Order and Disorder in the Approach to Equilibrium of a Classical Gas

D. J. Driebe[1] **and T. Petrosky**[1]

We study the approach to equilibrium of a classical gas. The initial condition corresponds to a Maxwell velocity distribution, but to a nonequilibrium binary correlation. We consider two cases. In the first, there are initially no spatial correlations, while in the second, initial correlations correspond to long-range spatial order. We show that the gas leaves the Maxwell velocity distribution function in the process of building up equilibrium correlations. The spatial correlations in the equilibrium state are seen to emerge from a self-organization process in the gas. Non-Markovian effects play an essential role in this process by coupling the velocity distribution and the binary correlations. For the case of initial long-range correlations we obtain "anti-Boltzmann" behavior in the evolution of the velocity distribution as the Boltzmann entropy decreases from the nonequilibrium to the equilibrium state. For this case we also have non-trivial behavior on a short time scale due to the non-Markovian effects. The approach used here is based on the theory of subdynamics as developed in pre-vious publications. The results obtained show the interplay between irreversible processes leading to disorder and to order in a classical gas.

KEY WORDS: Order and disorder; long-range correlations; anti-Boltzmann behavior; non-Markovian processes; subdynamics.

1. INTRODUCTION

As is well known, Boltzmann emphasized the close relationship between irreversibility and disorder. This point of view has been confirmed through numerical simulations.[1] However, this cannot be the whole story, as for a classical system at thermal equilibrium we have both disorder in the velocity distribution and order as expressed in two- or higher-order correlation functions. This spatial order also has to be the consequence of

---

[1] Center for Studies in Statistical Mechanics and Complex Systems, University of Texas at Austin, Austin, Texas 78712.

irreversible processes, i.e., starting with any initial condition, the system "self-organizes" the spatial order to be consistent with the equilibrium state.

From the Liouville equation, which gives the time evolution of the complete N-particle distribution function ρ, we can compute the time development of the velocity distribution (or "vacuum of correlation") ρ_0, two-particle spatial correlation ρ_2, or three-particle spatial correlation ρ_3.[2] As a result of the interactions, we have a "flow of correlations"[2,3]

$$\rho_0 \to \rho_2 \to \rho_3 \to \cdots \tag{1.1}$$

To visualize these processes, it is useful to introduce the $\mathscr{H}$-function[3]

$$\mathscr{H} = \int d\Gamma \, \rho^2 \tag{1.2}$$

where $d\Gamma$ is a volume element in phase space. We can easily decompose $\mathscr{H}$ into contributions coming from the various correlations

$$\mathscr{H} = \mathscr{H}_0 + \mathscr{H}_2 + \mathscr{H}_3 + \cdots \tag{1.3}$$

where

$$\mathscr{H}_i = \int d\Gamma \, \rho_i^2 \quad \text{for} \quad i = 0, 2, 3,\ldots \tag{1.4}$$

If we start with a system without correlations, we may expect the behavior represented schematically in Fig. 1. The total value of $\mathscr{H}$ is constant in time, since the evolution of ρ is unitary.

The behavior represented in Fig. 1 was predicted by Prigogine and verified by the numerical simulations of Orban and Bellemans,[1] as well as in a recent paper by Prigogine et al.[4] Here, as in the numerical simulation reported in ref. 4, we are interested in situations where we initially impose both the velocity distribution and the binary correlations ρ_2. In the numerical simulation, hard disks were used and were put at the nodes of a two-dimensional triangular lattice. The system was started therefore with "artificially high" spatial correlations.

---

[2] We are considering in this paper a spatially homogeneous system exclusively, so that the inhomogeneous component ρ_1 vanishes. The precise definition of, for example, ρ_2 is given by $\rho_2 \equiv \sum_k P^{(k,-k)}\rho$, where the definition of the projection operator $P^{(k,-k)}$ is given in (2.20) and below.

[3] Our choice of the $\mathscr{H}$-function allows the decomposition (1.3). Indeed, due to the orthogonality of each correlation subspace [see (2.19)], we have $\int d\Gamma \, \rho_i \rho_j = 0$ for $i \neq j$.
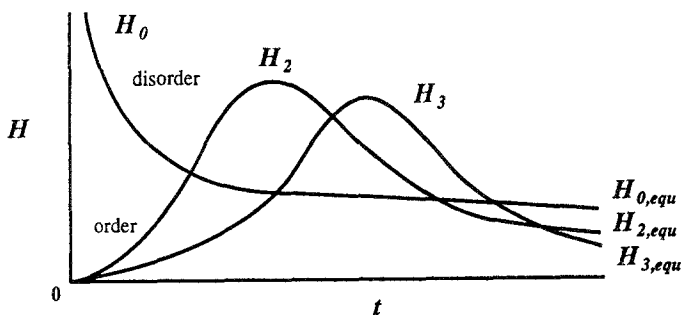
Fig. 1. Schematic representation of the typical behavior of the entropy components in a system started without correlations.

In this paper we shall consider soft interactions in dilute gases. Situations where initially there is either too little spatial order or, as was the case in the numerical simulations, too much spatial order are considered. Moreover, as was done in the numerical simulations, we start with a Maxwell velocity distribution. We expect quite different behavior from the two limiting situations. If there is initially too little order, $\mathcal{H}_2$ (and also $\mathcal{H}_3$, $\mathcal{H}_4$,...) in formula (1.4) will increase, and therefore $\mathcal{H}_0$ will initially decrease. As initially the velocity distribution is already Maxwellian, this decrease of $\mathcal{H}_0$ is realized by an increase in the temperature. In the second case, where we start with a long-range two-particle correlation so there is more spatial order than the equilibrium state, we find that eventually $\mathcal{H}_2$ decreases and $\mathcal{H}_0$ increases, an evolution which corresponds to a lowering of temperature. We have, in agreement with computer experiments, "anti-Boltzmann" behavior, as the entropy associated with the velocity distribution eventually decreases. For short times, though, the system cannot "feel" the long-range correlations and it behaves like the first case. This exemplifies in a rather dramatic way the influence of correlations on the evolution of the velocity distribution.

We shall see that these predictions can be verified through our kinetic approach. In order to obtain a quantitative description of these types of processes, we need to go beyond the traditional Markovian approximation used in kinetic theory, for example the $\lambda^2 t$ limit, where one considers the coupling constant λ going to zero while the time t increases, or the ct limit, where one considers the concentration c going to zero while the time t increases.[2] Indeed, we now need to retain finite values of the coupling constant or of the concentrations and thus include non-Markovian effects.

A classical gas is a large Poincaré system (LPS), and therefore, as discussed elsewhere, the eigenvalue problem associated with the Liouville operator L diverges.[5–7] The subdynamics theory avoids the divergence by

introducing a new type of analytic continuation which leads to a spectral representation of L involving *complex* eigenvalues.[7,8] In short, we associate a positive direction of time (in the lower half of the complex plane) to dynamical processes increasing (or preserving) the degree of correlation, while we associate a negative direction of time (in the upper half of the complex plane) to dynamical processes decreasing the degree of correlation. Here the degree of correlation is defined as the number of particles incolved in a correlation (see ref. 7 for more detail). The dynamics of correlations is therefore used to define in an intrinsic way the direction of time.

In the subdynamics theory, the evolution of the probability density $\rho(t)$ is expressed as a sum of independent evolutions in the various "subspaces" $\Pi^{(\nu)}$ corresponding to generalized eigenvectors of the Liouville operator.[8] (For the convenience of the reader we give in Appendix A a short summary of the subdynamics theory.) This superposition leads to a quantitative description of the non-Markovian processes that were introduced into kinetic theory some time ago.[2] As we shall see, the non-Markovian processes play an essential role in the coupling of the degrees of freedom of the gas, and correspond to a "self-organization" which prepares the long-time kinetic description.[3] These processes correspond to the induction period, preceding the kinetic regime, as discussed qualitatively by Bogolubov[9] and semiquantitatively by Green[10] and Cohen.[11] In those works the induction period was argued to last for a time on the order of the duration of a collision. As will be shown in detail, our formulation gives an explicit description of the induction period which may, for a system prepared initially with long-range correlations, last much longer.

In Section 2 we introduce the model and specify the initial conditions. In Section 3 we study the time evolution of the system as governed by the Liouville equation by using the subdynamics theory. In Sections 4 and 5 we discuss the velocity distribution, temperature shift, and entropy change for the cases of vanishing initial correlations and initial long-range correlations, respectively. Finally, in Section 6 we summarize our results.

2. THE MODEL AND THE INITIAL CONDITIONS

We consider a classical homogeneous gas interacting through two-body central forces (see Chapter 4 of ref. 2). The Hamiltonian of the N-particle system is

$$H = H_0 + \lambda V = \sum_{j=1}^{N} \frac{\mathbf{p}_j^2}{2m} + \lambda \sum_{j,n}^{N} V(|\mathbf{x}_j - \mathbf{x}_n|) \tag{2.1}$$

where λ is a small dimensionless coupling constant. We will take units with the mass of the particles $m = 1$ and so will make no distinction between the linear momentum $\mathbf{p}_j$ and the velocity $\mathbf{v}_j$ of particle j.

We are interested in studying the gas in the thermodynamic limit, i.e.,

$$N \to \infty, \qquad \Omega \to \infty; \qquad \frac{N}{\Omega} = c \tag{2.2}$$

where N is the number of particles, $\Omega = L^3$ is the volume of the gas, and c is the concentration. We start with the N-particle system in a box of volume L^3 and impose periodic boundary conditions. Hence, the interaction potential V can be expanded in the Fourier series

$$V(|\mathbf{x}_j - \mathbf{x}_n|) = \left(\frac{2\pi}{L}\right)^3 \sum_l V_l \exp[i l \cdot (\mathbf{x}_j - \mathbf{x}_n)] \tag{2.3}$$

The limit (2.2) is then taken at the appropriate place in the calculation, which leads, for example, to

$$\left(\frac{2\pi}{L}\right)^3 \sum_l \to \int d^3 l \quad \text{and} \quad \left(\frac{L}{2\pi}\right)^3 \delta^{\mathrm{Kr}}(\mathbf{k}) \to \delta(\mathbf{k}) \tag{2.4}$$

where $\delta^{\mathrm{Kr}}(\mathbf{k})$ is the Kronecker delta function and $\delta(\mathbf{k})$ is the Dirac delta function.

The N-particle distribution function ρ of the system evolves by the Liouville equation

$$i\frac{\partial}{\partial t}\rho(t) = L\rho(t) \tag{2.5}$$

where the Liouville operator (or Liouvillian) L is defined from

$$L\rho \equiv i\{H, \rho\} \tag{2.6}$$

with H the Hamiltonian and $\{H, \rho\}$ a Poisson bracket. Thus,

$$L = -i\frac{\partial H}{\partial v}\frac{\partial}{\partial x} + i\frac{\partial H}{\partial x}\frac{\partial}{\partial v} \tag{2.7}$$

For notational convenience we have used in (2.7), as elsewhere from now on when no ambiguity will occur,

$$x \equiv \{\mathbf{x}_1, \mathbf{x}_2 \cdots \mathbf{x}_N\} \tag{2.8}$$

$$v \equiv \{\mathbf{v}_1, \mathbf{v}_2 \cdots \mathbf{v}_N\} \tag{2.9}$$

and likewise for other sets of N quantities. The Liouvillian for the N-particle gas is thus obtained from (2.1) and (2.3) using (2.7) to give

$$L = L_0 + \lambda L_V \tag{2.10}$$

where

$$L_0 = -i \sum_{j=1}^{N} \mathbf{v}_j \cdot \frac{\partial}{\partial \mathbf{x}_j} \tag{2.11}$$

and

$$L_V = -\frac{8\pi^3}{\Omega} \sum_{j,n} \sum_{l} e^{il \cdot (\mathbf{x}_j - \mathbf{x}_n)} V_l l \cdot \partial_{jn} \tag{2.12}$$

where we have introduced the shorthand notation

$$\partial_{jn} \equiv \left(\frac{\partial}{\partial \mathbf{v}_j} - \frac{\partial}{\partial \mathbf{v}_n} \right) \tag{2.13}$$

We use a "superspace" description of the system where a phase function like $\rho(x, v)$ is regarded as a vector of the superspace.[7] To apply the subdynamics theory, the eigenfunctions of the unperturbed part of the Liouvillian are needed. They are defined from

$$L_0 | k; u) = l_{k;u} | k; u) \tag{2.14}$$

where

$$l_{k;u} = k \cdot u \tag{2.15}$$

From L_0 in (2.11)[4]

$$(x; v | k; u) = \Omega^{-N/2} e^{ik \cdot x} \delta(u - v) \tag{2.16}$$

where $\delta(u - v) = \prod_{i=1}^{N} \delta(\mathbf{u}_i - \mathbf{v}_i)$.

The matrix elements of L_V with respect to the unperturbed eigenstates of L_0 are

$$(k; u | L_V | k'; u') = \Omega^{-N} \int dx \, dv \, e^{-ik \cdot x} \delta(u - v) \, L_V e^{ik' \cdot x} \delta(u' - v)$$

$$= \frac{8\pi^3}{\Omega} \lambda \sum_{j,n} \sum_{l} V_l \delta^{Kr}(\mathbf{k}_j' - \mathbf{k}_j + l) \, \delta^{Kr}(\mathbf{k}_n' - \mathbf{k}_n - l)$$

$$\times \prod_{r \neq j,n} \delta^{Kr}(\mathbf{k}_r' - \mathbf{k}_r) \, l \cdot [\partial_{jn}' \delta(u' - u)] \tag{2.17}$$

where ∂_{jn}' is associated with the variables $\mathbf{u}_j'$ and $\mathbf{u}_n'$ [see (2.13)].

---

[4] We use eigenfunctions in the complete phase space, so the multiplicative factor v in L_0 accounts for the factor $\delta(u - v)$ in the eigenfunction. This makes the matrix elements of L_V in (2.17) numbers, in contrast to the choice of eigenfunctions in just x, k-space as in ref. 2, where the L_V "matrix elements" are then operators.

From the eigenstates of L_0 we introduce the (unperturbed) complete set of orthogonal projection operators $P_u^{(k)}$ defined as

$$\overset{(k)}{P_u} \equiv |k; u)(k; u| \qquad\qquad (2.18)$$

which satisfy

$$\overset{(k)}{P_u}\,\overset{(k')}{P_v} = \overset{(k)}{P_u}\,\delta^{\mathrm{Kr}}(k - k')\,\delta(u - v); \qquad \sum_k \int du\,\overset{(k)}{P_u} = 1 \qquad (2.19)$$

We are considering in this paper a homogeneous gas, i.e., where the state of the system is invariant with respect to a bulk translation of all particles. In this case only projections with $\sum_i \mathbf{k}_i = 0$ contribute.[2] Of special importance will be the $P^{(0)}$ projectors on the "vacuum of correlations" (the velocity distribution), and the $P^{(k, -k)}$ [here the notation $(k, -k)$ means $(\mathbf{k}_j = \mathbf{k}, \mathbf{k}_n = -\mathbf{k}, \mathbf{k}_{r \neq \{j,n\}} = 0)$] projectors on binary correlations (in the Fourier space). Expanding ρ in these unperturbed projectors, we have explicitly

$$\rho(x, v) = \sum_k \int du(x; v \mid \overset{(k)}{P_u} \mid \rho)$$

$$= \sum_k \int du(x; v \mid k; u)(k; u \mid \rho)$$

$$= \Omega^{-N}\{\rho_0(v) + (8\pi^3/\Omega)$$

$$\times \sum_{j,n} \sum_{\mathbf{k}} \rho_{\mathbf{k}, -\mathbf{k}}(\mathbf{v}_j, \mathbf{v}_n \mid ...)\exp[i\mathbf{k} \cdot (\mathbf{x}_j - \mathbf{x}_n)] + \cdots\} \qquad (2.20)$$

The notation $\rho_{\mathbf{k}, -\mathbf{k}}(\mathbf{v}_j, \mathbf{v}_n \mid ...)$ means that the Fourier component $\rho_{\mathbf{k}, -\mathbf{k}}$ has nonzero wave vectors of $\mathbf{k}$ and $-\mathbf{k}$ for the particles j and n, respectively. It is related to the projector $P^{(k, -k)}$ as

$$\overset{(k, -k)}{P}\rho = \rho_{\mathbf{k}, -\mathbf{k}}(\mathbf{v}_j, \mathbf{v}_n \mid ...)$$

The dots to the right of the bar schematically indicate the dependence of $\rho_{\mathbf{k}, -\mathbf{k}}$ on the velocities of the rest of the $N - 2$ particles with vanishing wave vectors. The volume dependence of each term in the second line of (2.20) is a result of the assumption that the distribution function depends smoothly on the space variables (see ref. 2 for a more detailed discussion of this decomposition). This property is preserved by the dynamics under time evolution.

The reduced s-particle distribution function is defined from the full N-particle distribution ρ as

$$f_s(x_1,\ldots, x_s; v_1,\ldots, v_s)$$

$$= \frac{N!}{(N-s)!} \int (d^3\mathbf{x})^{N-s} (d^3\mathbf{v})^{N-s} (d^3\mathbf{v})^{N-s} \rho(x, v) \qquad (2.21)$$

The N-particle velocity distribution $\rho_0(v)$ is by definition the $P^{(0)}$ component (the vacuum of correlation) of ρ. It is obtained by integrating ρ over all N positions. The one-particle velocity distribution function $\varphi(\mathbf{v})$ is obtained by integrating over all N positions and over $N-1$ velocities. For a homogeneous system it is related to $f_1(\mathbf{x}; \mathbf{v})$ by

$$f_1(\mathbf{x}; \mathbf{v}) = c\varphi(\mathbf{v}) \qquad (2.22)$$

The reduced two-particle correlation g_2 is as usual defined by

$$c^2 g_2(\mathbf{x}_\alpha, \mathbf{x}_\beta; \mathbf{v}_\alpha, \mathbf{v}_\beta) = f_2(\mathbf{x}_\alpha, \mathbf{x}_\beta; \mathbf{v}_\alpha, \mathbf{v}_\beta) - f_1(\mathbf{x}_\alpha; \mathbf{v}_\alpha) f_1(\mathbf{x}_\beta; \mathbf{v}_\beta) \quad (2.23)$$

For a homogeneous system there are simple relations[2] between each correlation function and the reduced Fourier components of ρ. For example, the two-particle correlation is related to $\rho_{k,-\mathbf{k}}$ by

$$g_2(\mathbf{x}_\alpha - \mathbf{x}_\beta; \mathbf{v}_\alpha, \mathbf{v}_\beta) = \int d^3\mathbf{k}\, \rho_{\mathbf{k},-\mathbf{k}}(\mathbf{v}_\alpha, \mathbf{v}_\beta)\, e^{i\mathbf{k}\cdot(\mathbf{x}_\alpha - \mathbf{x}_\beta)} \qquad (2.24)$$

where $\rho_{\mathbf{k},-\mathbf{k}}(\mathbf{v}_\alpha, \mathbf{v}_\beta)$ is the reduced Fourier coefficient obtained by integrating $\rho_{\mathbf{k},-\mathbf{k}}(\mathbf{v}_\alpha, \mathbf{v}_\beta |\ldots)$ over all velocity variables except those belonging to particles α and β.

We consider a weakly-coupled system so that the potential is always much smaller than the average kinetic energy of the particles. The inter-particle potential is chosen as

$$V = V_0 e^{-\eta |\mathbf{x}_j - \mathbf{x}_n|} \qquad (2.25)$$

which has the Fourier transform

$$V_k = \frac{\eta V_0}{\pi^2} \frac{1}{(k^2 + \eta^2)^2} \qquad (2.26)$$

The initial condition is taken to be (from now on we will not in general indicate the velocity variable dependence of the projection operators unless it is necessary)

$$\rho(0) = \left(\overset{(0)}{P} + \sum_{\mathbf{k}} \overset{(k,-k)}{P} \right) \rho(0) \qquad (2.27)$$

This means that we specify at $t = 0$ the velocity distribution and the binary correlation function. More specifically, we take

$$\rho_0(0) = \left(\frac{2\pi}{\beta}\right)^{-3N/2} \exp\left(-\frac{\beta}{2} \sum_{j=1}^{N} \mathbf{v}_j^2\right) \tag{2.28}$$

where $\beta = 1/k_B T_0$ (k_B is the Boltzmann constant and T_0 the initial temperature) and

$$g_2(0) = -\left(\frac{2\pi}{\beta}\right)^{-3} G\beta e^{-\sigma x_{\alpha\beta}} e^{-(v_\alpha^2 + v_\beta^2)/2} \tag{2.29}$$

where $x_{\alpha\beta} \equiv |\mathbf{x}_\alpha - \mathbf{x}_\beta|$, which corresponds to the N-particle Fourier coefficient

$$\rho_{\mathbf{k}, -\mathbf{k}}(0) = -\left(\frac{2\pi}{\beta}\right)^{-3N/2} \frac{G\sigma}{\pi^2} \frac{\beta}{(k^2 + \sigma^2)^2} \exp\left(-\frac{\beta}{2} \sum_{j=1}^{N} \mathbf{v}_j^2\right) \tag{2.30}$$

The specific choice of the initial two-particle correlation is made in order to make comparisions with the equilibrium correlation. Two parameters are introduced in the specification of g_2; G and σ, which measure, respectively, the amplitude and the range of the two-particle correlation. At equilibrium, to lowest order in λ, we would have [as will be seen later in (3.22)]

$$G = \lambda V_0, \qquad \sigma = \eta \tag{2.31}$$

3. TIME EVOLUTION OF THE SYSTEM

To calculate the evolution of the distribution function, we employ the theory of subdynamics to solve the Liouville equation. We start with the evolution of the velocity distribution. It is determined from the $P^{(0)}$ projection of ρ as decomposed in subdynamics as [see (A.15)]

$$\rho_0(v; t) = \overset{(0)}{P}\rho(t) = \overset{(0)}{P}[\exp(-i\overset{(0)}{\theta} t)]\overset{(0)}{A}(\overset{(0)}{P} + \overset{(0)}{D})\rho(0)$$

$$+ \sum_{(k \neq 0)} \overset{(0)(k)}{P\,C}[\exp(-i\overset{(k)}{\theta} t)]\overset{(k)}{A}(\overset{(k)}{P} + \overset{(k)}{D})\rho(0) \tag{3.1}$$

The definitions of the kinetic operators $A^{(v)}$, $C^{(v)}$, $D^{(v)}$, and $\theta^{(v)}$ are given in Appendix A. The first term in (3.1) gives the usual Boltzmann (or Fokker–Planck) type Markovian evolution in the $\Pi^{(0)}$ subspace. The second term corresponds to the excitation of the binary and higher correla-

tion modes. The superposition of these mechanisms leads to non-Markovian effects.[1,3] As will be discussed later in detail, the $\Pi^{(0)}$ subspace will dominate asymptotically in time. The subspaces other than $\Pi^{(0)}$ correspond to non-Markovian processes.

Let us now follow what happens in $\Pi^{(0)}$ space. By (3.1) we see that the evolution of the $P^{(0)}$ component of ρ in $\Pi^{(0)}$ space (i.e., $\rho_0^{(0)}$) satisfies the closed equation [see (A.17)]

$$i\, \partial \overset{(0)}{\rho_0}(t)/\partial t = \overset{(0)(0)}{\theta} \rho_0(t) \tag{3.2}$$

with the initial condition [see (A.7)]

$$\overset{(0)}{\rho_0}(0) = \overset{(0)(0)}{P\,\Pi} \rho(0) = \overset{(0)}{A}(\overset{(0)}{P} + \overset{(0)}{D})\rho(0) \tag{3.3}$$

As mentioned, the traditional approximation for weakly-coupled systems used in kinetic theory corresponds to the $\lambda^2 t$ limit where only contributions of $\mathcal{O}((\lambda^2 t)^n)$ (with $n = 0, 1,...$) are retained.[2] In this approximation, one neglects the second term in (3.3) (i.e., $D^{(0)} = 0$) and in the first term one replaces $A^{(0)}$ by 1. We then recover the usual Boltzmann (Fokker–Planck) description. In this approximation there is no coupling between the evolution of the velocity distribution and the correlations. We wish to go beyond this weakly coupled first approximation corresponding to traditional kinetic theory and include all terms of $\mathcal{O}(\lambda(\lambda^2 t)^n)$ and $\mathcal{O}(\lambda^2(\lambda^2 t)^n)$.

Using our choice for $\rho(0)$ from (2.28) and (2.30), then we have, up to $\mathcal{O}(\lambda^2)$,

$$\overset{(0)}{\rho_0}(0) = \left\{ \overset{(0)}{P} + \lambda \sum_k \overset{(0)(0)}{P\,D_1}\overset{(k,-k)}{}\overset{(0)}{P} + \lambda^2 \left[\overset{(0)(k)}{P\,A_2}\overset{(0)}{P} + \sum_k \overset{(0)(0)}{P\,D_2}\overset{(k,-k)}{}\overset{(0)}{P} \right] \right\} \rho(0) \tag{3.4}$$

Here $D_1^{(0)}$ and $D_2^{(0)}$ correspond, respectively, to the first- and second-order contributions to the destruction operator $D^{(0)}$, and $A_2^{(0)}$ to the lowest order (in λ^2) contribution to $A^{(0)}$. The important point is that the initial velocity distribution in this subspace depends explicitly on the state of the initial binary correlation function. This indicates a coupling between the velocity distribution and the correlation function.

Using the general forms of the operators D_1, A_2, and D_2 as given in Appendix A and the matrix elements of L_V from (2.17), we obtain here for the gas

$$\overset{(0)(0)}{P\,D_1}\overset{(k,-k)}{}\overset{(0)}{P} = \sum_{j=1}^N \int d^3k\, V_k \mathbf{k}\cdot \partial_{\alpha j} \frac{1}{\mathbf{k}\cdot \mathbf{v}_{\alpha j} - i\varepsilon} \tag{3.5}$$

$$\overset{(0)(0)}{P\,A_2}\overset{(0)}{P} = \frac{8\pi^3}{\Omega} \sum_{j=1}^N \int d^3k\, V_k^2 \mathbf{k}\cdot \partial_{\alpha j} \frac{1}{(\mathbf{k}\cdot \mathbf{v}_{\alpha j} - i\varepsilon)^2} \mathbf{k}\cdot \partial_{\alpha j} \tag{3.6}$$

$$\overset{(0)\,(0)\,(k,\,-k)}{P\;D_2\;P} = \sum_{j=1}^{N} \int d^3l \int d^3\mathbf{k}\; V_{k-l}V_l(\mathbf{k}-\mathbf{l})$$

$$\times \partial_{\alpha j} \frac{1}{(\mathbf{k}-\mathbf{l})\cdot\mathbf{v}_{\alpha j}-i\varepsilon}\,\mathbf{k}\cdot\partial_{\alpha j}\frac{1}{\mathbf{k}\cdot\mathbf{v}_{\alpha j}-i\varepsilon} \qquad (3.7)$$

In the above expressions, as in the following, we have integrated over the auxiliary velocity variables $u, u',...$ so the velocity dependence is on v only. The derivative operators $\partial_{\alpha j}$ are with respect to v and act on everything to their right.

Using (3.5)–(3.7) with the interaction (2.26) in (3.4), we obtain the initial condition $\rho_0^{(0)}(0)$, which we reduce to obtain the initial one-particle velocity distribution in $\Pi^{(0)}$ space (see Appendix B for details)

$$\overset{(0)}{\varphi}(\mathbf{v};0) = \left(\frac{2\pi}{\beta}\right)^{-3/2}\left\{1 - \left[\lambda\frac{8\pi cGV_0\beta^2}{(\eta+\sigma)^3} - \lambda^2\frac{\pi cV_0^2\beta^2}{\eta^3}\right]\right.$$

$$\left.\times\left[1 - 2\,_1F_1\left(\frac{1}{2};\frac{3}{2};\frac{\beta}{2}v^2\right)e^{-\beta v^2/2}\right]\right\}e^{-\beta v^2/2} \qquad (3.8)$$

where $_1F_1(\tfrac{1}{2};\tfrac{3}{2};\tfrac{1}{2}\beta v^2)$ is the confluent hypergeometric function. (Note that v here represents the magnitude $|\mathbf{v}|$ of the velocity of one particle.) The important point is that (3.8) corresponds to a nonequilibrium velocity distribution. From (3.2) this initial velocity distribution in $\Pi^{(0)}$ space evolves by the evolution operator $\theta^{(0)}$. Taking $\theta^{(0)}$ to $\mathcal{O}(\lambda^2)$, we have explicitly [see (A.16) with (A.11) in Appendix A]

$$\overset{(0)\,(0)\,(0)}{P\;\theta_2\;P} = \frac{8\pi^3}{\Omega}\sum_{j=1}^{N}\int d^3\mathbf{k}\;V_k^2\mathbf{k}\cdot\partial_{\alpha j}\frac{1}{\mathbf{k}\cdot\mathbf{v}_{\alpha j}-i\varepsilon}\,\mathbf{k}\cdot\partial_{\alpha j} \qquad (3.9)$$

This is the well-known Landau *collision operator* for weakly coupled gases.[2] Hence, to this approximation the velocity distribution in $\Pi^{(0)}$ space evolves by the Landau kinetic equation. There would be no point here in going to higher-order approximations in the kinetic equation (3.2), as this would simply introduce corrections in the relaxation time.

The fact that initial condition (3.8) is of the form of a Maxwellian plus a correction of $\mathcal{O}(\lambda)$ allows us to use the linearized form of the kinetic equation to obtain the asymptotic equilibrium velocity distribution as[12] (see Appendix C for details),

$$\varphi^{eq}(v) = (2\pi/\beta)^{-3/2}\exp(-\beta v^2/2) \qquad (3.10)$$

where $\bar\beta = 1/k_B T^{eq}$, and the equilibrium temperature is

$$T^{eq} = T_0\left[1 - \lambda\frac{8\pi cGV_0}{3(\eta+\sigma)^3 k_B^2 T_0^2} + \lambda^2\frac{\pi cV_0^2}{3\eta^3 k_B^2 T_0^2}\right] \qquad (3.11)$$

Since the evolution operator (3.9) preserves kinetic energy, we can also derive this result (3.11) by defining the temperature as an average of v^2 for (3.8).

One can see from (3.11) that different choices of the parameters G, characterizing the "strength," and σ, the inverse of the correlation length, in the initial two-particle correlation (2.29) lead to a temperature shift that may be positive, negative, or vanishing. In Sections 4 and 5 two special cases are considered.

The evolution of ρ_0 in $\Pi^{(2)} \equiv \Pi^{(k,-k)}$ space is given by

$$\overset{(2)}{\rho_0}(t) = \overset{(0)}{P}\overset{(2)}{\Pi}\rho(0) = \overset{(0)}{P}\overset{(2)}{C}[\exp(-i\overset{(2)}{\theta}t)]\,\overset{(2)}{A}(\overset{(2)}{P}+\overset{(2)}{D})\,\rho(0) \tag{3.12}$$

Up to order λ^2, then, we have the two contributions

$$\overset{(2)}{\rho}_{0|2} = \lambda\overset{(0)}{P}\overset{(2)}{C}_1[\exp(-i\overset{(2)}{\theta}t)]\,\overset{(2)}{P}\rho(0) \tag{3.13}$$

coming from the propagation in $P^{(2)}$ space of the initial two-particle correlation and then a transition to $P^{(0)}$ space, and

$$\overset{(2)}{\rho}_{0|0} = \lambda^2\overset{(0)}{P}\overset{(2)}{C}_1[\exp(-i\overset{(2)}{\theta}_t)]\,\overset{(2)}{D}_1\overset{(0)}{P}\rho(0) \tag{3.14}$$

arising from a diagonal transition consisting of a transition from $P^{(0)}$ to $P^{(2)}$, propagation in $P^{(2)}$, and then a transition back to $P^{(0)}$. The evolution operator $\theta^{(2)}$ to lowest order here has a term independent of λ since the unperturbed eigenvalue of L_0 in $P^{(2)}$ space is nonvanishing [see (A.16)]. This term represents the propagation of the correlations without any damping by collision with a third particle.

Carrying out the calculation in (3.13), similar to the derivation in Appendix B for (3.8), gives

$$\overset{(2)}{\rho}_{0|2} = \frac{8\pi^3}{\Omega}\left(\frac{2\pi}{\beta}\right)^{-3N/2}\frac{\eta V_0}{\pi^2}\frac{\sigma G}{\pi^2}\,\beta\,\frac{4\pi^2}{(\sigma^2-\eta^2)^3}$$

$$\times \sum_j \left\{\frac{1}{2}\left[\frac{3\sigma^2+\eta^2}{\sigma}e^{-\sigma v_{\alpha j}t} - \frac{\sigma^2+3\eta^2}{\eta}e^{-\eta v_{\alpha j}t}\right]\frac{1}{v_{\alpha j}^2}\right.$$

$$+\left[\frac{(\sigma^2-\eta^2)\,t}{2}(e^{-\sigma v_{\alpha j}t}+e^{-\eta v_{\alpha j}t})+\frac{\beta}{t}(e^{-\sigma v_{\alpha j}t}-e^{-\eta v_{\alpha j}t})\right]\frac{1}{v_{\alpha j}}$$

$$+\frac{(\sigma^2-\eta^2)\,\beta}{4}\left(\frac{e^{-\sigma v_{\alpha j}t}}{\sigma}+\frac{e^{-\eta v_{\alpha j}t}}{\eta}\right)\right\}e^{-\beta v_j^2/2} \tag{3.15}$$

and from (3.14) we have

$$
\overset{(2)}{\rho_{0|0}} = \frac{8\pi^3}{\Omega} \left(\frac{2\pi}{\beta}\right)^{-3N/2} \left(\frac{\eta V_0}{\pi^2}\right)^2 \beta \frac{\pi^2}{12} \sum_j \left\{ -3\eta^{-5}\frac{1}{v_{\alpha j}^2} - 3\eta^{-4}t\frac{1}{v_{\alpha j}} \right.
$$

$$
+ \frac{3}{2}\beta\eta^{-5} + \left(\frac{3}{2}\beta\eta^{-4}t + \eta^{-2}t^3\right)v_{\alpha j} + \frac{1}{2}\beta\eta^{-3}t^2 v_{\alpha j}^2 \bigg\}
$$

$$
\times e^{-\eta v_{\alpha j}t}e^{-\beta v_j^2/2} \tag{3.16}
$$

where we have again neglected damping due to a third particle. Note that $\rho_{0|2}^{(2)}$ decays to zero exponentially with the two time scales $\tau_\eta \sim (\eta\langle v\rangle)^{-1}$, being the duration of a collision, and $\tau_\sigma \sim (\sigma\langle v\rangle)^{-1}$, being the time for an average particle to cross the initial correlation length. The component $\rho_{0|0}^{(2)}$ is seen to decay with the duration-of-collision time scale $\tau_\eta \sim (\eta\langle v\rangle)^{-1}$. Hence, for the case of long-range initial correlations where $\sigma \ll \eta$ the contribution of the $\Pi^{(2)}$ subspace decays slower than the duration-of-collision time scale. Since the kinetic equation, such as the Boltzmann equation or the Landau equation, is valid when the contribution from $\Pi^{(0)}$ space becomes dominant, this means that the induction period for this case is much longer than the duration of collision τ_η.

The one-particle velocity distributions, from the reduction of (3.15) and (3.16), are found to be

$$
\overset{(2)}{\varphi_{0|2}}(v)
$$

$$
= \left(\frac{2\pi}{\beta}\right)^{-3/2} \lambda \frac{8\pi c G V_0 \beta^2}{(\sigma+\eta)^3} \frac{\exp(-\beta v^2)}{v} \frac{\sigma\eta}{(\sigma-\eta)^3}
$$

$$
\times \left\{ \frac{3\sigma^2+\eta^2}{\sigma}\left[\frac{1}{(2\pi)^{1/2}}\frac{(\beta v-\sigma t)^2}{\beta^{3/2}}\, {}_2F_2\left(1,1;\frac{3}{2},2;\frac{(\beta v-\sigma t)^2}{2\beta}\right) \right.\right.
$$

$$
+ \frac{\beta v-\eta t}{\beta}\, {}_1F_1\left(\frac{1}{2};\frac{3}{2};\frac{(\beta v-\sigma t)^2}{2\beta}\right)
$$

$$
- \frac{1}{(2\pi)^{1/2}}\frac{(\beta v+\sigma t)^2}{\beta^{3/2}}\, {}_2F_2\left(1,1;\frac{3}{2},2;\frac{(\beta v+\sigma t)^2}{2\beta}\right)
$$

$$
\left. + \frac{\beta v+\sigma t}{\beta}\, {}_1F_1\left(\frac{1}{2};\frac{3}{2};\frac{(\beta v+\sigma t)^2}{2\beta}\right)\right]
$$

$$
- \frac{\sigma^2+3\eta^2}{\eta}\left[\frac{1}{(2\pi)^{1/2}}\frac{(\beta v-\eta t)^2}{\beta^{3/2}}\, {}_2F_2\left(1,1;\frac{3}{2},2;\frac{(\beta v-\eta t)^2}{2\beta}\right)\right.
$$

$$
+ \frac{\beta v-\eta t}{\beta}\, {}_1F_1\left(\frac{1}{2};\frac{3}{2};\frac{(\beta v-\eta t)^2}{2\beta}\right)
$$

$$-\frac{1}{(2\pi)^{1/2}}\frac{(\beta v+\eta t)^2}{\beta^{3/2}}\ _2F_2\left(1,1;\frac{3}{2},2;\frac{(\beta v+\eta t)^2}{2\beta}\right)$$

$$+\frac{\beta v+\eta t}{\beta}\ _1F_1\left(\frac{1}{2};\frac{3}{2};\frac{(\beta v+\eta t)^2}{2\beta}\right)\Bigg]$$

$$+\left[\frac{\sigma^2-\eta^2}{2\beta}t+\frac{2}{t}+\frac{\sigma^2-\eta^2}{2\sigma}v\right]\exp\left(\frac{(\beta v-\sigma t)^2}{2\beta}\right)\mathrm{erfc}\left(\frac{-(\beta v-\sigma t)}{(2\beta)^{1/2}}\right)$$

$$-\left[\frac{\sigma^2-\eta^2}{2\beta}t+\frac{2}{t}-\frac{\sigma^2-\eta^2}{2\sigma}v\right]\exp\left(\frac{(\beta v+\sigma t)^2}{2\beta}\right)\mathrm{erfc}\left(\frac{\beta v+\sigma t}{(2\beta)^{1/2}}\right)$$

$$+\left[\frac{\sigma^2-\eta^2}{2\beta}t-\frac{2}{t}+\frac{\sigma^2-\eta^2}{2\eta}v\right]\exp\left(\frac{(\beta v-\eta t)^2}{2\beta}\right)\mathrm{erfc}\left(\frac{-(\beta v-\eta t)}{(2\beta)^{1/2}}\right)$$

$$-\left[\frac{\sigma^2-\eta^2}{2\beta}t-\frac{2}{t}-\frac{\sigma^2-\eta^2}{2\eta}v\right]\exp\left(\frac{(\beta v+\eta t)^2}{2\beta}\right)\mathrm{erfc}\left(\frac{\beta v+\eta t}{(2\beta)^{1/2}}\right)\Bigg\}$$

$$(3.17)$$

and

$$\overset{(2)}{\varphi}_{0|0}(v)$$

$$=-\left(\frac{2\pi}{\beta}\right)^{-3/2}\lambda^2\frac{\pi c V_0^2\beta^2}{\eta^3}\frac{\exp(-\beta v^2)}{v}$$

$$\times\Bigg\{-\frac{1}{(2\pi)^{1/2}}\frac{(\beta v-\eta t)^2}{\beta^{3/2}}\ _2F_2\left(1,1;\frac{3}{2},2;\frac{(\beta v-\eta t)^2}{2\beta}\right)$$

$$-\frac{\beta v-\eta t}{\beta}\ _1F_1\left(\frac{1}{2};\frac{3}{2};\frac{(\beta v-\eta t)^2}{2\beta}\right)$$

$$+\frac{1}{(2\pi)^{1/2}}\frac{(\beta v+\eta t)^2}{\beta^{3/2}}\ _2F_2\left(1,1;\frac{3}{2},2;\frac{(\beta v+\eta t)^2}{2\beta}\right)$$

$$-\frac{(\beta v+\eta t)}{\beta}\ _1F_1\left(\frac{1}{2};\frac{3}{2};\frac{(\beta v+\eta t)^2}{2\beta}\right)$$

$$+\left[\left(-\beta^{-1}\eta t+\frac{1}{3}\beta^{-2}\eta^3 t^3+\frac{1}{6}\beta^{-3}\eta^5 t^5\right)+\left(\frac{1}{2}\eta t-\frac{1}{6}\beta^{-1}\eta^3 t^3\right)v^2\right]$$

$$\times\left[\exp\left(\frac{(\beta v-\eta t)^2}{2\beta}\right)\mathrm{erfc}\left(\frac{-(\beta v-\eta t)}{(2\beta)^{1/2}}\right)\right.$$

$$-\exp\left(\frac{(\beta v+\eta t)^2}{2\beta}\right)\mathrm{erfc}\left(\frac{\beta v+\eta t}{(2\beta)^{1/2}}\right)\Bigg]$$

$$+ \left[\left(\frac{1}{2} - \frac{1}{2} \beta^{-1} \eta^2 t^2 - \frac{1}{6} \beta^{-2} \eta^4 t^4 \right) v + \left(\frac{1}{6} \eta^2 t^2 \right) v^3 \right]$$

$$\times \left[\exp \left(\frac{(\beta v - \eta t)^2}{2\beta} \right) \mathrm{erfc} \left(\frac{-(\beta v - \eta t)}{(2\beta)^{1/2}} \right) \right.$$

$$\left. + \exp \left(\frac{(\beta v + \eta t)^2}{2\beta} \right) \mathrm{erfc} \left(\frac{\beta v + \eta t}{(2\beta)^{1/2}} \right) \right]$$

$$\left. + \left(\frac{2\beta}{\pi} \right)^{1/2} (\beta^{-1} \eta t) v \right\} \tag{3.18}$$

In the above two expressions $_2F_2$ is the generalized hypergeometric function, $_1F_1$ is the confluent hypergeometric function as appears in (3.8), and erfc is the complementary error function.

Both $\varphi_{0|2}^{(2)}(v)$ and $\varphi_{0|0}^{(2)}(v)$ behave asymptotically like $1/t$ for t large. It looks as though we have found long-time-tail behavior here, but the $1/t$ decay is due to the fact that we only considered the flow part and neglected collision with a third particle in the time evolution operator $\theta^{(2)}$. If we were to go to the next order in λ, there would appear an exponentially decaying factor due to the three-body collision.

Since the contributions from $\varPi^{(2)}$ space decay, the $\varPi^{(0)}$ space velocity distribution dominates for long times. Actually, the entire N-particle asymptotic equilibrium state is in the $\varPi^{(0)}$ subspace.[12] At equilibrium the two-particle correlation function (to order λ) is given by

$$\rho_{k,-k}^{\mathrm{eq}}(v) = \lambda \overset{(k,-k)(0)}{P} C_1 \rho_0^{\mathrm{eq}}(v) \tag{3.19}$$

It becomes then a functional of the velocity distribution. Here $C_1^{(0)}$ is given by [see (A.11)]

$$\overset{(k,-k)(0)}{P} \overset{(0)}{C_1} P = \frac{8\pi^3}{\Omega} \sum_{j=1}^{N} V_k \frac{1}{\mathbf{k} \cdot \mathbf{v}_{\alpha j} - i\varepsilon} \mathbf{k} \cdot \partial_{\alpha j} \tag{3.20}$$

From the equilibrium velocity distribution (3.10) we obtain therefore

$$\rho_{k,-k}^{\mathrm{eq}}(v_\alpha, v_\beta) = -\lambda (2\pi/\beta)^{-3} \beta V_k \exp[-\tfrac{1}{2}\beta(v_\alpha^2 + v_\beta^2)] \tag{3.21}$$

This leads to [cf. (2.29) and (2.31)]

$$g_2^{\mathrm{eq}}(x_{\alpha\beta}; v_\alpha, v_\beta) = -\lambda (2\pi/\beta)^{-3} \beta V_0 \exp(-\eta x_{\alpha\beta}) \exp[-\tfrac{1}{2}\beta(v_\alpha^2 + v_\beta^2)] \tag{3.22}$$

4. INITIAL VANISHING CORRELATIONS

If in (2.29) we take $G = 0$, then we have a vanishing initial two-particle correlation. The equilibrium temperature is then, from (3.11),

$$T^{eq} = T_0 \left[1 + \lambda^2 \frac{\pi c V_0^2}{3\eta^3 k_B^2 T_0^2} \right] \tag{4.1}$$

Hence, there is a temperature increase as the system evolves to equilibrium. Notice that it is independent of the sign of the potential.

This temperature increase is anticipated by the general considerations of Section 1. As the correlations "order" has to increase, the velocity "order" has to decrease to meet the constraint of the constancy of the Gibbs entropy. Moreover, as we already start with a Maxwell distribution, this leads naturally to an increase of temperature. In Fig. 2 the velocity distributions for this case are shown. Plotted for a certain choice of parameters are the initial distribution corresponding to the one-particle form of (2.28), the initial distribution in $\Pi^{(0)}$ space (3.8) with $G = 0$, and the final equilibrium distribution (3.10).

Since the initial and final velocity distributions are both Maxwellian and the temperature increases, the Boltzmann entropy increases also. Specifically, the Boltzmann entropy density is given by

$$s_1 = -k_B \int d^3\mathbf{v} \, f_1 \log f_1 \tag{4.2}$$

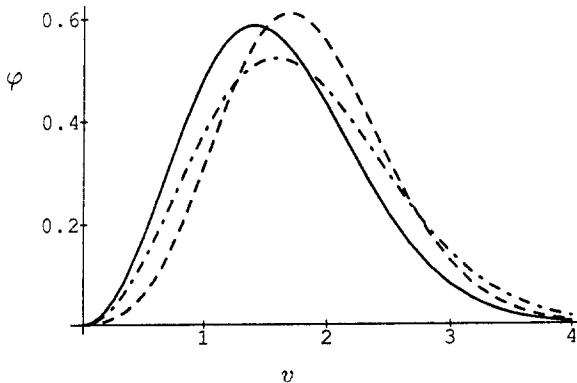Fig. 2. Evolution of the velocity distribution when the system initially has no correlations. The solid line is the initial distribution, the dashed line is the initial distribution in $\Pi^{(0)}$ space, and the dot-dashed line is the equilibrium distribution. The parameters have been chosen as $c = 1$, $V_0 = 1$, $\beta = 1$, and $\eta = 1$, and to exaggerate the effect we choose a moderately large value of $\lambda = 0.5$.

Using our initial and final velocity distributions gives

$$s_1^{eq} - s_1^0 \simeq \lambda^2 c k_B \left(\frac{\pi c V_0^2}{2\eta^3 k_B^2 T_0^2} \right) > 0 \tag{4.3}$$

Thus, the "disorder" associated with the velocity distribution has increased.

5. INITIAL LONG-RANGE CORRELATIONS

To consider the evolution from an initial state with long-range correlations, let us take in (2.29) $G = \lambda V_0$ and $\sigma \ll \eta$. For this case Eq. (3.11) gives us

$$T^{eq} = T_0 \left[1 - \lambda^2 \frac{7\pi c V_0^2}{3\eta^3 k_B^2 T_0^2} \right] \tag{5.1}$$

showing that there is a *decrease* in temperature as the system evolves to equilibrium. In Fig. 3 the velocity distributions as were given for the previous case are shown.

Let us discuss in greater detail the evolution of the velocity distribution starting with (3.1) for $t = 0$ correct to order λ^2 [see also (3.4) and (3.14)]. We first consider the case $G = 0$ studied in the previous section, where the initial velocity distribution is

$$\rho_0(v; t=0) = \overset{(0)}{P}(1 + \lambda^2 \overset{(0)}{A_2}) \overset{(0)}{P} \rho(0) + \lambda^2 \overset{(0)}{P} \overset{(2)}{C_1} \overset{(2)}{D_1} \overset{(0)}{P} \rho(0) \tag{5.2}$$

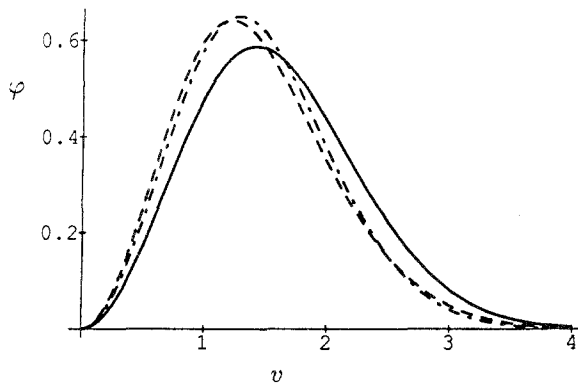Fig. 3. Evolution of the velocity distribution when the system has long-range correlations initially. The solid line is the initial distribution, the dashed line is the initial distribution in $\Pi^{(0)}$ space, and the dot-dashed line is the equilibrium distribution. The parameters have been chosen as $c = 1$, $V_0 = 1$, $\beta = 1$, $G = 0.5$, $\sigma = 0.2$, $\eta = 1.8$, and $\lambda = 0.5$.

The initial condition is distributed over the "kinetic subspace" $\Pi^{(0)}$ and the correlation subspace $\Pi^{(2)}$. The initial condition corresponds to a Maxwell distribution; however, in each subspace there is a non-Maxwellian contribution. The important point is that the correlation space $\Pi^{(2)}$ dies out exponentially over a time of the order of the duration of a collision, as can be seen in (3.16). Therefore, after this time we have a non-Maxwellian distribution (coming from $\Pi^{(0)}$) for ρ itself, and $\Pi^{(0)}\rho(0)$ acts as a "post-initial condition" for the slow kinetic evolution determined by Eq. (3.2).[13]

However, for the case $G \neq 0$ considered in this section we now have the additional contributions to (5.2) of [see (3.4) and (3.13)]

$$\overset{(0)}{\rho}_{0|2}(0) = \lambda \overset{(0)}{P} \overset{(0)}{D_1} \overset{(2)}{P} \rho(0) \tag{5.3}$$

from $\Pi^{(0)}$ space and

$$\overset{(2)}{\rho}_{0|2}(0) = \lambda \overset{(0)}{P} \overset{(2)}{C_1} \overset{(2)}{P} \rho(0) \tag{5.4}$$

from $\Pi^{(2)}$ space. At $t = 0$ these terms cancel. However, (5.4) decays slowly, typically on the time scale of the duration for a particle to cross the initial correlation length. Therefore, after the duration of the collision, the system does not yet have the time to "feel" the effect of the initial correlations. Thus, for short times, the temperature first increases (as does the value of the initial correlations), then the decay of the inner correlations cools the
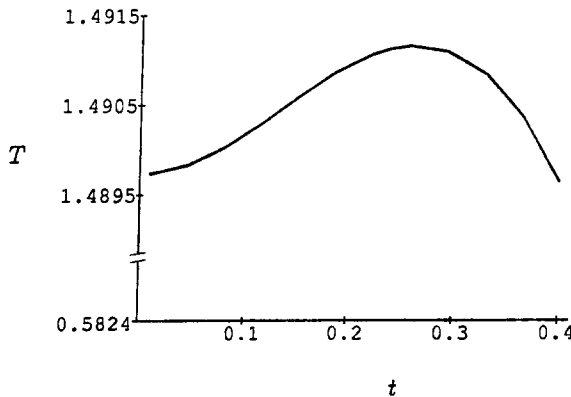
Fig. 4. Evolution of the temperature for very short times in the case of initial long-range correlations with parameters $c = 1$, $V_0 = 1$, $\beta = 1$, $G = 0.5$, $\sigma = 0.2$, $\eta = 1.2$, and $\lambda = 0.5$. The plot is obtained from numerical integration of $\frac{1}{2}v^2$ times the complete velocity distribution obtained from Eqs. (3.8), (3.17), and (3.18). The initial temperature is 1.4897 and the equilibrium temperature of 0.5824 is reached in a much longer time scale than is shown in the figure.

system. This cooling of the system corresponds to a decrease in the Boltzmann entropy. Specifically, we have

$$s_1^{eq} - s_1^0 \simeq -\lambda^2 c k_B \left(\frac{7\pi c V_0^2}{2\eta^3 k_B^2 T_0^2} \right) < 0 \qquad (5.5)$$

Thus, for this case we have "anti-Boltzmann' behavior as the system evolves to equilibrium. The evolution of the temperature for this case for a representative choice of parameters is shown in Fig. 4.

6. CONCLUSION

The interplay between correlations and the velocity distribution presents interesting features. The analysis of the evolution of the distribution function by using the theory of subdynamics allows us to couple the velocity distribution and the correlations by explicitly considering non-Markovian effects. The initial specification of the correlations determines a redefined initial velocity distribution which evolves kinetically to the asymptotic equilibrium form of the distribution function.

In the absence of initial correlations the non-Markovian effects extend only over a duration of a collision. The system evolves to equilibrium with an increase in temperature and a concomitant increase of the Boltzmann entropy. In contrast, in the presence of initial long-range correlations we find non-Markovian effects which extend over the time for a particle of average velocity to cross the initial correlation length. In this case there can be a small increase in temperature initially before the system cools to the equilibrium state. This nontrivial behavior and detailed description of the prekinetic stage can only be obtained with a dynamical analysis which goes beyond the traditional Markovian approximations used in kinetic theory. With the long-range correlation initial condition the Boltzmann entropy *decreases* from the initial nonequilibrium state to the final equilibrium state. Thus, for this case we may say that the system displays "anti-Boltzmann" behavior.

If we are interested only in the final temperature of the system, we can obtain the result (3.11) from the law of energy conservation and equipartition (see Appendix D). However, as we have shown, the subdynamics theory goes beyond the phenomenological macroscopic theory and describes a detailed dynamical evolution toward equilibrium. The subdynamics theory provides a systematic description of the microscopic non-Markovian evolution of the system by decoupling it from the Markovian evolution. This is in contrast to the theory using the generalized master equation, which provides a complicated description of the non-Markovian evolution (see ref. 14, for example).

APPENDIX A

We give here a brief summary of the subdynamics theory which we apply to the problem at hand. The reader is referred to ref. 7 for more details.

The main idea of the subdynamics theory is the introduction of projection operators for the complete Liouvillian that allows us to decompose the time evolution of the system into generalized eigenstates of the Liouvillian (see ref. 8 for details). Projection operators $\overset{(v)}{\Pi}$ are constructed with the following properties:

$$\overset{(v)}{\Pi}L = L\overset{(v)}{\Pi} \tag{A.1a}$$

$$\sum_v \overset{(v)}{\Pi} = 1 \tag{A.1b}$$

$$\overset{(v)}{\Pi}\overset{(v')}{\Pi} = \overset{(v)}{\Pi}\delta_{vv'} \tag{A.1c}$$

The $\Pi^{(v)}$ are extensions, analytic in λ, of the projection operators, denoted $P^{(v)}$, of an eigenstate of the unperturbed Liouvillian L_0, satisfying

$$\overset{(v)}{P}L_0 = L_0\overset{(v)}{P} = l_v\overset{(v)}{P} \tag{A.2a}$$

$$\sum_v \overset{(v)}{P} = 1 \tag{A.2b}$$

$$\overset{(v)}{P}\overset{(v')}{P} = \overset{(v)}{P}\delta_{vv'} \tag{A.2c}$$

where l_v is an eigenvalue.

In the form of a perturbation series,

$$\overset{(v)}{\Pi} = \overset{(v)}{P} + \lambda\overset{(v)}{\Pi_1} + \lambda^2\overset{(v)}{\Pi_2} + \cdots \tag{A.3}$$

the projector $\Pi^{(v)}$ is given from (A.1a) and (A.1c) by: for the diagonal components,

$$\overset{(v)}{P}\overset{(v)}{\Pi_n}\overset{(v)}{P} = -\sum_{m=1}^{n-1} \overset{(v)}{P}\overset{(v)}{\Pi_{n-m}}\overset{(v)}{\Pi_m}\overset{(v)}{P} \tag{A.4a}$$

$$\overset{(v')}{P}\overset{(v)}{\Pi_n}\overset{(v')}{P} = +\sum_{m=1}^{n-1} \overset{(v')}{P}\overset{(v)}{\Pi_{n-m}}\overset{(v)}{\Pi_m}\overset{(v')}{P} \qquad (v' \neq v) \tag{A.4b}$$

and for off-diagonal components $v' \neq v''$,

$$\overset{(v')}{P}\overset{(v)}{\Pi_n}\overset{(v'')}{P} = \frac{1}{l_{v'} - l_{v''} + i\varepsilon_{v'v''}} \overset{(v')}{P}[\overset{(v)}{\Pi_{n-1}}L_V - L_V\overset{(v)}{\Pi_{n-1}}]\overset{(v'')}{P} \tag{A.5}$$

where

$$\varepsilon_{v'v''} = \begin{cases} -\varepsilon & \text{if} \quad d_{v'} > d_{v''} \\ -\varepsilon & \text{if} \quad d_{v'} = d_{v''} \\ +\varepsilon & \text{if} \quad d_{v'} < d_{v''} \end{cases} \tag{A.6}$$

and ε is a positive infinitesimal, $\varepsilon \to 0+$. Here, the index d_v of the "degree of correlation" in (A.6) is the key of the analytic continuation of the small denominator, which is chosen by the consideration of the natural time ordering of states. If a state in $P^{(v)}$ subspace needs at least j interactions λV to arise from a state in the minimum or "vacuum of correlations" subspace, then that state has a degree of correlation $d_v = j$.

As has been discussed in detail in ref. 7, $\Pi^{(v)}$ can be decomposed in the form

$$\overset{(v)}{\Pi} = (\overset{(v)}{P} + \overset{(v)}{C})\,\overset{(v)}{A}\,(\overset{(v)}{P} + \overset{(v)}{D}) \tag{A.7}$$

Here the kinetic operators $A^{(v)}$, $C^{(v)}$, and $D^{(v)}$ are defined through the relations

$$\overset{(v)}{A} = \overset{(v)}{P}\,\overset{(v)}{\Pi}\,\overset{(v)}{P} \tag{A.8a}$$

$$\overset{(v)}{C}\,\overset{(v)}{A} = \overset{(v)}{Q}\,\overset{(v)}{\Pi}\,\overset{(v)}{P} \tag{A.8b}$$

$$\overset{(v)}{A}\,\overset{(v)}{D} = \overset{(v)}{P}\,\overset{(v)}{\Pi}\,\overset{(v)}{Q} \tag{A.8c}$$

where $Q^{(v)}$ is the projector orthogonal to $P^{(v)}$ defined by

$$\overset{(v)}{Q} \equiv 1 - \overset{(v)}{P} \tag{A.9}$$

These kinetic operators are related to each other through the formula

$$\overset{(v)}{A} = \overset{(v)}{P}(1 + \overset{(v)}{D}\,\overset{(v)}{C})^{-1} \tag{A.10}$$

By iterating recursion formulas in Eqs. (A.4) and (A.5) and using the series expansion of $A^{(v)}$ in (A.10), we obtain the perturbation series of $\Pi^{(v)}$. Here, we display the first few results of this series: For $C^{(v)}$, we obtain

$$\overset{(v')}{P}\,\overset{(v)}{C_0}\,\overset{(v)}{P} = 0$$

$$\overset{(v')}{P}\,\overset{(v)}{C_1}\,\overset{(v)}{P} = \frac{1}{l_{v'} - l_v + i\varepsilon_{v'v}}\,\overset{(v')}{P}\,L_V\,\overset{(v)}{P} \tag{A.11}$$

$$\overset{(v')}{P}\,\overset{(v)}{C_2}\,\overset{(v)}{P} = \sum_{v''} \frac{1}{l_{v'} - l_v + i\varepsilon_{v'v}}\,\overset{(v')}{P}\,L_V\,\overset{(v'')}{P}\,\frac{1}{l_{v''} - l_v + i\varepsilon_{v''v}}\,\overset{(v'')}{P}\,L_V\,\overset{(v)}{P}$$

$$\vdots$$

for $D^{(v)}$, we obtain

$$\overset{(v)}{P}\overset{(v)}{D_0}\overset{(v')}{P} = 0$$

$$\overset{(v)}{P}\overset{(v)}{D_1}\overset{(v')}{P} = \overset{(v)}{P}L_V\overset{(v')}{P}\frac{1}{l_v - l_{v'} + i\varepsilon_{vv'}}$$

$$\overset{(v)}{P}\overset{(v)}{D_2}\overset{(v')}{P} = \sum_{v''} \overset{(v)}{P}L_V\overset{(v'')}{P}\frac{1}{l_v - l_{v''} + i\varepsilon_{vv''}} \overset{(v'')}{P}L_V\overset{(v')}{P}\frac{1}{l_v - l_{v'} + i\varepsilon_{vv'}}$$

$$\vdots$$

(A.12)

and for $A^{(v)}$, we obtain

$$\overset{(v)}{A_0} = \overset{(v)}{P}$$

$$\overset{(v)}{A_1} = 0$$

$$\overset{(v)}{A_2} = -\overset{(v)}{D_1}\overset{(v)}{C_1}$$

$$\vdots$$

(A.13)

The time evolution of the distribution function in each $\Pi^{(v)}$ subspace is given by

$$\overset{(v)}{\rho}(t) \equiv \overset{(v)}{\Pi}\rho(t) = [\exp(-iLt)]\overset{(v)}{\Pi}\rho(0) \tag{A.14}$$

where

$$[\exp(-iLt)]\overset{(v)}{\Pi} = (\overset{(v)}{P} + \overset{(v)}{C})[\exp(-i\overset{(v)}{\theta}t)]\overset{(v)}{A}(\overset{(v)}{P} + \overset{(v)}{D}) \tag{A.15}$$

and the non-Hermitian evolution operator $\theta^{(v)}$ in each subspace is defined by

$$\overset{(v)}{\theta} \equiv l_v \overset{(v)}{P} + \lambda \overset{(v)}{P}L_V\overset{(v)}{C}\overset{(v)}{P} \tag{A.16}$$

From (A.15) it is easy to see that the following closed kinetic equation holds in each subspace:

$$i\,\partial\overset{(v)}{\rho_v}(t)/\partial t = \overset{(v)}{\theta}\overset{(v)}{\rho_v}(t) \tag{A.17}$$

where $\rho_v^{(v)} = P^{(v)}\Pi^{(v)}\rho$.

We wish to point out that one of the important aspects of the subdynamical decomposition is that the equilibrium distribution function lies entirely in the $\Pi^{(0)}$ subspace.[12] Also, all contributions to the normalization of the distribution function for any time are coming entirely from $\Pi^{(0)}$.

APPENDIX B

Here we outline some steps in the calculation of (3.8). Let us consider just the second term in (3.4),

$$\overset{(0)}{\rho}_{0|2} = \lambda \sum_{\mathbf{k}} \overset{(0)}{P} \overset{(0)}{D_1} \overset{(2)}{P} \rho(0) \tag{B.1}$$

From (3.5), using (2.30) and (2.26), we have then

$$\overset{(0)}{\rho}_{0|2} = -\lambda \frac{8\pi^3}{\Omega} \left(\frac{2\pi}{\beta}\right)^{-3N/2} \frac{\eta V_0}{\pi^2} \frac{\sigma G}{\pi^2} \beta$$

$$\times \sum_{j=1}^{N} \int d^3\mathbf{k} \frac{1}{(k^2 + \eta^2)^2} \frac{1}{(k^2 + \sigma^2)^2} \mathbf{k} \cdot \partial_{\alpha j} \frac{1}{\mathbf{k} \cdot \mathbf{v}_{\alpha j} - i\varepsilon} e^{-\beta v_j^2/2} \tag{B.2}$$

Carrying out the differentiation by $\mathbf{v}$ and then doing the 3-dimensional integration over $\mathbf{k}$ gives

$$\overset{(0)}{\rho}_{0|2} = \lambda \frac{8\pi^3}{\Omega} \left(\frac{2\pi}{\beta}\right)^{-3N/2} \frac{\eta V_0}{\pi^2} \frac{\sigma G}{\pi^2} \beta \sum_{j=1}^{N} \frac{\pi^2 \beta^2}{\sigma \eta (\eta + \sigma)^3}$$

$$\times \left\{ -1 + \frac{1}{\beta v_{\alpha j}^2} \right\} e^{-\beta v_j^2/2} \tag{B.3}$$

We reduce to a one-particle velocity distribution by integrating over $\mathbf{v}_j$. The sum over j gives a factor N and $N/\Omega = c$. The integration of the first term in (B.3), being just a Gaussian integral, is trivial. For the second term we use

$$\int d^3\mathbf{v}_j \frac{e^{-\beta v_j^2/2}}{v_{\alpha j}^2} = (2\pi)^{3/2} \beta^{-1/2} e^{-\beta v_x^2/2} F_1 \left(\frac{1}{2}; \frac{3}{2}; \frac{\beta}{2} v^2\right) \tag{B.4}$$

where $_1F_1(\frac{1}{2}; \frac{3}{2}; \frac{1}{2}\beta v^2)$ is the confluent hypergeometric function. It is related to the error function with imaginary argument and has the integral representation

$$_1F_1\left(\frac{1}{2}; \frac{3}{2}; \xi^2\right) = \frac{\sqrt{\pi}}{2i\xi} \operatorname{erf}(i\xi) = \frac{1}{\xi} \int_0^\xi e^{u^2} du \tag{B.5}$$

We thus have for this contribution to the one-particle distribution

$$\overset{(0)}{\varphi_{0|2}} = \left(\frac{2\pi}{\beta}\right)^{-3/2} \lambda \frac{8\pi c G V_0 \beta^2}{(\eta+\sigma)^3} \left[1 - 2 \, {}_1F_1\left(\frac{1}{2};\frac{3}{2};\frac{\beta}{2}v^2\right) e^{-\beta v^2/2}\right] e^{-\beta v^2/2}$$

(B.6)

The other terms in (3.8) are obtained from (3.4) in a similar fashion. We note, though, that the D_2 term vanishes because of the specific form of $\rho_{\mathbf{k},-\mathbf{k}}(0)$ that we have chosen.

APPENDIX C

We follow Chapter 13 of ref. 12 to obtain the asymptotic equilibrium velocity distribution (3.10). The evolution of the initial velocity distribution (3.8) is governed by Eq. (3.2), where the time evolution operator is the Landau collision operator (3.9). The distribution (3.8) is of the form

$$\varphi(\mathbf{v}; 0) = \{1 + \lambda\chi(\mathbf{v}; 0)\} \, \varphi^0(\mathbf{v})$$

(C.1)

where $\varphi^0(\mathbf{v})$ is the equilibrium distribution, and χ is of $\mathcal{O}(\lambda)$. We may consider the linearized collision operator obtained by substituting (C.1) in (3.2), using (3.9) and keeping only terms linear in χ. The function $\chi(\mathbf{v}; t)$ then satisfies the linear Landau equation. χ is expanded in eigenfunctions ϕ_n of the linearized collision operator and then the solution is expressed as

$$\chi(\mathbf{v}; t) = \sum_{n=1}^{\infty} \gamma_n \phi_n e^{\lambda_n^0 t}$$

(C.2)

The linearized collision operator has a fivefold degeneracy of the zero eigenvalue, $\lambda^0 = 0$, with five mutually orthogonal and normalized eigenfunctions $\phi_1,..., \phi_5$. As $t \to \infty$ the distribution becomes

$$\varphi(\mathbf{v}; \infty) = \{1 + \gamma_1\phi_1(\mathbf{v}) + \cdots + \gamma_5\phi_5(\mathbf{v})\} \, \varphi^0(v)$$

(C.3)

where $\varphi^0(v)$ is a Maxwellian. The coefficients γ_n are determined from the initial distribution by

$$\gamma_n = \int d^3\mathbf{v} \, \varphi^0(v) \, \chi(\mathbf{v}; 0) \, \phi_n$$

(C.4)

From (3.8) we find $\gamma_1 = \gamma_2 = \gamma_3 = \gamma_4 = 0$ and

$$\gamma_5 = \int d^3\mathbf{v} \left(\frac{2\pi}{\beta}\right)^{-3/2} \left[\lambda \frac{8\pi c G V_0 \beta^2}{(\eta+\sigma)^3} - \lambda^2 \frac{\pi c V_0^2 \beta^2}{\eta^3}\right]$$

$$\times \left[1 - 2 \, {}_1F_1\left(\frac{1}{2};\frac{3}{2};\frac{\beta}{2}v^2\right) e^{-\beta v^2/2}\right]\left(\frac{2}{3}\right)^{1/2}\left(-\frac{3}{2}+\frac{\beta}{2}v^2\right)e^{-\beta v^2/2}$$

$$= \frac{1}{2}\left(\frac{2}{3}\right)^{1/2}\left[\lambda \frac{8\pi c V_0 \beta^2}{(\eta+\sigma)^3} - \lambda^2 \frac{\pi c V_0^2 \beta^2}{\eta^3}\right]$$

(C.5)

Then

$$\varphi(\mathbf{v}; \infty) = \left(\frac{2\pi}{\beta}\right)^{-3/2} \left\{1 - \frac{1}{2}\left[\lambda \frac{8\pi c G V_0 \beta^2}{(\eta + \sigma)^3} - \lambda^2 \frac{\pi c V_0^2 \beta^2}{\eta^3}\right]\left(1 - \frac{\beta}{3}v^2\right)\right\} e^{-\beta v^2/2}$$

(C.6)

But (C.6) is just the expansion up to $\mathcal{O}(\lambda^2)$ of (3.10) with the temperature (3.11).

APPENDIX D

We show here how to obtain the result for the temperature shift (3.11) using energy conservation and the equipartition theorem. The energy density at a point $\mathbf{x}$ is given by[12]

$$E(\mathbf{x}; t) = c^{-1} \left\{\int d\mathbf{x}_1 \, d\mathbf{v}_1 \frac{1}{2} \mathbf{v}_1^2 \delta(\mathbf{x} - \mathbf{x}_1) f_1(\mathbf{x}_1; \mathbf{v}_1; t)\right.$$

$$+ \frac{1}{2}\lambda \int d\mathbf{x}_1 \, d\mathbf{x}_2 \, d\mathbf{v}_1 \, d\mathbf{v}_2 \, V(\mathbf{x}_1 - \mathbf{x}_2) \delta(\mathbf{x} - \mathbf{x}_1)$$

$$\left. \times f_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{v}_1, \mathbf{v}_2; t)\right\}$$

(D.1)

The two-particle distribution f_2 is given from g_2 and the one-particle distribution by using (2.23). The initial distributions are given in (2.28) and (2.29). The final distributions are independent of the initial distributions and can be obtained from ordinary equilibrium statistical mechanics. The initial energy is thus

$$E_0 = \frac{3}{2} k_B T_0 - 4\pi\lambda c V_0 \left[\frac{G}{(\eta + \sigma)^3 k_B T_0} - \frac{1}{\eta^3}\right]$$

(D.2)

and the equilibrium energy is

$$E^{eq} = \frac{3}{2} k_B T^{eq} - 4\pi\lambda c V_0 \left[\frac{\lambda V_0}{(2\eta)^3 k_B T^{eq}} - \frac{1}{\eta^3}\right]$$

(D.3)

By conservation of energy the two expressions above are equal and so we can calculate T^{eq} as a function of T_0,

$$T^{eq} = \frac{1}{2}T_0 - \frac{4\pi c\lambda V_0 G}{3(\eta + \sigma)^3 k_B^2 T_0} + \frac{1}{3k_B}\left\{\left[\frac{3}{2}k_B T_0 - \frac{4\pi c\lambda V_0 G}{(\eta + \sigma)^3 k_B T_0}\right]^2\right.$$

$$\left. + \frac{3\pi c\lambda^2 V_0^2}{\eta^3}\right\}^{1/2}$$

(D.4)

If we calculate this result to $\mathcal{O}(\lambda^2)$, we recover the result (3.11) obtained by our dynamical approach.

ACKNOWLEDGMENTS

REFERENCES

1. B. J. Alder and T. Wainwright, in *Transport Processes in Statistical Mechanics*, I. Prigogine, ed. (Wiley-Interscience, New York, 1958). J. Orban and A. Bellemans, *Phys. Lett.* **24A**:620 (1967); J. Orban and A. Bellemans, *J. Stat. Phys.* **1**:467 (1969).
2. I. Prigogine, *Non-Equilibrium Statistical Mechanics* (Wiley-Interscience, New York, 1962).
3. T. Petrosky and I. Prigogine, *Can. J. Phys.* **68**:670 (1990).
4. I. Prigogine, E. Kestemont, and M. Mareschal, in *Microscopic Simulations of Complex Flow*, M. Mareschal, ed. (Plenum Press, New York, 1990).
5. T. Petrosky and I. Prigogine, *Physica A* **147**:439 (1988).
6. C. George, *Physica* **65**:277 (1973).
7. T. Petrosky and H. Hasegawa, *Physica A* **160**:351 (1989).
8. T. Petrosky and I. Prigogine, *Physica A* **175**:146 (1991).
9. N. N. Bogolubov, *J. Phys. (USSR)* **10**:265 (1946).
10. M. S. Green, *J. Chem. Phys.* **25**:836 (1956).
11. E. G. D. Cohen, *Physica* **28**:1025, 1045 (1962).
12. R. Balescu, *Equilibrium and Non-Equilibrium Statistical Mechanics* (Wiley, New York, 1975).
13. C. George, *Physica* **37**:182 (1967).
14. P. Resibois and M. DeLeener, *Classical Kinetic Theory of Fluids* (Wiley, New York, 1977).