cdot p)^2/2\right]}{|D(-k;ik\cdot p)|^2}\left[\beta(\hat{k}\cdot p)+\hat{k}\cdot\frac{\partial}{\partial p}\right]\right\}\varphi(p;t) \tag{57}$$

where [compare with Eq. (40)]

$$D(-k;ik\cdot p) = 1+(2\pi)^d n\beta\hat{V}(k) \times\left\{\int_0^\infty dv\,v\exp(-\tfrac{1}{2}v^2)\cos(v\beta^{1/2}\hat{k}\cdot p) - i(\tfrac{1}{2}\beta\pi)^{1/2}(\hat{k}\cdot p)\exp\left[-\tfrac{1}{2}\beta(\hat{k}\cdot p)^2\right]\right\} \tag{58}$$

The Maxwell distribution (3) is a stationary solution of Eq. (57). Multiplying both sides of Eq. (57) by $[\exp(\beta p^2/2)\varphi(\mathrm{p};\mathrm{t})]$, and integrating over variable p one finds

$$\frac{1}{2}\frac{\partial}{\partial t}\int dp\exp(\tfrac{1}{2}\beta p^2)\left[\varphi(p;t)\right]^2 = -\epsilon^{1+1/d}(2\pi)^d n(\tfrac{1}{2}\pi\beta)^{1/2}\int dp\int dk\,|k|\left[\hat{V}(k)\right]^2 \times\frac{\exp\left\{\frac{1}{2}\beta\left[p^2-(\hat{k}\cdot p)^2\right]\right\}}{|D(-k;ik\cdot p)|^2}\left\{\left[\beta(\hat{k}\cdot p)+\hat{k}\cdot\frac{\partial}{\partial p}\right]\varphi(p;t)\right\}^2 \tag{59}$$

The right-hand side of Eq. (59) is strictly negative, unless $\varphi = \varphi^{\mathrm{eq}}$, in which case it vanishes. Hence, if the distribution φ belongs to the class of functions for which the integral appearing in Eq. (59) exists, it tends to the equilibrium Maxwell distribution in the long-time limit. It follows that the thermalization of particle 1 does occur on the time scale $t\sim\epsilon^{-1-1/\mathrm{d}}$.

It is interesting to note that the kinetic equation (57) has the form of the linearized Landau equation (or rather its generalization to the ring approximation) for the momentum distribution of a test particle in a plasma (see Ref. 7, p. 233). Its solution depends on time through the product $(\epsilon^{1+1/d}t)$. This implies that the coefficient of self-diffusion D_s is of the order $\epsilon^{1+1/d}$.

Equation (57) simplifies considerably in the high-temperature (low-density) regime

$$n\beta\hat{V}(k) \ll 1 \tag{60}$$

where function D can be replaced by 1. It there takes the form

$$\frac{\partial\varphi(p;t)}{\partial t} = A_d^\epsilon \frac{\partial}{\partial p}\cdot\left[\mathsf{T}(p)\cdot\left(\beta p + \frac{\partial}{\partial p}\right)\right]\varphi(p;t) \tag{61}$$

where

$$A_d^\epsilon = \epsilon^{1+1/d}(2\pi)^d n(2\pi\beta)^{1/2}\int_0^\infty |k|^d[\hat{V}(k)]^2 d|k| \tag{62}$$

and the tensor $\mathsf{T}(p)$ is given by

$$\mathsf{T}(p) = \tfrac{1}{2}\int d\hat{k}\,\hat{k}\,\hat{k}\exp\left[-\tfrac{1}{2}\beta(\hat{k}\cdot p)^2\right] \tag{63}$$

Equation (61) has a universal character in the sense that the whole dependence on the pair potential V enters only through the multiplicative constant A_d^ϵ. It can be obtained alternatively by considering the self-diffusion in an ideal fluid, which means that the thermal bath in which particle 1 propagates is assumed to be an ideal gas. In order to see it, let us notice that Eq. (25), describing the evolution of the correlation function g^1, reduces in this situation to

$$\begin{aligned}\left(\frac{\partial}{\partial\tau_0} + p_1\cdot\frac{\partial}{\partial r_1} + p_2\cdot\frac{\partial}{\partial r_2}\right)&g^1(r_{12}, p_1, p_2; \tau_0, \tau_1)\\ &= -F(r_{12})\cdot\left(\frac{\partial}{\partial p_1} - \frac{\partial}{\partial p_2}\right)\tilde{f}_1^0(p_1;\tau_1)n\varphi^{\text{eq}}(p_2)\end{aligned} \tag{64}$$

as $F(r_{23}) = 0$, and $g^1(r_{23}, p_2, p_3; \tau_0, \tau_1) = 0$. The Fourier transform of g^1 can be thus readily calculated yielding

$$\begin{aligned}\hat{g}^1(k, p_1, p_2; \tau_0, \tau_1) &= \exp(-ik\cdot p_{12}\tau_0)\,\hat{g}^1(k, p_1, p_2; 0, \tau_1)\\ &\quad + i\int_0^{\tau_0} d\mu\,\exp(-i\mu k\cdot p_{12})\,\hat{V}(k)k\\ &\quad \cdot\left(\frac{\partial}{\partial p_1} - \frac{\partial}{\partial p_2}\right)\tilde{f}_1^0(p_1;\tau_1)n\varphi^{\text{ep}}(p_2)\end{aligned} \tag{65}$$

After inserting this result into Eq. (33) one can perform all the integrations involved in an explicit way. The result of lengthy but simple calculations is again the kinetic equation (61) [of course under the assumption that the correlation term

$$\begin{aligned}\Lambda^{\text{corr}}(p_1;\tau_0,\tau_1) = &-i(2\pi)^d\int dp_2\int dk\,k\\ &\cdot\frac{\partial}{\partial p_1}\hat{V}(k)\,\hat{g}^1(k, p_1, p_2; 0, \tau_1)\exp(-i\tau_0 k\cdot p_{12})\end{aligned} \tag{66}$$

vanishes when $\tau_0 \to \infty$; see the remark following Eq. (56)]. Clearly, one would expect on physical grounds that the self-diffusion process described by Eq. (57) tends to the one taking place in an ideal gas in the high-temperature (low-density) limit. So the fact that the same equation (61) is found by the two methods described above is satisfactory.

In one dimension Eq. (61) reads

$$\frac{\partial \varphi(p;t)}{\partial t} = A_1^\epsilon \frac{\partial}{\partial p} \left\{ \exp\left(-\frac{\beta p^2}{2} \right) \left(\beta p + \frac{\partial}{\partial p} \right) \right\} \varphi(p;t) \tag{67}$$

where A_1^ϵ is given by Eq. (62) with $d = 1$.

In general the tensor $\mathsf{T}(p)$ is diagonal in the system of reference whose, say, z axis is oriented along the vector p. In three dimensions one then finds

$$\begin{aligned} \mathsf{T}_{xx}(p) = \mathsf{T}_{yy}(p) &= \pi \int_0^1 d\mu \, (1 - \mu^2) \exp(-\beta p^2 \mu^2 / 2) \\ \mathsf{T}_{zz}(p) &= 2\pi \int_0^1 d\mu \; \mu^2 \exp(-\beta p^2 \mu^2 / 2) \end{aligned} \tag{68}$$

Equation (61) has the structure of a Fokker–Planck equation describing diffusion in momentum space [the same can be said about the general equation (57)]. In one dimension the corresponding coefficient of dynamical friction and the diffusion tensor are both proportional to $\exp(-\beta p^2/2)$ [see Eq. (67)], and thus vanish exponentially when $p \to \infty$. When $d = 3$, the coefficient of dynamical friction is given by

$$\eta = 4\pi\beta \int_0^1 d\mu \; \mu^2 \exp(-\beta p^2 \mu^2 / 2) \tag{69}$$

[see Eq. (68)], so that

$$\eta \simeq (2\pi)^{3/2} / \beta^2 |p|^3, \qquad \text{when } |p| \to \infty$$

Also the components of the diffusion tensor vanish in three dimensions according to power laws. I have already stressed the universal character of Eq. (61). The mathematical study of its solutions would thus be of interest. This question will be left open here.

7. THE LORENTZ GAS

The final part of my considerations will be concerned with the study of the Lorentz gas. In this case the heat bath is replaced by a medium of noninteracting, immobile (infinitely heavy) scattering centers, distributed uniformly in space. The diffusing particle 1 interacts with them through the scaled potential (9).

One can treat the Lorentz gas as the limiting case of the motion of a particle with a unit mass in an ideal gas heat bath, when the mass M of the ideal gas particles tends to infinity. The pair correlation function $\hat{g}^1$ [see Eq. (65)] then takes the form

$$\hat{g}^1(k, p_1, p_2; \tau_0, t_1) = \exp\left[-ik \cdot \left(\frac{p_1 - p_2}{M} \right) \tau_0 \right] \hat{g}^1(k, p_1, p_2; 0, \tau_1) + i \int_0^{\tau_0} d\mu \exp\left[-i\mu k \cdot \left(\frac{p_1 - p_2}{M} \right) \right] \hat{V}(k) k \cdot \left(\frac{\partial}{\partial p_1} - \frac{\partial}{\partial p_2} \right) \tilde{f}_1^0(p_1; \tau_1) n \varphi_M^{\text{eq}}(p_2) \tag{70}$$

where

$$\varphi_M^{\text{eq}}(p) = (\beta / 2\pi M)^{d/2} \exp(-\beta p^2 / 2M) \tag{71}$$

Inserting this result into Eq. (33) one finds the following collision term:

$$\Lambda_M^{\text{coll}}(p; \tau_1) = (2\pi)^d n \left(\frac{\pi \beta M}{2} \right)^{1/2} \int dk [\hat{V}(k)]^2 \times \left(k \cdot \frac{\partial}{\partial p} \right) \left\{ \exp\left[-\frac{\beta M}{2k^2} (k \cdot p)^2 \right] \times \frac{1}{|k|} \left[\beta(k \cdot p) + k \cdot \frac{\partial}{\partial p} \right] \right\} \tilde{f}_1^0(p; \tau_1) \tag{72}$$

The limit $M \to \infty$ can be calculated with the use of the relation

$$\lim_{M \to \infty} \frac{1}{|k|} \left(\frac{M\beta}{2\pi} \right)^{1/2} \exp\left[-\frac{\beta M}{2k^2} (k \cdot p)^2 \right] = \delta(k \cdot p) \tag{73}$$

The kinetic equation describing the Lorentz gas reads

$$\frac{\partial \varphi(p; t)}{\partial t} = \epsilon^{1 + 1/d} n \pi (2\pi)^d \int dk [\hat{V}(k)]^2 \times \left(k \cdot \frac{\partial}{\partial p} \right) \delta(k \cdot p) \left(k \cdot \frac{\partial}{\partial p} \right) \varphi(p; t) \qquad d \geqslant 2 \tag{74}$$

The integration over k can be done owing to the relation

$$\int dk \, [\hat{V}(k)]^2 kk \, \delta(k \cdot p) = \alpha_d (\mathbb{1} - \hat{p}\hat{p}) / |p| \tag{75}$$

where $\mathbb{1}$ is a unit tensor, and

$$\alpha_d = \frac{1}{d - 1} \sigma_{d-1} \int_0^\infty d|k| \, |k|^d [\hat{V}(k)]^2 \tag{76}$$

σ_{d-1} being the area of a unit sphere in a $(d-1)$-dimensional space. Using Eq. (75) one can rewrite the kinetic equation (74) in the form

$$\frac{\partial\varphi(p;t)}{\partial t} = \epsilon^{1+1/d} n\pi(2\pi)^d \frac{\alpha_d}{|p|}\left\{\Delta_d - \left[\frac{\partial^2}{\partial|p|^2} + \frac{d-1}{|p|}\frac{\partial}{\partial|p|}\right]\right\}\varphi(p;t) \tag{77}$$

The differential operator in curly brackets is the difference between the d-dimensional Laplace operator Δ_d and its radial part. It follows that the collision term vanishes when the momentum distribution φ is spherically symmetric. In other words, any spherically symmetric momentum distribution provides a stationary solution of the kinetic equation (77). In the case of the Lorentz gas the thermalization process does not occur. Only the deviation of the angular distribution of momentum from an isotropic one evolves in time, vanishing when $t \to \infty$. [When $d = 3$, one may represent φ as a series of spherical functions and verify that its projection on spherical functions of order l decays like $\exp(-\gamma_l t)$, with $\gamma_l \sim l(l+1)/|p|^3$.]

8. FINAL REMARKS

The mean-field limit has important physical applications in dynamical theory of inhomogeneous fluids (e.g., Vlasov's equation in plasma physics). The characteristic time scale is there $t \sim \epsilon^{-1/d}$. I have shown that for systems at constant density (Vlasov's force vanishes) dynamical effects occur on a much larger time scale ($t \sim \epsilon^{-1-1/d}$), and are described (in the case of self-diffusion) by kinetic equation (57). A natural question arises whether there are situations in which real behavior of fluids is adequately described by it. Here the only remark I could make was to indicate a striking analogy between the results of the present study and those leading to the Balescu–Lenard equation in hot plasma theory (generalized Landau equation).

In the theory of van der Waals fluids one assumes pair potentials of the form

$$V(q) = V^s(q) + \epsilon V^L(\epsilon^{1/d} q) \tag{78}$$

Only the long-range part V^L is scaled according to Eq. (9). The short-range repulsive part V^s is not. It would be of great interest to extend the theory of dynamical phenomena to this case. In particular, this seems necessary for understanding the origin of the difference in orders of magnitude of the self-diffusion coefficient D_s obtained here ($D_s \sim \epsilon^{1+1/d}$; see Section 6) and of the correction to D_s due to long-range forces found for three-dimensional van der Waals fluids (with short-range repulsion) by Seghers, Résibois, and Pomeau[8] ($\delta D_s \sim \epsilon^{2/3}$).

Let me finally remark that condition (50) is not the only one to be imposed on the pair potential V in order to guarantee that the theory is well defined. Supplementary restrictions should be added to ensure the existence of the thermodynamic limit of reduced distributions [see Eq. (4)] and local thermodynamical parameters. The discussion of these restrictions can be found in the literature on the static properties of van der Waals fluids.[9]

APPENDIX

At equilibrium the second equation of hierarchy (14) reads

$$\left[-\frac{\partial}{\partial r_1}+\epsilon\beta F(r_{12})\right]n_2^{\epsilon,\mathrm{eq}}(r_{12})=-\beta\int dr_3\,F(r_{13})n_3^{\epsilon,\mathrm{eq}}(r_{12},r_{13},r_{23}) \quad \text{(A1)}$$

where $n_s^{\epsilon,\mathrm{eq}}(r_1,\ldots,r_s)$ is the equilibrium number density of s-tuples of particles with positions $(r_1,\ldots,r_s)$. The asymptotic representation (20) takes the form

$$\begin{aligned} n_2^{\epsilon,\mathrm{eq}}(r_{12}) &= n^2+\epsilon g^{1,\mathrm{eq}}(r_{12}) \\ n_3^{\epsilon,\mathrm{eq}}(r_{12},r_{13},r_{23}) &= n^3+\epsilon n\left[g^{1,\mathrm{eq}}(r_{12})+g^{1,\mathrm{eq}}(r_{13})+g^{1,\mathrm{eq}}(r_{23})\right] \end{aligned} \quad \text{(A2)}$$

Inserting Equations (A2) into Eq. (A1) one finds (terms$\sim\epsilon$)

$$-\frac{\partial}{\partial r_1}g^{1,\mathrm{eq}}(r_{12})+\beta F(r_{12})n^2=-n\beta\int dr_3\,F(r_{13})g^{1,\mathrm{eq}}(r_{23}) \quad \text{(A3)}$$

Applying the Fourier transform to the above equation yields the relation

$$\hat{g}^{1,\mathrm{eq}}(k)+n^2\beta\hat{V}(k)=-(2\pi)^d n\beta\hat{V}(k)\,\hat{g}^{1,\mathrm{eq}}(k) \quad \text{(A4)}$$

equivalent to Eq. (34) in Section 4.

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