Journal of Statistical Physics, Vol. 5, No. 1/2, 1972

Nonequilibrium Statistical Mechanics of Finite Classical Systems—II

C. J. Myerscough[1]

Received June 22, 1971

The work of the previous paper is applied to the study of weakly interacting systems. Either by "quasilinear" techniques or by analyzing the perturbation series for the smoothed probability density, it is possible to derive a master equation equivalent to that of Brout and Prigogine without requiring the size of the system to become infinite. The properties of this equation are discussed. The equation is self-consistent provided the interactions are weak enough; however, examination of higher terms in the perturbation series shows that their effect might make the master equation invalid for times longer than that taken by a typical particle to cross the containing vessel. In many physical cases, the relaxation time will be shorter than this; also, further studies may show the higher terms to be less important than they seem.

KEY WORDS: Coarse-grained probability density; smoothed probability density; avoidance of infinite system limit; weak-interaction master equation; diagram techniques; nonequilibrium statistical mechanics; kinetic theory.

1. INTRODUCTION

In a previous paper (Myerscough,[1] hereafter referred to as I), we showed how the use of a certain smoothed probability density allows us to discuss some simple results of statistical mechanics for a finite system. In this paper, we treat the extremely important problem of a finite, weakly interacting system, showing how a master equation similar to that first derived by Brout

[1] Central Electricity Research Laboratories, Leatherhead, Surrey, England. Formerly at Department of Applied Mathematics and Theoretical Physics, University of Cambridge, England.

and Prigogine[2] may be derived by either of the methods commonly used. We shall also investigate the validity of the approximations made in this derivation, and show that we require the condition (I.52) to be true.

Thus we consider systems satisfying periodic conditions as set out in Section 3 of I and such that the interparticle interaction V of (I.25) is small, but nonzero.

By $V(\mathbf{x}_1, \mathbf{x}_2)$ being small, we mean that its average value is very much smaller than a typical particle kinetic energy. We write

$$H(\mathbf{X}) = \epsilon \hat{H}(\mathbf{X}), \qquad V(\mathbf{x}_1, \mathbf{x}_2) = \epsilon \hat{V}(\mathbf{x}_1, \mathbf{x}_2) \tag{1}$$

etc., where

$$V(\mathbf{x}_1, \mathbf{x}_2) \sim v_0^2/2 \tag{2}$$

v_0 being a typical particle speed, and $\epsilon \ll 1$. From (I.25),

$$H(\mathbf{X}) \sim \tfrac{1}{2}N(N-1)\,\epsilon v_0^2/2 = \epsilon' N v_0^2/2, \qquad \text{where} \quad \epsilon' = (N-1)\,\epsilon \tag{3}$$

ϵ' gives the order of magnitude of the ratio of potential to kinetic energy in the system. If N is large, $\epsilon' \sim N\epsilon$.

Equation (I.38) gives coupled equations for the spatial Fourier components of $\bar{\rho}$:

$$\frac{\partial \bar{\rho}_{\mathbf{K}}}{\partial t}(\mathbf{V}, t) + i\mathbf{K}\cdot\mathbf{V}\bar{\rho}_{\mathbf{K}} + i\sigma^2\mathbf{K}\cdot\frac{\partial \bar{\rho}_{\mathbf{K}}}{\partial \mathbf{V}} + \epsilon\sum_{\mathbf{K}'} F_{-\mathbf{K}'}\cdot\frac{\partial}{\partial \mathbf{V}}\bar{\rho}_{\mathbf{K}+\mathbf{K}'} = 0 \tag{4}$$

with initial conditions $\bar{\rho}_{\mathbf{K}}(V, 0)$ given. $\mathbf{K}$ runs through all lattice vectors. Then,

$$\rho_{\mathbf{K}}(\mathbf{V}, t) = \sum_{n=0}^{\infty} \epsilon \bar{\rho}_{n\mathbf{K}}(\mathbf{V}, t) \tag{5}$$

where

$$\frac{\partial \bar{\rho}_{0\mathbf{K}}}{\partial t}(\mathbf{V}, t) + i\mathbf{K}\cdot\mathbf{V}\bar{\rho}_{0\mathbf{K}} + i\sigma^2\mathbf{K}\cdot\frac{\partial \bar{\rho}_{0\mathbf{K}}}{\partial \mathbf{V}} = 0 \tag{6}$$

$$n \geqslant 1, \qquad \frac{\partial \bar{\rho}_{n\mathbf{K}}}{\partial t}(\mathbf{V}, t) + i\mathbf{K}\cdot\mathbf{V}\bar{\rho}_{n\mathbf{K}} + i\sigma^2\mathbf{K}\cdot\frac{\partial \bar{\rho}_{n\mathbf{K}}}{\partial \mathbf{V}} + \sum_{\mathbf{K}'} F_{-\mathbf{K}'}\cdot\frac{\partial \bar{\rho}_{n-1,\mathbf{K}+\mathbf{K}'}}{\partial \mathbf{V}} = 0 \tag{7}$$

$$\bar{\rho}_{0\mathbf{K}}(\mathbf{V}, 0) = \bar{\rho}_{\mathbf{K}}(\mathbf{V}, 0) \tag{8}$$

$$n \geqslant 1, \qquad \bar{\rho}_{n\mathbf{K}}(\mathbf{V}, 0) = 0 \tag{9}$$

If all the $\bar{\rho}_{n\mathbf{K}}$ were bounded in time, the sum (5) would remain arbitrarily near $\bar{\rho}_{0\mathbf{K}}$, which is the solution of the interactionless problem, as $t \to \pm\infty$

for small enough ϵ. Since this does not occur, at least some of the $\bar{\rho}_{nk}$ must increase indefinitely in magnitude—the series (5) contains secular terms and we cannot approximate $\bar{\rho}_{\mathbf{K}}$ by the sum of the first few.

2. QUASILINEAR THEORY; A MASTER EQUATION

First we shall study the weak-interaction case by adapting the method of Nakajima,[3] Zwanzig,[4,5] Montroll,[6] and Sandri.[7] A time-independent solution of (4) will be such that, for $\mathbf{K} \neq \mathbf{0}$,

$$\bar{\rho}_{\mathbf{K}}(V)/\bar{\rho}_0(V) = O(\epsilon) \tag{10}$$

We assume that if at time zero this is true, the evolution of $\bar{\rho}$ and $\bar{\rho}_{\mathbf{K}}$ is such that it remains so. We shall see later that this assumption is self-consistent.

With $\mathbf{K} = \mathbf{0}$, (4) gives (exactly)

$$[\partial \bar{\rho}_0(\mathbf{V}, t)/\partial t] + \sum_{\mathbf{K}} \mathbf{F}_{-\mathbf{K}'} \, \partial \rho_{\mathbf{K}}(V, t)/\partial \mathbf{V} = 0 \tag{11}$$

Since $\mathbf{F}_0 = \mathbf{0}$, this means that $\partial \bar{\rho}_0/\partial t$ is of order ϵ^2; $\bar{\rho}_0$ will change very slowly indeed. For $\mathbf{K} \neq \mathbf{0}$, to first order in ϵ only,

$$[\partial \bar{\rho}_{\mathbf{K}}(V, t)/\partial t] + i\mathbf{K} \cdot \mathbf{V}\bar{\rho}_{\mathbf{K}} + i\sigma^2\mathbf{K} \cdot (\partial \bar{\rho}_{\mathbf{K}}/\partial \mathbf{V}) + \mathbf{F}_{\mathbf{K}} \cdot [\partial \bar{\rho}_0(\mathbf{V}, t)/\partial \mathbf{V}] = 0 \tag{12}$$

As before, we are given the value of each $\bar{\rho}_{\mathbf{K}}$ at $t = 0$.

Exactly as (I.79), the solution of (12) is

$$\begin{aligned}\bar{\rho}_{\mathbf{K}}(\mathbf{V}, t) = {} & \bar{\rho}_{\mathbf{K}}(\mathbf{V} - i\mathbf{K}\sigma^2 t, 0) \exp(-i\mathbf{K} \cdot \mathbf{V}t - \tfrac{1}{2}\sigma^2\mathbf{K}^2 t^2) \\ & - \int_0^t d\tau[\exp(-i\mathbf{K} \cdot \mathbf{V} - \tfrac{1}{2}\sigma^2 K^2\tau^2)]\, F_{\mathbf{K}} \cdot (\partial/\partial \mathbf{V})\, \bar{\rho}_0(\mathbf{V} - i\mathbf{K}\sigma^2\tau, t - \tau)\end{aligned} \tag{13}$$

We now assume that *at all times*, $\bar{\rho}_0(\mathbf{V}, t)$ varies slowly on scale σ. That is [cf. (I.41)],

$$\sigma/\mu(t) \ll 1, \qquad \text{where} \quad \mu(t) \sim [1/\bar{\rho}_0(\mathbf{V}, t)] |\, \partial \bar{\rho}_0(\mathbf{V}, t)/\partial \mathbf{V} \,| \tag{14}$$

We shall show later that this assumption also is self-consistent. Assuming that $\bar{\rho}_{\mathbf{K}}(\mathbf{V}, 0)$ satisfies (I.41), we can say that once a *positive* time greater than $(\sigma K)^{-1}$ has elapsed, for $\mathbf{K} \neq \mathbf{0}$,

$$\begin{aligned}\bar{\rho}_{\mathbf{K}}(\mathbf{V}, t) = {} & -\int_0^\infty d\tau[\exp(-i\mathbf{K} \cdot \mathbf{V}\tau - \tfrac{1}{2}\sigma^2 K^2\tau^2)] \\ & \times \mathbf{F}_{\mathbf{K}} \cdot (\partial/\partial \mathbf{V})\, \bar{\rho}_0(\mathbf{V} - i\mathbf{K}\sigma^2\tau, t - \tau)\end{aligned} \tag{15}$$

If we wanted to consider negative times—to follow the system backward—we would have to replace ∞ by $-\infty$ in (14).

We shall consider this expression for $\bar{\rho}_{\mathbf{K}}$ in more detail in the next section. Here, we are interested in the evolution of $\bar{\rho}_0$: For this, we substitute (13) in (11),

$$\partial\bar{\rho}_0(\mathbf{V}, t)/\partial t = -\sum_{\mathbf{K}} \mathbf{F}_{-\mathbf{K}} \cdot (\partial/\partial\mathbf{V})\, \bar{\rho}_{\mathbf{K}}(\mathbf{V} - i\mathbf{K}\sigma^2 t, 0) \exp(-i\mathbf{K}\cdot\mathbf{V}t - \tfrac{1}{2}\sigma^2K^2t^2)$$
$$+ \int_0^t d\tau \sum_{\mathbf{K}} \mathbf{F}_{-\mathbf{K}} \cdot (\partial/\partial\mathbf{V})\, [\exp(-i\mathbf{K}\cdot\mathbf{V}\tau - \tfrac{1}{2}\sigma^2K^2\tau^2)]$$
$$F_{\mathbf{K}} \cdot (\partial/\partial\mathbf{V})\, \bar{\rho}_0(\mathbf{V} - i\mathbf{K}\sigma^2\tau, t - \tau) \tag{16}$$

Equation (16), like (13), is exact. The vast majority of the **K** in the two terms of this will have magnitudes about λ_I^{-1} and λ^{-1}, respectively, provided λ_I and λ are both much less then l. So, once a time much greater than λ_I/σ and λ/σ has elapsed,

$$\partial\bar{\rho}_0(\mathbf{V}, t)/\partial t = \sum_{\mathbf{K}} \mathbf{F}_{-\mathbf{K}} \cdot (\partial/\partial\mathbf{V}) \int_0^\infty d\tau \exp(-i\mathbf{K}\cdot\mathbf{V}\tau - \tfrac{1}{2}\sigma^2K^2\tau^2)$$
$$\times\, \mathbf{F}_{\mathbf{K}} \cdot (\partial/\partial\mathbf{V})\bar{\rho}_0(\mathbf{V} - i\mathbf{K}\sigma^2\tau, t - \tau) \tag{17}$$

However, as in Section 8 of I, we can do better than this. The sums over **K** in (16) have just the form (I.50), and so, provided (I.52) is satisfied—that is, the time l/v_0 that a particle takes to cross the containing vessel is much greater than both λ_I/σ and λ/σ—

$$l/v_0 \gg \lambda/\sigma, \quad \lambda_I/\sigma \tag{18}$$

(17) will be valid once

$$t \gg \lambda_I/v_0, \quad \lambda/v_0 \tag{19}$$

Furthermore, provided ϵ is sufficiently small that $\bar{\rho}_0$ changes little in a time of order λ/v_0,

$$(\lambda/v_0\bar{\rho}_0)|\, \partial\bar{\rho}_0/\partial t\, | \ll 1 \tag{20}$$

we may replace $t - \tau$ by t in (17). We shall investigate the condition on ϵ that this requires in Section 6. Doing so, we obtain a closed Markovian master equation for $\bar{\rho}_0$:

$$\partial\bar{\rho}_0(\mathbf{V}, t)/\partial t = \tfrac{1}{2}\sum_{\mathbf{K}} H_{\mathbf{K}}^2\, \mathbf{K} \cdot (\partial/\partial\mathbf{V}) \int_{-\infty}^{\infty} d\tau[\exp(-i\mathbf{K}\cdot\mathbf{V}\tau - \tfrac{1}{2}\sigma^2K^2\tau^2)]$$
$$\times\, \mathbf{K} \cdot \bar{\mathbf{g}}(\mathbf{V} - i\sigma^2\mathbf{K}\tau, t) \tag{21}$$

where we have observed the effect of replacing τ by $-\tau$, and **K** by $-$**K**, in the summation. To avoid future ambiguity, we write

$$\bar{\mathbf{g}}(\mathbf{V}) = \partial\bar{\rho}_0(\mathbf{V})/\partial\mathbf{V} \tag{22}$$

Now, complete the square in τ, that is, substitute

$$y = \sigma[\tau + (i\mathbf{K} \cdot \mathbf{V}/\sigma^2 K^2)] \tag{23}$$

so that

$$\mathbf{V} - i\sigma^2\mathbf{K}\tau = V_\perp - i\sigma\mathbf{K}y \tag{24}$$

where $\mathbf{V}_\perp = \mathbf{V} - (\mathbf{V} \cdot \mathbf{K})\,\mathbf{K}/K^2$ is the perpendicular from $\mathbf{V}$ to $\mathbf{K}$. Using Cauchy's theorem to move the contour of y integration back to the real axis,

$$\begin{aligned} \partial\bar{\rho}_0(\mathbf{V}, t)/\partial t &= (1/2\sigma) \sum_{\mathbf{K}} H_{\mathbf{K}} H_{-\mathbf{K}}(\mathbf{K} \cdot \partial/\partial\mathbf{V}) \exp(-(\mathbf{K} \cdot \mathbf{V})^2/2\sigma^2 K^2] \\ &\quad \times \int_{-\infty}^{\infty} dy[\exp(-K^2y^2/2)]\, \mathbf{K} \cdot \bar{\mathbf{g}}(\mathbf{V}_\perp - i\sigma\mathbf{K}y, t) \end{aligned} \tag{25}$$

Using (14), we have the approximate form

$$\begin{aligned} \partial\bar{\rho}_0(\mathbf{V}, t)/\partial t &= [(2\pi)^{1/2}/2\sigma K][1 + O(\sigma^2/\mu^2)] \sum_{\mathbf{K}} H_{\mathbf{K}} H_{-\mathbf{K}}(\mathbf{K} \cdot \partial/\partial\mathbf{V}) \\ &\quad \times \{\exp[-(\mathbf{K} \cdot \mathbf{V})^2/2\sigma^2K^2]\}\, \mathbf{K} \cdot \bar{\mathbf{g}}(\mathbf{V}_\perp, t) \end{aligned} \tag{26}$$

At first sight, both these equations seem bizarre, for they give $\partial\bar{\rho}_0(\mathbf{V})/\partial t$ in terms of the values of $\bar{\rho}_0$ at quite different points $\mathbf{V}_\perp$. However, in Section 5, we shall show that they have all the properties we expect of a master equation for a weakly interacting system. We note here that for large negative times, the result of changing ∞ to $-\infty$ in (16) or (17) is to give (21), (25), and (26) with the sign of the right-hand side reversed. And, indeed, this reversal of sign also comes about if we make the substitution $\mathbf{V} \to -\mathbf{V}$, $t \to -t$ in any of these equations.

3. THE NON-SPATIALLY-HOMOGENEOUS COMPONENTS OF $\bar{\rho}$, CONSISTENCY OF THE APPROXIMATION (10)

Let us now return to (15). First, consider the order of magnitude of $\bar{\rho}_{\mathbf{K}}$ that it gives. An integration by parts suggests (and more detailed calculations, similar to those below, confirm) that the result of the time integration is just to give about $(\mathbf{K} \cdot \mathbf{V})^{-1}$ times the average value of the integrand. The magnitude of $\mathbf{F}_{\mathbf{K}}$ is about Kh, where h is the magnitude of a typical component $V_{\mathbf{K}_1,\mathbf{K}_2}$. The magnitude of $\partial\bar{\rho}_0/\partial\mathbf{V}$ is about μ^{-1} times that of $\bar{\rho}_0$. So,

$$|\,\bar{\rho}_{\mathbf{K}}/\bar{\rho}_0\,| \sim (1/Kv_0)\, Kh(1/\mu) = h/v_0\mu \tag{27}$$

The magnitude of h is given by observing that

$$\int_{\mu_1} d^3x_1 \int_{\mu_2} d^3x_2\, |\, V(\mathbf{x}_1, \mathbf{x}_2)|^2 \sim \epsilon^2 v_0{}^4 l^6 \tag{28}$$

so that

$$\sum_{\mathbf{K}_1,\mathbf{K}_2} V_{\mathbf{K}_1,\mathbf{K}_2} V_{-\mathbf{K}_1,-\mathbf{K}_2} \sim \epsilon^2 v_0^{\,4} \tag{29}$$

and, using the results of the discussion at the end of Section 4 of I,

$$h \sim \epsilon v_0^{\,2}(\lambda/l)^{3/2} \tag{30}$$

Later, we shall justify assuming that for all t, $\mu \sim v_0$. So, provided $\epsilon(\lambda/l)^{3/2} \ll 1$, the approximation (10) is definitely valid.

In (15), we cannot replace $t - \tau$ by t in the integrand unless we assume that $\bar{\rho}_0$ varies little over a time λ/σ (rather than λ/v_0 in the derivation of the master equation). Furthermore, (15) cannot be valid until a time much longer than λ/σ or λ_l/σ has elapsed. However, in Section 6, we shall prove that there exists a time τ_0, the relaxation time, over which $\bar{\rho}_0$ tends to a limit. There will therefore exist a shorter time, τ_1, say, such that once $t > \tau_1$, $\bar{\rho}_0$ varies little over time λ/σ. Once a time larger than both τ_1 and λ_1/σ has elapsed, we can write

$$\bar{\rho}_{\mathbf{K}}(\mathbf{V}, t) = -\int_0^\infty d\tau[\exp(-i\mathbf{K}\cdot\mathbf{V}\tau - \tfrac{1}{2}\sigma^2K^2\tau^2)]\, F_{\mathbf{K}} \cdot \partial\bar{\rho}_0(\mathbf{V} - i\mathbf{K}\sigma^2\tau, t)/\partial\mathbf{V} \tag{31}$$

We split this expression into two by contour integration (Fig. 1)

$$\bar{\rho}_{\mathbf{K}}(\mathbf{V}, t) = -F_{\mathbf{K}} \cdot (I_{\mathbf{K}} + J_{\mathbf{K}}) \tag{32}$$

where

$$\begin{aligned} I_{\mathbf{K}} &= \int_{AB} d\tau[\exp(-i\mathbf{K}\cdot\mathbf{V}\tau - \tfrac{1}{2}\sigma^2K^2\tau^2)]\, \bar{\mathbf{g}}(\mathbf{V} - i\sigma^2\mathbf{K}\tau, t) \\ &= (-i/\sigma)\{\exp[-(\mathbf{K}\cdot\mathbf{V})^2/2\sigma^2K^2]\} \\ &\quad \times \int_0^{(\mathbf{K}\cdot\mathbf{V})/\sigma K^2} g(\mathbf{V} - \sigma\mathbf{K}y, t) \exp(\tfrac{1}{2}K^2\{y - [(\mathbf{K}\cdot\mathbf{V})/\sigma K^2]^2\})\, dy \end{aligned} \tag{33}$$

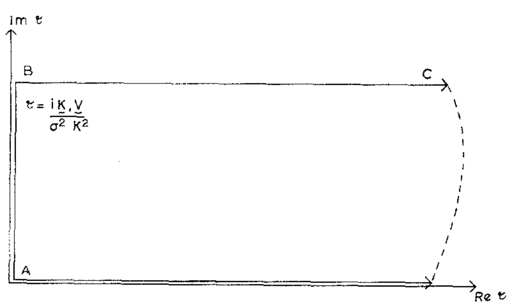

Fig. 1. Contour used in evaluating Eq. (31).

and

$$J_{\mathbf{K}} = \int_{BC} d\tau [\exp(-i\mathbf{K} \cdot \mathbf{V}\tau - \tfrac{1}{2}\sigma^2 K^2 \tau^2)]\, \bar{\mathrm{g}}(\mathbf{V} - i\sigma^2 \mathbf{K}\tau, t)$$
$$= (1/\sigma)\{\exp[-(\mathbf{K} \cdot \mathbf{V})^2/2\sigma^2 K^2]\}$$
$$\int_0^\infty dy [\exp(-\tfrac{1}{2}K^2 y^2)]\, \bar{\mathrm{g}}(\mathbf{V}_\perp - i\mathbf{K}\sigma y, t) \tag{34}$$

We easily verify that

$$\begin{aligned} i\mathbf{K} \cdot \mathbf{V}(-\mathbf{F}_{\mathbf{K}} \cdot \mathbf{I}_{\mathbf{K}}) + i\mathbf{K}\sigma^2 \cdot (\partial/\partial\mathbf{V})(-\mathbf{F}_{\mathbf{K}} \cdot \mathbf{I}_{\mathbf{K}}) + F_{\mathbf{K}} \cdot \partial\bar{\rho}_0/\partial\mathbf{V} &= 0 \\ i\mathbf{K} \cdot \mathbf{V}(-\mathbf{F}_{\mathbf{K}} \cdot \mathbf{J}_{\mathbf{K}}) + i\mathbf{K}\sigma^2 \cdot (\partial/\partial\mathbf{V})(-\mathbf{F}_{\mathbf{K}} \cdot \mathbf{J}_{\mathbf{K}}) &= 0 \end{aligned} \tag{35}$$

that is,

$$i\mathbf{K} \cdot \mathbf{V}\bar{\rho}_{\mathbf{K}} + i\sigma^2\mathbf{K} \cdot (\partial\bar{\rho}_{\mathbf{K}}/\partial\mathbf{V}) + \mathbf{F}_{\mathbf{K}} \cdot (\partial\bar{\rho}_0/\partial\mathbf{V}) = 0 \tag{36}$$

This is in accord with (10); since $\bar{\rho}_{\mathbf{K}}$ is determined from $\bar{\rho}_0$, and $\partial\bar{\rho}_0/\partial t$ is of order ϵ^2, $\partial\bar{\rho}_{\mathbf{K}}/\partial t$ is of order ϵ^3. In particular, if $\bar{\rho}_0$ is a time-independent solution of (25), the $\bar{\rho}_{\mathbf{K}}$ for $\mathbf{K} \neq 0$ determined by (31), together with $\bar{\rho}_0$, form a time-independent solution of (11) and (12).

From (33), $I_{\mathbf{K}} = -I_{\mathbf{K}}$. So, when (32) is substituted in (11), the $I_{\mathbf{K}}$ terms cancel, leaving (25).

Provided $\sigma/\mu \ll 1$,

$$J_{\mathbf{K}} = \{\exp[-(\mathbf{K} \cdot \mathbf{V})^2/2\sigma^2 K^2]\}(1/\sigma K)(\pi/2)^{1/2}\, \bar{\mathrm{g}}(\mathbf{V}_\perp, t) \tag{37}$$

and (25) reduces to (26). Equation (37) still satisfies (35). For $|\mathbf{V} \cdot \mathbf{K}|/K \gg \sigma$,

$$I_{\mathbf{K}} = [\bar{\mathrm{g}}(\mathbf{V}, t)/i\mathbf{V} \cdot \mathbf{K}][1 + O(\sigma/\mu) + O(\sigma K/\mathbf{V} \cdot \mathbf{K})] \tag{38}$$

while for $\mathbf{K} \cdot \mathbf{V} = 0$, $\mathbf{I}_{\mathbf{K}} = \mathbf{0}$.

4. THE CASE $\sigma = 0$

When $\sigma = 0$, (13) becomes

$$\rho_{\mathbf{K}}(\mathbf{V}, t) = \rho_{\mathbf{K}}(\mathbf{V}, 0)[\exp(-i\mathbf{K} \cdot \mathbf{V}t)]$$
$$- \int_0^t d\tau [\exp(-i\mathbf{K} \cdot \mathbf{V}\tau)]\, \mathbf{F}_{\mathbf{K}} \cdot \partial\bar{\rho}_0(\mathbf{V}, t - \tau)/\partial\mathbf{V} \tag{39}$$

As in Section 2.3, this expression oscillates indefinitely as $t \to \infty$, and may even be periodic. Substitution in (11) gives an expression for $\partial\bar{\rho}_0/\partial t$ with similar properties.

The procedure used by most authors to obtain a closed equation for ρ_0 from (39) and (11) similar to that derived for $\bar{\rho}_0$ in Section 2 is that of Section 9 of I; to allow the side of the vessel containing the system to become infinite, so that $\rho(\mathbf{X}, \mathbf{V}, t)$ is given by (I.54). We then arrive at

$$\partial\bar{\rho}_0(\mathbf{V}, t)/\partial t = \pm\pi \int d^{3N}K\,\mathbf{F}^{\dagger}(-\mathbf{K}) \cdot (\partial/\partial\mathbf{V})\,\delta(\mathbf{K}\cdot\mathbf{V}) \times F^{\dagger}(\mathbf{K}) \cdot (\partial/\partial\mathbf{V})\,\rho_0(\mathbf{V}, t) \tag{40}$$

once $|t| > \lambda_l/v_0$, the sign being that of t. This equation was first derived, using perturbative techniques similar to those of sections 8 and 9 by Brout and Prigogine[3]; it was obtained in this way by Zwanzig.[4]

We also have

$$\rho^{+}(\mathbf{K}, \mathbf{V}, t) = [\pm\pi\,\delta(\mathbf{K}\cdot\mathbf{V}) - P(1/i\mathbf{K}\cdot\mathbf{V})]\,\mathbf{F}^{\dagger}(\mathbf{K}) \cdot \partial\rho_0(\mathbf{V}, t)/\partial\mathbf{V} \tag{41}$$

where the P denotes the Cauchy principal value function. This must be interpreted with care; any expression involving an integral over $\mathbf{K}$ of the left-hand side will tend to the corresponding integral of the right-hand side in a time of order $(v_0k_0)^{-1}$, where k_0 is a linear dimension of the volume of $\mathbf{K}$ integration, assuming ρ_0 varies little over this time.

We can easily show that the expressions we have obtained for $\bar{\rho}_{\mathbf{K}}$ in Section 3 [and, therefore, our modified Brout–Prigogine equation (25)] may all be derived from the results of this section by integrating over $\mathbf{V}$. Figure 2 shows how $\mathbf{I}_{\mathbf{K}}$ and $\mathbf{J}_{\mathbf{K}}$ form approximations to the terms of (41).

Our work gives a meaning to expressions involving generalized functions

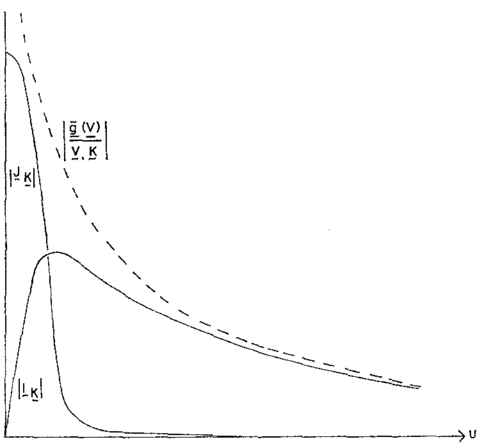

Fig. 2. Behavior of $\mathbf{I}_{\mathbf{K}}$ and $\mathbf{J}_{\mathbf{K}}$.

by integrating over $\mathbf{V}$ rather than over $\mathbf{K}$. Equations (25) and (40) are different realizations of the generalized function expression for $\partial\rho_0/\partial t$:

$$\partial\rho_0(\mathbf{V}, t)/\partial t = \pi \sum_{\mathbf{K}} H_{\mathbf{K}} H_{-\mathbf{K}} (\mathbf{K} \cdot \partial/\partial\mathbf{V})[\delta(\mathbf{K} \cdot \mathbf{V})]\, \mathbf{K} \cdot \partial\rho_0(\mathbf{V}, t)/\partial\mathbf{V} \tag{42}$$

Some properties of (40) are discussed by Prigogine.[8] In the next section, we shall discuss the corresponding properties of (25), and we shall find it very convenient on occasion to consider the behavior of functionals of ρ (rather than $\bar{\rho}$), using (42). It will always be possible to obtain the same results more tediously by coupling (25) with the inversion formula (I.39).

5. PROPERTIES OF THE MASTER EQUATION (25). CONSISTENCY OF APPROXIMATIONS (14) AND (20)

Write (25) as

$$\partial\bar{\rho}_0/\partial t = J\bar{\rho}_0 \tag{43}$$

where

$$J\bar{\rho}_0 = (1/2\sigma) \sum_{\mathbf{K}} H_{\mathbf{K}} H_{-\mathbf{K}} (\mathbf{K} \cdot \partial/\partial\mathbf{V})\{\exp[-(\mathbf{K} \cdot \mathbf{V})^2/2\sigma^2 K^2]\}$$
$$\times \int_{-\infty}^{\infty} dy[\exp(-\tfrac{1}{2}K^2 y^2)]\, \mathbf{K} \cdot \bar{g}(\mathbf{V}_\perp - i\sigma\mathbf{K}y) \tag{44}$$

(a) The significance of the peculiar form $V_\perp = \mathbf{V} - (\mathbf{V} \cdot \mathbf{K})\, \mathbf{K}/K^2$ in the expression for J becomes clear if we observe that any function $f(\mathbf{V})$ depending on V through $V^2/2$ only, $f(\mathbf{V}) = \alpha(V^2/2)$, say, is such that

$$Jf(V) = (1/2\sigma) \sum_{\mathbf{K}} H_{\mathbf{K}} H_{-\mathbf{K}} (\mathbf{K} \cdot \partial/\partial\mathbf{V})\{\exp[-(\mathbf{K} \cdot \mathbf{V})^2/2\sigma^2 K^2]\}$$
$$\times \int_{-\infty}^{\infty} dy[\exp(-\tfrac{1}{2}K^2 y^2)]\, \mathbf{K} \cdot (\mathbf{V}_\perp - i\mathbf{K}\sigma y)\, \alpha'[(\mathbf{V}_\perp - i\mathbf{K}\sigma y)^2] \tag{45}$$

But $\mathbf{K} \cdot \mathbf{V}_\perp = 0$, and $(\mathbf{V}_\perp - i\mathbf{K}\sigma y)^2 = V_\perp{}^2 - K^2\sigma^2 y^2$. The integrand in (45) is thus an odd function of y, and so the integral is zero. Any such $f(\mathbf{V})$ is a time-independent solution of (43).

(b) If we write $u = (\mathbf{V} \cdot \mathbf{K})/K$, $\mathbf{V} = \mathbf{V}_\perp + (u\mathbf{K}/K)$, then

$$\int d^{3N}V\, \alpha(V^2/2)\, J\bar{\rho}_0 \tag{46}$$

is the sum of terms which are integrals of odd functions of u, and so vanish, for any function α.

In particular, total probability is conserved by (43), and total energy to order ϵ^2.

(c) However, our operator J is not exactly self-adjoint. With a similar notation to (46),

$$\begin{aligned}
&\int d^{3N}V\,\bar{\rho}_1(\mathbf{V})\,J\bar{\rho}_2(\mathbf{V}) \\
&\quad = -(1/2\sigma^2)\sum_{\mathbf{K}} H_{\mathbf{K}}H_{-\mathbf{K}}\int d^{3N-1}V_\perp \int_{-\infty}^{\infty} du \int_{-\infty}^{\infty} du' \\
&\qquad \times \{\exp[-(1/2\sigma^2)(u^2+u'^2)]\}\,\mathbf{K}\cdot\bar{\mathbf{g}}_1(\mathbf{u},\mathbf{V}_\perp)\,\mathbf{K}\cdot\bar{\mathbf{g}}_2(-iu',\mathbf{V}_\perp) \\
&\quad = [1+O(\sigma/\mu)^2]\int d^{3N}V\,\bar{\rho}_2(\mathbf{V})\,J\bar{\rho}_1(\mathbf{V}) \qquad (47)
\end{aligned}$$

expanding $\mathbf{g}_1$ and $\mathbf{g}_2$ about u and $u' = 0$ in a Taylor series. Provided (14) is valid, we can regard J as self-adjoint.

(*d*) To show that (14) is self-consistent, we show that the equation (26) obtained by using it is such that local minima of $\bar{\rho}_0(\mathbf{V})$ tend to increase with time, and local maxima to decrease. [Incidentally, we may easily prove that (25) also has the properties (a)–(c) above.]

Since $\mathbf{V}_\perp$ and u are independent components of V,

$$\partial\mathbf{g}(\mathbf{V}_\perp, t)/\partial u = 0$$

so that (26) may be written

$$\partial\bar{\rho}_0(\mathbf{V},t)/\partial t = -\sum_{\mathbf{K}}[(2\pi)^{1/2}/\sigma^3]\,H_{\mathbf{K}}H_{-\mathbf{K}}u[\exp(-u^2/2\sigma^2)]\,\mathbf{K}\cdot\mathbf{g}(V_\perp, t) \qquad (48)$$

Writing $\mathbf{V}_\perp = \mathbf{V} - u\mathbf{K}/K$ and expanding the last term as a Taylor series, we find that

$$\begin{aligned}
\left[1+O\left(\frac{\sigma}{\mu}\right)^2\right]\frac{\partial\bar{\rho}_0}{\partial t} &= -\sum_{\mathbf{K}}\frac{K(2\pi)^{1/2}}{2\sigma^3}\,H_{\mathbf{K}}H_{-\mathbf{K}}\left(\exp-\frac{u^2}{2\sigma^2}\right) \\
&\quad \times\left[u\,\frac{\partial\bar{\rho}_0(\mathbf{V})}{\partial u} - u^2\,\frac{\partial^2\rho_0(\mathbf{V})}{\partial u\,\partial u}\right] \qquad (49)
\end{aligned}$$

So

$$\frac{\partial\bar{\rho}_0}{\partial\mathbf{V}} = \mathbf{0}, \qquad \frac{\partial^2\rho_0(\mathbf{V})}{\partial\mathbf{V}\,\partial\mathbf{V}} \text{ positive definite} \to \frac{\partial\bar{\rho}_0(\mathbf{V})}{\partial t} > 0, \quad \text{etc.}$$

This must in the long term cause μ to increase. If (14) is true initially, it will remain so.

(e) In order to discuss the Markovian approximation (20), we must estimate the magnitude of $J\bar{\rho}_0$. In the sum over $\mathbf{K}$ in (44), the only $\mathbf{K}$ that will contribute significantly are those such that

$$|\mathbf{V}\cdot\mathbf{K}/\sigma K| \sim 1 \tag{50}$$

The proportion of possible $\mathbf{K}$ satisfying this condition is about σ/v_0 (we ignore the case of $|\mathbf{V}|$ very small, of order σ). From (29),

$$\sum_{\mathbf{K}} H_{\mathbf{K}} H_{-\mathbf{K}} \sim (\epsilon')^2\, v_0{}^4 \tag{51}$$

and so the magnitude of $J\bar{\rho}_0$ is of order

$$(1/\sigma)(\epsilon')^2 v_0{}^4(\lambda^{-1}/\mu)(\sigma/v_0)(\lambda^{-1}/\mu)(1/\lambda^{-1})\,\bar{\rho}_0 = [(\epsilon')^2\, v_0{}^3/\mu^2\lambda]\,\bar{\rho}_0$$

Initially, $\mu \sim v_0$, and we have shown that μ increases with t. So $|\partial\bar{\rho}_0/\partial t|$ is always less than $\tau_0^{-1}\bar{\rho}_0$, where

$$\tau_0 = \lambda/(\epsilon')^2\, v_0 \tag{52}$$

Thus if $\epsilon' \ll 1$, (20) will always be valid. Indeed, if $\epsilon'(\sigma/v_0)^{-1/2} \ll 1$, the expressions for $\bar{\rho}_{\mathbf{K}}$ that we have derived in Section 3 will be valid once $t > \lambda/\sigma$ and λ_I/σ.

6. THE EVOLUTION OF $\bar{\rho}_0$

As we have already seen, once a time of orler λ/v_0 has elapsed, the effect on $\bar{\rho}$ of initial conditions on $\bar{\rho}_{\mathbf{K}}$ for $\mathbf{K} \neq \mathbf{0}$ will have disappeared; $\bar{\rho}_0$ will have changed very little over this time provided $\lambda_I \sim \lambda$ and $\epsilon' \ll 1$. Thus the behavior of $\bar{\rho}_0$ and $\bar{\rho}_{\mathbf{K}}$ for large positive times will be given within our approximation by assuming that, from time zero, $\bar{\rho}_0$ has evolved according to (25), while the $\bar{\rho}_{\mathbf{K}}$ for $\mathbf{K} \neq \mathbf{0}$ are obtained by substituting this $\bar{\rho}_0$ in (32) (how large these times have to be we have already discussed in Section 3). These are the "post-initial conditions" of Balescu.[9]

In order to prove that $\bar{\rho}_0$ tends to a limit as $t \to \infty$, we adopt the usual approach of finding a functional of $\bar{\rho}_0$,

$$I(t) = \int d^{3N}V\, f(\bar{\rho}_0(V, t)) \tag{53}$$

that varies monotonically with time, is bounded, and is constant only when $\bar{\rho}_0$ is a time-independent solution of (25).

Owing to the non-self-adjoint nature of J, we have to search a little harder than usual. While (42) is meaningless on its own, it may be used to consider the behavior of functionals of ρ_0. For example, set

$$Q(t) = \tfrac{1}{2}\int \rho_0{}^2(\mathbf{V}, t)\, d^{3N}V \tag{54}$$

where ρ_0 is defined from $\bar{\rho}_0$ by (I.39) and $\bar{\rho}_0$ satisfies (25). Then, either using (42) or, more tediously, (I.39) and (25),

$$dQ/dt = -\pi \sum_{\mathbf{K}} H_{\mathbf{K}} H_{-\mathbf{K}} \int d^{3N}V\, [\delta(\mathbf{K} \cdot \mathbf{V})]\, (\mathbf{K} \cdot \partial \rho_0(\mathbf{V}, t)/\partial \mathbf{V})^2 \tag{55}$$

So, $dQ/dt < 0$, and $dQ/dt = 0$ only when

$$\mathbf{K} \cdot \mathbf{V} = 0, \qquad H_{\mathbf{K}} \neq \mathbf{0} \rightarrow \mathbf{K} \cdot \partial \rho_0(\mathbf{V}, t)/\partial \mathbf{V} = 0 \tag{56}$$

It is a consequence of the proof of Fermi's theorem (see I, Section 5) that (56) holding for all $\mathbf{K}$ implies that ρ_0 depends on $\mathbf{V}$ through $V^2/2$ only.

Since $Q(t)$ is bounded below, it must tend to a limiting value, at which $dQ/dt = 0$: Since Q is a continuous functional of ρ_0, this implies that ρ_0 as defined by (I.39) from $\bar{\rho}_0$ satisfying (25) must tend to a limit isotropic in $\mathbf{V}$ as $t \rightarrow \infty$. The term $\bar{\rho}_0$ must do so too, in a time of order τ_0. We call τ_0 the relaxation time.

$\bar{\rho}_{\mathbf{K}}$ will have reached its limit once the larger of times λ_l/σ and τ_0 has elapsed; we may then show that the limit of ρ is equal to the result of smoothing the phase average of $\rho(\mathbf{X}, \mathbf{V}, 0)$.

Exactly similarly, we may consider negative times. Once $t < -\lambda/v_0$ and $-\lambda_l/v_0$, the evolution of $\bar{\rho}_0$ is according to (25) with the sign reversed. Now, $dQ/dt > 0$; as $t \rightarrow -\infty$, $\bar{\rho}_0$ tends to the same limit.

7. AN EQUATION FOR THE ONE-PARTICLE REDUCED DENSITY FUNCTION

As we have already observed in Section 10 of *I*, we are often interested only in the behavior of the reduced probability density function $\bar{f}_s$ for small s, in particular, for $s = 1$. We now obtain an equation for the evolution of $\bar{f}_1$ once a large, positive time has elapsed. The result of integrating (26) over all velocity variables except v_1 is (with the notation of Section 4 of I)

$$\begin{aligned}
&\frac{\partial \bar{f}_{10}(\mathbf{v}_1, t)}{\partial t} \\
&\quad = (N-1) \sum_{\mathbf{k}_1, \mathbf{k}_2} V^2_{\mathbf{k}_1, \mathbf{k}_2} \mathbf{k}_1 \cdot \frac{\partial}{\partial \mathbf{v}_1} \int d^3 v_2 \frac{(2\pi)^{1/2}}{\sigma(k_1{}^2 + k_2{}^2)^{1/2}} \\
&\qquad \times \left[\exp - \frac{(\mathbf{k}_1 \cdot \mathbf{v}_1 + \mathbf{k}_2 \cdot \mathbf{v}_2)^2}{2\sigma^2(k_1{}^2 + k_2{}^2)}\right] \\
&\qquad \times \bar{h}_2 \left[\mathbf{v}_1 - \frac{(\mathbf{v}_1 \cdot \mathbf{k}_1 + \mathbf{v}_2 \cdot \mathbf{k}_2)}{k_1{}^2 + k_2{}^2} \mathbf{k}_1, \mathbf{v}_2 - \frac{(\mathbf{v}_1 \cdot \mathbf{k}_1 + \mathbf{v}_2 \cdot \mathbf{k}_2)}{k_1{}^2 + k_2{}^2} \mathbf{k}_2, t\right]
\end{aligned} \tag{57}$$

where

$$\bar{h}_2(\mathbf{v}_1, \mathbf{v}_2, t) = \mathbf{k}_1 \cdot (\partial \bar{f}_{20}/\partial v_1) + \mathbf{k}_2 \cdot (\partial \bar{f}_{20}/\partial \mathbf{v}_2) \tag{58}$$

$\bar{f}_{10}$ and $\bar{f}_{20}$ are the spatially homogeneous components of the reduced densities $\bar{f}_1$ and $\bar{f}_2$.

Owing to the presence of an integration over $\mathbf{v}_2$, it causes only a proportional error of order $(\sigma/\mu)^2$, where μ is, as before, the scale of variation of $\bar{f}_{10}$ and $\bar{f}_{20}$ with $\mathbf{v}_1$ and $\mathbf{v}_2$, to replace

$$\frac{(2\pi)^{1/2}}{(\mathbf{k}_1{}^2 + \mathbf{k}_2{}^2)^{1/2}\sigma}\left[\exp - \frac{(\mathbf{k}_1 \cdot \mathbf{v}_1 + \mathbf{k}_2 \cdot \mathbf{v}_2)^2}{2\sigma^2(k_1{}^2 + k_2{}^2)}\right] \quad \text{by} \quad \pi\delta(\mathbf{k}_1 \cdot \mathbf{v}_1 + \mathbf{k}_2 \cdot \mathbf{v}_2) \tag{59}$$

This error is the same as we made in using (26) instead of (25). So (57) becomes

$$\partial\bar{f}_{10}/\partial t = (N-1) \sum_{\mathbf{k}_1,\mathbf{k}_2} V^2_{\mathbf{k}_1,\mathbf{k}_2}\pi \times \int d^3v_2\, D_{\mathbf{k}_1,\mathbf{k}_2}[\delta(\mathbf{k}_1 \cdot \mathbf{v}_1 + \mathbf{k}_2 \cdot \mathbf{v}_2)]\, D_{\mathbf{k}_1,\mathbf{k}_2}\bar{f}_{20}(\mathbf{v}_1, \mathbf{v}_2, t) \tag{60}$$

where

$$D_{\mathbf{k}_1,\mathbf{k}_2} = \mathbf{k}_1 \cdot (\partial/\partial\mathbf{v}_1) + \mathbf{k}_2 \cdot (\partial/\partial\mathbf{v}_2) \tag{61}$$

This is of a standard form [cf. (4.3.1) of Prigogine[8]], allowing for the more complicated structure of V introduced by the periodic conditions.

If we now assume that all the particles are uncorrelated, as in (I.61),

$$\bar{f}_{20}(\mathbf{v}_1, \mathbf{v}_2, t) = \bar{f}_{10}(\mathbf{v}_1, t)\bar{f}_{10}(\mathbf{v}_2, t) \tag{62}$$

and (60) becomes

$$\partial\bar{f}_{10}(\mathbf{v}_1, t)/\partial t = (N-1)\pi \sum_{\mathbf{k}_1,\mathbf{k}_2} V^2_{\mathbf{k}_1,\mathbf{k}_2} \int d^3v_2\, D_{\mathbf{k}_1,\mathbf{k}_2}[\delta(\mathbf{k}_1 \cdot \mathbf{v}_1 + \mathbf{k}_2 \cdot \mathbf{v}_2)] \times D_{\mathbf{k}_1,\mathbf{k}_2}\bar{f}_{10}(\mathbf{v}_1, t)\bar{f}_{10}(\mathbf{v}_2, t) \tag{63}$$

which is very similar to the Landau or "pseudo-Boltzmann" equation [(4.3.4) of Prigogine[8]]. As there, we can prove much more about the behavior of $\bar{f}_{10}$ than (25) gives us, for

$$\begin{aligned}
&(d/dt) \int \bar{f}_{10}(\mathbf{v}_1, t) \log \bar{f}_{10}(\mathbf{v}_1, t)\, d^3\mathbf{v}_1 \\
&= (N-1)\pi \sum_{\mathbf{k}_1,\mathbf{k}_2} V^2_{\mathbf{k}_1,\mathbf{k}_2} \int d^3v_1 \int d^3v_2\, [\log \bar{f}_{10}(v_1)]\, D_{\mathbf{k}_1,\mathbf{k}_2} \\
&\qquad \times [\delta(\mathbf{k}_1 \cdot \mathbf{v}_1 + \mathbf{k}_2 \cdot \mathbf{v}_2)]\, D_{\mathbf{k}_1,\mathbf{k}_2}\bar{f}_{10}(\mathbf{v}_1)\bar{f}_{10}(\mathbf{v}_2) \\
&= \tfrac{1}{2}(N-1)\pi \sum_{\mathbf{k}_1,\mathbf{k}_2} V^2_{\mathbf{k}_1,\mathbf{k}_2} \int d^3v_1 \int d^3v_2\, \{\log[\bar{f}_{10}(\mathbf{v}_1)\bar{f}_{10}(\mathbf{v}_2)]\} \\
&\qquad \times D_{\mathbf{k}_1,\mathbf{k}_2}[\delta(\mathbf{k}_1 \cdot \mathbf{v}_1 + \mathbf{k}_2 \cdot \mathbf{v}_2)]\, D_{\mathbf{k}_1,\mathbf{k}_2}\bar{f}_{10}(\mathbf{v}_1)\bar{f}_{10}(\mathbf{v}_2)
\end{aligned}$$

[by the symmetry of the integrand in $\mathbf{v}_1$ and $\mathbf{v}_2$]

$$= -\tfrac{1}{2}(N-1)\pi \sum_{\mathbf{k}_1,\mathbf{k}_2} V^2_{\mathbf{k}_1,\mathbf{k}_2} \int d^3v_1 \int d^3v_2 \frac{\delta(\mathbf{k}_1 \cdot \mathbf{v}_1 + \mathbf{k}_2 \cdot \mathbf{v}_2)}{\bar{f}_{10}(\mathbf{v}_1)\bar{f}_{10}(\mathbf{v}_2)}$$

$$\times [D_{\mathbf{k}_1,\mathbf{k}_2}\bar{f}_{10}(\mathbf{v}_1)\bar{f}_{10}(\mathbf{v}_2)]^2 < 0 \tag{64}$$

This result is known as an H-theorem. We note the use we made of the logarithmic integrand; it is the only functional of $\bar{f}_{10}$ for which the proof works, while the proof that $dQ/dt < 0$ in Section 6 works for many functionals Q of $\bar{\rho}$ (including $\int \rho \log \rho$).

From (61), we can prove that $\bar{f}_{10}$ tends to a Maxwellian form as $t \to \infty$ (or, once again, as $t \to -\infty$). The reason why this happens is that our assumption of no velocity correlations between the particles is only self-consistent when the system is large.[8] In this case, as we have already pointed out in Section 10 of I, the single-particle reduced density corresponding to a time-independent solution of the Liouville equation must be Maxwellian.

We can also obtain (63) from the BBGKY hierarchy (I.59) following the work of Frieman.[9]

8. THE PERTURBATION SERIES FOR $\bar{\rho}$

We now discuss the general problem of the evolution of the spatial Fourier components of $\bar{\rho}$ as given by the set of equations (5)–(9), without restriction on the magnitude of the parameter ϵ.

Equations (6) and (8) give, as (I.48),

$$\bar{\rho}_{0,\mathbf{K}_0}(\mathbf{V}, t) = \bar{\rho}_{\mathbf{K}_0}(\mathbf{V} - i\mathbf{K}_0\sigma^2 t, 0) \exp(-i\mathbf{K}_0 \cdot \mathbf{V}t - \tfrac{1}{2}\sigma^2 \mathbf{K}_0{}^2 t^2) \tag{65}$$

while in general

$$\bar{\rho}_{n,\mathbf{K}_0}(\mathbf{V}, t) = (-1)^n \underset{\tau_0+\tau_1+\cdots+\tau_n=t}{\int_0 d\tau_0 \int_0 d\tau_1 \cdots \int_0 d\tau_n} \sum_{\mathbf{K}_1,\ldots,\mathbf{K}_n} [\exp(-i\mathbf{K}_0 \cdot \mathbf{V}\tau_0)]$$

$$\times \mathbf{F}_{-(\mathbf{K}_1-\mathbf{K}_0)} \cdot (\partial/\partial\mathbf{V})[\exp(-i\mathbf{K}_1 \cdot \mathbf{V}\tau_1)]\, \mathbf{F}_{-(\mathbf{K}_2-\mathbf{K}_1)} \cdot \partial/\partial\mathbf{V}$$

$$\times \cdots [\exp(-i\mathbf{K}_{n-1} \cdot \mathbf{V}\tau_1)]\, \mathbf{F}_{-(\mathbf{K}_n-\mathbf{K}_{n-1})} \cdot (\partial/\partial\mathbf{V})[\exp(-i\mathbf{K}_n \cdot \mathbf{V}\tau_n)]$$

$$\times \bar{\rho}_{\mathbf{K}_n}(\mathbf{V} - i\sigma^2(\mathbf{K}_0\tau_0 + \cdots + \mathbf{K}_n\tau_n))$$

$$\times \exp[-\tfrac{1}{2}\sigma^2(\mathbf{K}_0\tau_0 + \cdots + \mathbf{K}_n\tau_n)^2] \tag{66}$$

In the next section, we show that the resummation techniques of the Brussels school (Prigogine and Balescu,[10] Prigogine and Résibois,[11] Prigogine,[12] Chapter 11) can be used on the series (5). The idea behind their work is a generalization of that of the above sections: they attempt to show that eventually the spatially homogeneous component $\rho_0(\mathbf{V}, t)$ of ρ evolves with time according to a closed equation, while the other components $\rho_{\mathbf{K}}$ are determined from current and previous values of ρ_0. In particular, we shall find an additional condition for the weak interaction calculation—we have shown so far only that our framework of approximations (10) and (20) is self-consistent.

We refer to Prigogine and Balescu,[10] Prigogine,[8] Chapter 7, or Balescu,[12] Chapter 1 for an explanation of the method by which any term of the perturbation series for ρ may be represented by a "diagram." The representation itself is still perfectly valid when applied to the perturbation series for $\bar{\rho}$, since the only assumption made is that $H_{\mathbf{K}}$ is of the form (I.2) (corresponding to two-particle interactions). This implies that if $\mathbf{K}_i$ and $\mathbf{K}_{i+1}$ are consecutive wave vectors in (66), for the term to be nonzero, only two of their N 3-components can differ,

$$\mathbf{k}_{i,l} = \mathbf{k}_{i+1,l} \qquad (l \neq p, q) \tag{67}$$

say. However, the law of conservation of wave vectors

$$\mathbf{k}_{i,p} + \mathbf{k}_{i,q} = \mathbf{k}_{i+1,p} + \mathbf{k}_{i+1,q} \tag{68}$$

being a consequence of (I.16), is *not* true; the best we can say is that when $\lambda \ll l$,

$$\mathbf{k}'_{i,p} + \mathbf{k}'_{i,q} = (\mathbf{k}'_{i+1,p} + \mathbf{k}'_{i+1,q})[1 + O(\lambda/l)] \tag{69}$$

Here, $\mathbf{k}'$ is some vector obtained from $\mathbf{k}$ by changing the signs of one or more components. This is the nearest we can get to (68) in veiw of the requirements (I.18).

Furthermore, since the Laplace transform of a particular term is no longer an algebraic product of operators, we can no longer work out the behavior of a particular diagram from the behavior of its vertices. We shall demonstrate this first for the weak-interaction case in section 10.

9. THE PRIGOGINE–RÉSIBOIS RESUMMATION

We write

$$G(\mathbf{V}, t) = \sum_{s=2}^{\infty} \epsilon^s G_s(\mathbf{V}, t) \tag{70}$$

where the *operator* $G_s(\mathbf{V}, t)$ is defined by

$$G_s(\mathbf{V}, t)\bar{f}(\mathbf{V}) = (-1)^s \underset{\tau_1+\cdots+\tau_{s-1}=t}{\int_0 d\tau_1 \cdots \int_0 d\tau_{s+1}} \sum_{\mathbf{K}_1,\ldots,\mathbf{K}_{s-1}\neq 0} F_{-\mathbf{K}_1} \cdot (\partial\rho/\partial\mathbf{V})$$

$$\times [\exp(-i\mathbf{K}_1 \cdot \mathbf{V}\tau_1)]\mathbf{F}_{-(\mathbf{K}_2-\mathbf{K}_1)} \cdot (\partial/\partial\mathbf{V})[\exp(-i\mathbf{K}_2 \cdot \mathbf{V}\tau_2)] \cdots \mathbf{F}_{\mathbf{K}_{s-1}} \cdot (\partial/\partial\mathbf{V})$$

$$\times \bar{f}(\mathbf{V} - i\sigma^2(\mathbf{K}_1\tau_1 + \cdots + \mathbf{K}_{s-1}\tau_{s-1}))$$

$$\times \exp[-\tfrac{1}{2}\sigma^2(\mathbf{K}_1\tau_1 + \cdots + \mathbf{K}_{s-1}\tau_{s-1})^2] \tag{71}$$

for any analytic function $\bar{f}(\mathbf{V})$ derivable from an analytic function $f(\mathbf{V})$ by means of our smoothing process. G_s is a linear integrodifferential functional operator acting on $\bar{f}$ when $\sigma \neq 0$, rather than just a differential operator, as it is when $\sigma = 0$.

Similarly, we define an operator $D_{\mathbf{K}}(\mathbf{V}, t)$ for $\mathbf{K} \neq 0$ by

$$D_{\mathbf{K}}(\mathbf{V}, t) = \sum_{s=1}^{\infty} \epsilon^s D_{s\mathbf{K}}(\mathbf{V}, t) \tag{72}$$

$$D_{s\mathbf{K}}(\mathbf{V}, t)\bar{f}(\mathbf{V}) = (-1)^s \underset{\tau_1+\cdots+\tau_s=t}{\int_0 d\tau_1 \cdots \int_0 d\tau_s} \sum_{\mathbf{K}_1,\ldots,\mathbf{K}_{s-1}\neq 0} \mathbf{F}_{-\mathbf{K}_1} \cdot (\partial/\partial\mathbf{V})$$

$$\times [\exp(-i\mathbf{K}_1 \cdot \mathbf{V}\tau_1)]\,\mathbf{F}_{-(\mathbf{K}_2-\mathbf{K}_1)} \cdot (\partial/\partial\mathbf{V})$$

$$\times [\exp(-i\mathbf{K}_2 \cdot \mathbf{V}\tau_2)] \cdots \mathbf{F}_{-(\mathbf{K}-\mathbf{K}_{s-1})} \cdot (\partial/\partial\mathbf{V})$$

$$\times [\exp(-i\mathbf{K} \cdot \mathbf{V}\tau_s)]\,\bar{f}(\mathbf{V} - i\sigma^2(\mathbf{K}_1\tau_1 + \cdots + \mathbf{K}\tau_s))$$

$$\times \exp[-\tfrac{1}{2}\sigma^2(\mathbf{K}_1\tau_1 + \cdots + \mathbf{K}\tau_s)^2] \tag{73}$$

Every term of the integrand of (66) with $\mathbf{K}_0 = \mathbf{0}$ can be expressed uniquely as a product of terms of the expressions G and $D_{\mathbf{K}}$, just as in the theory of Prigogine and Résibois. Thus

$$\bar{\rho}_0(\mathbf{V}, t) = \sum_{n=0}^{\infty} \underset{t_0+\tau_1+t_1+\tau_2+\cdots+\tau_n+t_n=t}{\int_0 dt_0 \int_0 d\tau_1 \int_0 dt_1 \int_0 d\tau_2 \cdots \int_0 d\tau_n \int_0 dt_n}\, G(\mathbf{V}, \tau_1)$$

$$\times \cdots G(\mathbf{V}, \tau_n)\,\bar{\rho}_0(\mathbf{V}, 0) + \sum_{n=0}^{\infty} \underset{t_0+\tau_1+\cdots+\tau_n+t_n+\tau'=t}{\int_0 dt_0 \int_0 d\tau_1 \cdots \int_0 d\tau_n \int_0 dt_n \int_0 d\tau'}$$

$$G(\mathbf{V}, \tau_1) \cdots G(\mathbf{V}, \tau_n) \sum_{\mathbf{K}\neq 0} D_{\mathbf{K}}(\mathbf{V}, \tau')\,\bar{\rho}_{\mathbf{K}}(\mathbf{V}, 0) \tag{74}$$

This gives us the integral equation

$$\bar{\rho}_0(\mathbf{V}, t) = \bar{\rho}_0(\mathbf{V}, 0) + \sum_{\mathbf{K}\neq 0} \int_0^t d\tau' \, D_{\mathbf{K}}(\mathbf{V}, \tau') \, \bar{\rho}_{\mathbf{K}}(\mathbf{V}, 0)$$

$$+ \underset{t_0+\tau_1+t_1=t}{\int_0 dt_0 \int_0 d\tau_1 \int_0 dt_1} \, G(\mathbf{V}, \tau_1) \, \bar{\rho}_0(\mathbf{V}, t_1) \tag{75}$$

equivalent to the differential equation

$$\partial\bar{\rho}_0(\mathbf{V}, t)/\partial t = A(\mathbf{V}, t) + \int_0^t G(\tau) \, \bar{\rho}_0(\mathbf{V}, t - \tau) \, d\tau \tag{76}$$

where

$$A(\mathbf{V}, t) = \sum_{\mathbf{K}\neq 0} D_{\mathbf{K}}(\mathbf{V}, t) \, \bar{\rho}_{\mathbf{K}}(\mathbf{V}, 0) \tag{77}$$

All this is simply formal manipulation of the series solution, and is exactly true. If, however, we can now prove that

$$A(\mathbf{V}, t) \to 0; \qquad t^{1+\delta} G(\mathbf{V}, t) \bar{f}(\mathbf{V}) \to 0 \quad (\delta > 0) \tag{78}$$

as $|t| \to \infty$, for any reasonably well-behaved $\bar{f}(\mathbf{V})$, then for large, positive times, we have, as promised, a closed equation for the evolution of $\bar{\rho}_0$

$$\partial\bar{\rho}_0(\mathbf{V}, t)/\partial t = \int_0^\infty G(\mathbf{V}, \tau) \, \bar{\rho}_0(\mathbf{V}, t - \tau) \, d\tau \tag{79a}$$

provided that $\bar{\rho}_0$ remains reasonably well-behaved. Similarly, for large, negative times,

$$\partial\bar{\rho}_0(\mathbf{V}, t)/\partial t = -\int_{-\infty}^0 G(\mathbf{V}, \tau) \, \bar{\rho}_0(\mathbf{V}, t - \tau) \, d\tau \tag{79b}$$

We observe that so far our work has made no mention of whether $\sigma \neq 0$ or $\sigma = 0$; (79a) or (79b) will be valid in either case provided (77) holds. The resummation leading to (76) was first performed, and the conditions (78) first explicitly stated, for $\sigma = 0$ in Refs. 10 and 11; we shall always refer to (79) as the Prigogine–Résibois master equation.

In just the same way, we can carry over the work on inhomogeneous components of Prigogine and Henin[13] (see also Prigogine,[8] Chapter 11). The $\bar{\rho}_{\mathbf{K}}$ for $\mathbf{K} \neq \mathbf{0}$ can be split into *created* and *propagated* parts. We would like to prove that the propagated part tends to zero.

10. THE WEAK-INTERACTION CASE

The results of Sections 2 and 3 may easily be derived from our general equations above. As there, we assume that the parameter ϵ is very small;

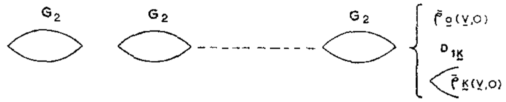

Fig. 3. Diagrams summed in weak-interaction approximation.

if we retain only the lowest powers of ϵ in (70) and (72), (78) is satisfied; (79a) gives (21). Expressions for the inhomogeneous components may also be derived, and give the results of Section 3.

In this approximation, we are of course keeping only terms in which alternate $\mathbf{K}_i$ are zero, that is, of the diagrammatic form shown (Fig. 3), in the expansion of $\bar{\rho}_0$. These are the same terms as are kept in the derivation of (40) from the perturbation series for ρ.[2,8]

There, however, the time dependence of these diagrams is obtained by convoluting the separate components. If we assume the spatial Fourier spectrum continuous, we can show that in the weak-interaction case, each *diagonal fragment* contributes a factor $\epsilon^2 t$, while *creation fragments* and *destruction fragments* merely add constant operators proportional to ϵ. That is, the terms represented by the above diagrams have as many powers of t in them as there are rings, and as many powers of ϵ in them as there are vertices.

When $\sigma \neq 0$, the behavior of compound terms is more complicated. For example,

$$G_2\bar{\rho}_0 = \sum_{\mathbf{K}_1} \int_0^t d\tau_0 \int_0^t d\tau_1 \int_0^t d\tau_2 \, \mathbf{F}_{-\mathbf{K}_1} \cdot (\partial/\partial \mathbf{V})$$
$$\times [\exp(-i\mathbf{K}_1 \cdot \mathbf{V}\tau_1 - \tfrac{1}{2}\sigma^2 K^2 \tau_1{}^2)] \, \mathbf{F}_{\mathbf{K}_1} \cdot (\partial/\partial \mathbf{V}) \, \bar{\rho}_0(\mathbf{V} - i\sigma^2 \mathbf{K}_1 \tau_1, 0) \tag{80}$$

It is easily seen that this expression equals $tJ\bar{\rho}_0(\mathbf{V}, 0)$ to within constant and decaying terms, where J was defined in (44). The behavior of the corresponding term in the expansion of ρ_0, with a continuous spectrum of $\mathbf{K}$, as analyzed in the above references, is essentially the same. However, the next term in the expansion is

$$\sum_{\mathbf{K}_1, \mathbf{K}_3} \underset{\tau_0 + \cdots + \tau_4 = t}{\int_0 d\tau_0 \cdots \int_0 d\tau_4} \mathbf{F}_{-\mathbf{K}_1} \cdot (\partial/\partial \mathbf{V})[\exp(-i\mathbf{K}_1 \cdot \mathbf{V}\tau_1)] \, \mathbf{F}_{\mathbf{K}_1} \cdot (\partial/\partial \mathbf{V})$$
$$\times \mathbf{F}_{-\mathbf{K}_3} \cdot (\partial/\partial \mathbf{V})[\exp(-i\mathbf{K}_3 \cdot \mathbf{V}\tau_3)] \, \mathbf{F}_{\mathbf{K}_3} \cdot (\partial/\partial \mathbf{V}) \, \bar{\rho}_0(\mathbf{V} - i\sigma^2(\mathbf{K}_1\tau_1 + \mathbf{K}_3\tau_3))$$
$$\times \exp[-\tfrac{1}{2}\sigma^2(\mathbf{K}_1\tau_1 + \mathbf{K}_3\tau_3)^2] \tag{81}$$

Unless

$$\mathbf{K}_1 + \alpha \mathbf{K}_3 = \mathbf{0} \tag{82}$$

for some (rational) $\alpha < 0$, $|\mathbf{K}_1\tau_1 + \mathbf{K}_3\tau_3| \to \infty$ as $\tau_1, \tau_3 \to \infty$. The τ_1 and τ_3 integrations may then be regarded as independent, and the result is proportional to t^2 (plus lower-order terms). However, if (82) is true, substitute $\tau_3' = \tau_3 - \alpha\tau_1$; then, $|\mathbf{K}_1\tau_1 + \mathbf{K}_3\tau_3| = |\mathbf{K}_3\tau_3'| \to \infty$ as $\tau_1, \tau_3 \to \infty$ if τ_3' remains bounded. The integral turns out to involve powers of t higher than the second.

We note that these effects show themselves in (25); the perturbative solution of this equation is just

$$\bar{\rho}_0(\mathbf{V}, t) = \sum_{n=0}^{\infty} (t^n/n!)\, J^n\, \bar{\rho}_0(\mathbf{V}, 0) \tag{83}$$

(this, of course, we only expect to represent $\bar{\rho}_0$ for large, positive t). Though the $n = 2$ term here seems to be of order t^2, in fact,

$$\begin{aligned} J^2\bar{\rho}_0(\mathbf{V}, 0) = \tfrac{1}{4} \sum_{\mathbf{K}_1,\mathbf{K}_3} \int_{-\infty}^{\infty} d\tau_1 \int_{-\infty}^{\infty} d\tau_3\, &\mathbf{F}_{-\mathbf{K}_1} \cdot (\partial/\partial\mathbf{V})[\exp(-i\mathbf{K}_1 \cdot \mathbf{V}\tau_1)] \\ &\times \mathbf{F}_{\mathbf{K}_1} \cdot (\partial/\partial\mathbf{V})\, \mathbf{F}_{-\mathbf{K}_3} \cdot (\partial/\partial\mathbf{V})[\exp(-i\mathbf{K}_3 \cdot \mathbf{V}\tau_3)]\, \mathbf{F}_{\mathbf{K}_3} \cdot (\partial/\partial\mathbf{V}) \\ &\bar{\rho}_0\big(\mathbf{V} - i\sigma^2(\mathbf{K}_1\tau_1 + \mathbf{K}_3\tau_3)\big) \exp[-\tfrac{1}{2}\sigma^2(\mathbf{K}_1\tau_1 + \mathbf{K}_3\tau_3)^2] \end{aligned} \tag{84}$$

When (82) is true, this integral diverges; the approximation (84) for the fourth-order term is invalid; the term is of higher order in t.

Despite the presence of these anomalous terms in our series for $\bar{\rho}_0$, we have shown that the corresponding equation (25) does have all the properties we expect of it. This reduces our pessimism when we tackle the problem of investigating the terms of the series (65) and (66) that we have omitted in the weak-interaction approximation, and find similar difficulties occurring when the wave vectors $\mathbf{K}_1$ in a term are parallel or linearly dependent.

11. SOME SECULAR TERMS IN G

We now attempt to discuss the effects of higher powers of ϵ, representing repeated collisions or multiple-body interactions. Prigogine and Résibois[11] discuss the $\sigma = 0$ infinite system case using Laplace transforms and complex variable theory to discuss higher terms in the expansion (70) of G. They make more plausible, though they do not prove, the assertion that each higher term G_3, G_4,..., of G separately satisfies (78), and so that (79) may be extended to all orders in the interaction strength. A recent paper by de Pazzis[14] considers this matter in more detail.

When $\sigma \neq 0$, however, Laplace transforms are not very useful, as remarked before. For example,

$$G_3(\mathbf{V}, t)\bar{f}(\mathbf{V}) = -\underset{\tau_1+\tau_2=t}{\int_0 d\tau_1 \int_0 d\tau_2} \sum_{\mathbf{K}_1,\mathbf{K}_2\neq\mathbf{0}} \mathbf{F}_{-\mathbf{K}_1} \cdot (\partial/\partial\mathbf{V})[\exp(-i\mathbf{K}_1 \cdot \mathbf{V}\tau_1)]$$
$$\times \mathbf{F}_{-(\mathbf{K}_2-\mathbf{K}_1)} \cdot (\partial/\partial\mathbf{V})[\exp(-i\mathbf{K}_2 \cdot \mathbf{V}\tau_2)]$$
$$\times \mathbf{F}_{\mathbf{K}_2} \cdot (\partial/\partial\mathbf{V})\bar{f}(\mathbf{V} - i\sigma^2(\mathbf{K}_1\tau_1 + \mathbf{K}_2\tau_2))$$
$$\times \exp[-\tfrac{1}{2}\sigma^2(\mathbf{K}_1\tau_1 + \mathbf{K}_2\tau_2)^2] \tag{85}$$

Now, if $\tau_1 + \tau_2 = t$ and $\mathbf{K}_2 \neq \mathbf{K}_1$,

$$(\mathbf{K}_1\tau_1 + \mathbf{K}_2\tau_2)^2 = [\mathbf{K}_1 t + (\mathbf{K}_2 - \mathbf{K}_1)\,\tau_2]^2$$
$$= (\mathbf{K}_2 - \mathbf{K}_1)^2\{\tau_2 + [\mathbf{K}_1 \cdot (\mathbf{K}_2 - \mathbf{K}_1)t/(\mathbf{K}_2 - \mathbf{K}_1)^2]\}^2$$
$$+ t^2\{\mathbf{K}_1{}^2 - [(\mathbf{K}_1 \cdot (\mathbf{K}_2 - \mathbf{K}_1))^2/(\mathbf{K}_2 - \mathbf{K}_1)^2]\} \tag{86}$$

It follows that all terms of (85) except those in which

$$\mathbf{K}_2 - \alpha\mathbf{K}_1 = \mathbf{0} \tag{87}$$

for some (rational) $\alpha \neq 1$, must have magnitude less than various powers of

$$t \exp\left(-\tfrac{1}{2}\sigma^2 t^2\{\mathbf{K}_1{}^2 - [(\mathbf{K}_1 \cdot (\mathbf{K}_2 - \mathbf{K}_1))^2/(\mathbf{K}_2 - \mathbf{K}_1)^2]\}\right)$$

Thus almost all these terms will tend to zero in a time of order λ/σ, and provided (I.52) holds, their sum is very likely to tend to zero in a time of order λ/v_0.

But consider the term

$$-\underset{\tau_1+\tau_2=t}{\int_0 d\tau_1 \int_0 d\tau_2}\, \mathbf{F}_{-\mathbf{K}_1} \cdot (\partial/\partial\mathbf{V})\, \mathbf{F}_{-\mathbf{K}_1(\alpha-1)} \cdot [(\partial/\partial\mathbf{V}) + i\mathbf{K}_1\tau_1]$$
$$\times \{\exp[-i\mathbf{K}_1 \cdot \mathbf{V}(\tau_1 + \alpha\tau_2)]\}\, \mathbf{F}_{\alpha\mathbf{K}_1} \cdot (\partial/\partial\mathbf{V})\bar{f}(\mathbf{V} - i\sigma^2\mathbf{K}_1(\tau_1 + \alpha\tau_2))$$
$$\times \exp[-\tfrac{1}{2}\sigma^2 K_1{}^2(\tau_1 + \alpha\tau_2)^2] \tag{88}$$

Substituting

$$\tau_1 + \alpha\tau_2 = \tau' \tag{89}$$

and changing the variable of integration from τ_1 to τ', we have

$$\frac{1}{\alpha - 1}\int_{\alpha t}^{t} d\tau'\, \mathbf{F}_{-\mathbf{K}_1} \cdot \frac{\partial}{\partial\mathbf{V}}\mathbf{F}_{-\mathbf{K}_{1(\alpha-1)}} \cdot \left[\frac{\partial}{\partial\mathbf{V}} + \frac{i\mathbf{K}_1(\alpha t - \tau')}{\alpha - 1}\right]$$
$$\times [\exp(-i\mathbf{K}_1 \cdot \mathbf{V}\tau')]\, \mathbf{F}_{\alpha\mathbf{K}_1} \cdot \frac{\partial}{\partial\mathbf{V}}\bar{f}(\mathbf{V} - i\sigma^2\mathbf{K}_1\tau') \exp[-\tfrac{1}{2}\sigma^2\mathbf{K}_1{}^2(\tau')^2] \tag{90}$$

If $\alpha < 0$, and $t > 1/\sigma K$, the limits of integration may be replaced by $-\infty$ and ∞; assuming $\bar{f}$ varies slowly with $\mathbf{V}$, this gives us some constant terms plus

$$\frac{\alpha t\sqrt{2\pi}}{(\alpha-1)^2\sigma K_1}\mathbf{F}_{-\mathbf{K}_1}\cdot\frac{\partial}{\partial\mathbf{V}}\mathbf{F}_{-\mathbf{K}_{1(\alpha-1)}}\cdot i\mathbf{K}_1\left[\exp-\frac{(\mathbf{K}_1\cdot\mathbf{V})^2}{2\sigma^2 K_1{}^2}\right]\mathbf{F}_{\alpha\mathbf{K}_1}\cdot\mathbf{g}(\mathbf{V}_\perp) \tag{91}$$

Thus $G_3(\mathbf{V}, t)\bar{f}(\mathbf{V})$, far from decreasing, contains terms which increase linearly with t! The integral expression (77) for $\partial\bar{\rho}_0/\partial t$ will contain terms of order t^2; it seems unlikely that we can approximate it by (78). However, as the size of the system increases, the time taken for these secular terms in G_3 to have an appreciable effect becomes longer and longer, as we shall now show.

The total number of possible $\mathbf{K}_1$, $\mathbf{K}_2$ in (85) is equal to the number of $\mathbf{K}_1$, $\mathbf{K}_2$ we can find such that

$$\mathbf{F}_{-\mathbf{K}_1\neq 0},\quad \mathbf{F}_{\mathbf{K}_2\neq 0},\quad F_{+(\mathbf{K}_1-\mathbf{K}_2)}\neq 0 \tag{92}$$

Using (I.22) we are restricted to terms whose diagrammatic representation is one of the two types shown in Fig. 4, that is, in the first type, only the pth and qth 3-components of either $\mathbf{K}_1$ or $\mathbf{K}_2$ are nonzero, while in the second type, the p and q components of $\mathbf{K}_1$, and the j and p components of $\mathbf{K}_2$, are nonzero. Assuming that $l \gg \lambda$, the total number of terms of the first type is about

$$\tfrac{1}{2}N(N-1)(l/\lambda)^6 \tag{93}$$

while the total number of the second type is about

$$\tfrac{1}{6}N(N-1)(N-2)(l/\lambda)^3 \tag{94}$$

(In the first type, $\mathbf{k}_{1p}$ and $\mathbf{k}_{2p}$ may differ; in the second type, they must be the same.) Since the magnitudes of almost all terms apart from the secular ones are about the same, the major contribution to the decaying part of G_3 will come from the class of diagrams with more representatives. Which class this is depends on the magnitude of

$$n_0 = N(\lambda/l)^3 \tag{95}$$

the average number of particles in a sphere of radius λ. When this is small, as for a rarified gas with short-range interactions, the first type predominates

Fig. 4. Two types of third-order term.

(two-body interactions, leading to an equation of Boltzmann type); when it is large, as for a plasma, the second type predominates (Balescu[12]).

Terms in which $\mathbf{K}_1$ and $\mathbf{K}_2$ are parallel occur only among the first type. There are about l/λ possible $\mathbf{K}_2$ for each of the $\frac{1}{2}N(N-1)(l/\lambda)^3$ possible $\mathbf{K}_1$:

$$\tfrac{1}{2}N(N-1)(l/\lambda)^4 \tag{96}$$

secular terms in all.

The effect of the secular terms in (76) will be negligible as long as

$$\left|\int_0^\infty G_{3,\mathrm{NSC}}(\mathbf{V},\tau)\bar{f}(\mathbf{V})\,d\tau\right| \gg \left|\int_0^t G_{3,\mathrm{SEC}}(\mathbf{V},\tau)\bar{f}(\mathbf{V})\,d\tau\right| \tag{97}$$

where the expression on the left contains all the nonsecular terms, and the expression on the right all the secular terms, in G_3. Write Q as the typical magnitude of the expressions

$$\mathbf{F}_{-\mathbf{K}_1}\cdot(\partial/\partial\mathbf{V})\,\mathbf{F}_{-(\mathbf{K}_2-\mathbf{K}_1)}\cdot(\partial/\partial\mathbf{V})\,\mathbf{F}_{\mathbf{K}_2}\cdot(\partial/\partial\mathbf{V})\,\bar{f}(\mathbf{V}) \tag{98}$$

Then the magnitude of the left-hand side of (97) will be about

$$\left.\begin{aligned} &\tfrac{1}{2}N(N-1)(l/\lambda)^6\,Q(\lambda/v_0)^2, && n_0 \ll 1\\ &\tfrac{1}{6}N(N-1)(N-2)\,Q(\lambda/v_0)^2(l/\lambda)^3, && n_0 \gg 1\end{aligned}\right. \tag{99}$$

[only a proportion $(\sigma/v_0)^2$ of the terms in this sum, satisfying

$$|\,\mathbf{V}\cdot\mathbf{K}_1'\,|/\sigma K_1' \sim 1 \qquad \text{and} \qquad |\,\mathbf{V}\cdot\mathbf{K}_2'\,|/\sigma K_2' \sim 1,$$

where $\mathbf{K}_1'$ and $\mathbf{K}_2'$ are certain linear combinations of $\mathbf{K}_1$ and $\mathbf{K}_2$, will be nonzero; these will have magnitude $Q/(\sigma K_0)^2$, where $K_0 \sim 1/\lambda$].

Integrating (91) with respect to time just adds a factor t; thus the magnitude of the right-hand side of (97) is about

$$\tfrac{1}{2}N(N-1)(l/\lambda)^4\,t^2 Q\mu\lambda/\lambda v_0 \tag{100}$$

[again, only a proportion σ/v_0 of the terms contribute, but the magnitude of each of these is $Q\mu\lambda/\sigma$, since, comparing (91) with (98), a $\partial/\partial\mathbf{V}$ is replaced by a $\mathbf{K}_1/K_1$]. The ratio of (100) to (99) is about $(tv_0/l)^2\,\mu/v_0$ or $(1/n_0)(tv_0/l)\,\mu/v_0$. Since, as before, $\mu < v_0$, secular terms will be negligible as long as

$$tv_0/l \ll 1 \tag{101}$$

i.e., provided a particle moving with the typical speed v_0 has not yet succeeded in crossing the containing vessel.

It is easy to extend this proof to consider secular terms in G_s of the form represented by the diagram shown in Fig. 5 with all intermediate wave

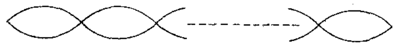

Fig. 5. Example of a general secular term.

vectors parallel. Though these increase with t like t^{2s-5}, they will have negligible effect compared to the nonsecular terms in G_s.

However, the terms of G_s (occurring for $s > 4$) in which not all the $\mathbf{K}_1, \ldots, \mathbf{K}_{s-1}$ are parallel, but between which there does exist some linear relation, are more troublesome. We can show that these secular terms are only negligible in effect compared to the nonsecular terms of the same order as long as

$$(\lambda/l)^2(tv_0/\lambda)^{s-1} \ll 1 \tag{102}$$

As s increases, the time required for this condition to be violated becomes shorter and shorter.

It is clear, then, that we cannot formulate a general criterion for the neglect of secular terms and the validity of (24). Even a condition for the weak-interaction approximation eludes us; for this, we would need

$$\left| \int_0^t G_{s,\mathrm{SEC}}(\mathbf{V}, t') \bar{f}(\mathbf{V})\, dt' \right| \ll \bar{f}(\mathbf{V})/\tau_0 \tag{103}$$

for all $s > 2$, and t up to the relaxation time $\tau_0 = \lambda/(\epsilon')^2 v_0$. This is certainly true for terms of the form (102) provided $\tau_0 v_0/l \ll 1 - \bar{\rho}_0$ reaches its limit in a time much shorter than it takes a particle to cross the containing vessel. However, (103) would be true only if, roughly speaking

$$[v_0(\epsilon')^{s+1}/\lambda](\lambda/l)^2(tv_0/\lambda)^{s-1} \ll (1/\tau_0) \qquad (t < \tau_0)$$

i.e.,

$$(\lambda/l)^2[1/(\epsilon')^{s-2}] \ll 1 \tag{104}$$

which will always break down for large enough s.

12. CONCLUSION

We have seen how a self-consistent theory of weakly interacting systems of finite size may be obtained either by "quasilinear" approximation or by perturbation theory. This equation has all the properties we would expect, and is indeed the Brout–Prigogine equation in another form. However, when we attempt to go to higher interaction strengths, difficulties arise owing to a finite proportion of sets of nonzero wave vectors being linearly dependent. In particular, when strings of consecutive parallel wave vectors occur, the behavior of terms of the series is quite different from that normally encountered. A physical explanation of these anomalous terms may be "resonant" particles colliding again and again on successive circuits of the toroidal Γ-space.

We are presently investigating methods of incorporating these terms. One suspects their collective effect is of little importance; suppose, for example, we have but one degree of freedom—one particle moving in a potential well. A series solution for ρ can be written down, and every term will similar to those analyzed in the last section. In fact, rather than being a series in powers of $\epsilon^2 t$ to highest order, (5) is a series in powers of ϵt^2. As we would then expect, a physical analysis of the problem (considering the period of oscillation of a particle in the well) shows that $\bar{\rho}$ will reach its limiting value in a time of order $\epsilon^{-1/2}$ [rather than $\tau_0 \sim \epsilon^{-2}$ of (52)]. In other words, it should be possible in the general expansion (5) to sum over classes of these awkward terms to obtain something well-behaved. This would be a further, or possibly an alternative, resummation of the series.

All this suggests that our work can be developed further to cover wider classes of finite systems. Even our work so far has, however, made it clear that the infinite limit is not a necessary part of the derivation of several important results of nonequilibrium statistical mechanics. As remarked in the introduction to I, it is not desirable that it should be necessary.

ACKNOWLEDGMENTS

This work was done during the tenure of a Junior Research Fellowship at Churchill College, Cambridge, and of a Research Studentship awarded by the Central Electricity Generating Board. My thanks are due to Drs. J. P. Dougherty and B. D. Josephson for their advice and help.

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