Physica **75** (1974) 1–36 © *North-Holland Publishing Co.*

THE NONEXISTENCE OF THE LINEAR DIFFUSION EQUATION BEYOND FICK'S LAW

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Received 31 January 1974

Synopsis

The self-diffusion of a tagged particle in a 3-dimensional fluid of identical particles cannot be described by a linear diffusion equation which contains corrections to Fick's law proportional to $\nabla^4 n$, $\nabla^6 n$, ... For long times a $t^{\frac{1}{2}}$ divergence is found for the super-Burnett coefficient, the proportionality coefficient of the ∇^4-term, both from the mode–mode coupling theory and the kinetic theory of hard spheres. Furthermore, higher asymptotic corrections of the form $t^{-2+2^{-n}}$ ($n = 2, 3, \ldots$) to the $t^{-3/2}$-time tail of the velocity autocorrelation function are calculated from both theories and the results are compared.

1. *Introduction.* It is widely believed that as a consequence of the long-time tail in the velocity autocorrelation function of a tagged particle[1–5]) the super-Burnett coefficient in the linear diffusion equation does not exist.

Here we shall prove this statement in a more explicit way with the help of the phenomenological mode–mode coupling theory and the kinetic theory of hard spheres. The reason why the proof is carried out along two lines is the following. The mode–mode coupling formulae, which are valid for small wave numbers and frequencies, are so simple and generally applicable that it is interesting to know up to which order in wave number and frequency they may be used. To that end we study in this section the diffusion of a tagged particle, in a fluid of identical particles and we derive formal expressions for the diffusion coefficient and the super-Burnett coefficient. In section 2 the super-Burnett coefficient is calculated from the phenomenological theory which is not restricted to the low-density regime, and in sections 3 and 4 from the kinetic theory of hard spheres at low densities, and the results are compared. We end in section 5 with some conclusions which may be drawn from the previous sections.

Consider now a classical fluid of N identical particles with mass m, interacting with central, pairwise-additive forces contained in a three-dimensional volume V. The particles have spatial coordinates $\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N$, and velocities $\boldsymbol{v}_1, \boldsymbol{v}_2, \ldots, \boldsymbol{v}_N$, denoted by the phase point Γ. The tagged particle is taken to be particle 1.

The diffusion process is then described by the function $G^s(\boldsymbol{r}, t)$ which is the probability of finding the tagged particle at time t at the position $\boldsymbol{\rho} + \boldsymbol{r}$, when it was initially ($t = 0$) at the position $\boldsymbol{\rho}$. $G^s(\boldsymbol{r}, t)$ is essentially the Green's function determining completely the decay of any reasonable initial density disturbance. This function is defined as

$$G^s(\boldsymbol{r}, t) = V\langle n(\boldsymbol{\rho}, 0)\, n(\boldsymbol{\rho} + \boldsymbol{r}, t)\rangle = \langle \delta(\Delta\boldsymbol{r}_1(t) - \boldsymbol{r})\rangle, \tag{1.1}$$

where $\Delta\boldsymbol{r}_1(t) = \boldsymbol{r}_1(t) - \boldsymbol{r}_1(0)$, the brackets denote an average over an equilibrium ensemble, and

$$n(\boldsymbol{r}, t) = \delta(\boldsymbol{r}_1(t) - \boldsymbol{r}), \tag{1.2}$$

is the microscopic density of the tagged particle. The time dependence of a microscopic function, $h(\Gamma, t)$, is given by

$$h(\Gamma, t) = e^{tL} h(\Gamma), \tag{1.3}$$

where L is the Liouville operator.

It will be convenient to consider Fourier transforms of a function $f(\boldsymbol{r})$, defined as

$$f_{\boldsymbol{k}} = \int_V d\boldsymbol{r}\, e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} f(\boldsymbol{r}), \tag{1.4}$$

of which the inverse is given by

$$f(\boldsymbol{r}) = (1/V) \sum_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} f_{\boldsymbol{k}}. \tag{1.5}$$

For large volumes we may replace the sum $V^{-1}\sum_{\boldsymbol{k}}$ by an integral $(2\pi)^{-3}\int d\boldsymbol{k}$. We also define an inner product in the space of phase functions as

$$\langle f \mid g\rangle = \langle f^* g\rangle, \tag{1.6}$$

where the asterisk stands for complex conjugation. The spatial Fourier transform of $G^s(\boldsymbol{r}, t)$ can now be written as

$$G^s_{\boldsymbol{k}}(t) = \langle n_{\boldsymbol{k}} \mid n_{\boldsymbol{k}}(t)\rangle = \langle e^{-i\boldsymbol{k}\cdot\Delta\boldsymbol{r}_1(t)}\rangle, \tag{1.7}$$

where $n_k = \exp(-i\boldsymbol{k}\cdot\boldsymbol{r}_1)$ and

$$\Delta\boldsymbol{r}_1(t) = \boldsymbol{r}_1(t) - \boldsymbol{r}_1(0) = \int_0^t \mathrm{d}t'\, \boldsymbol{v}_1(t'), \tag{1.8}$$

is the spatial displacement of the tagged particle.

Next we consider the equation of motion for $G_k^s(t)$. From eq. (1.3) we obtain

$$\frac{\partial}{\partial t} n_k(t) = L n_k(t) = -ikj_k(t), \tag{1.9}$$

where the tagged-particle current density is

$$j_k = \hat{\boldsymbol{k}}\cdot\boldsymbol{v}_1\, \mathrm{e}^{-i\boldsymbol{k}\cdot\boldsymbol{r}_1} \tag{1.10}$$

and $\hat{\boldsymbol{k}} = \boldsymbol{k}/k$ denotes a unit vector.

We also need the Laplace transform of a function $f(t)$, defined as

$$f_z = \int_0^\infty \mathrm{d}t\, \mathrm{e}^{-zt} f(t), \tag{1.11}$$

so that the Fourier–Laplace transform of $G^s(\boldsymbol{r}, t)$ is equal to

$$G_{kz}^s = \langle n_k|\,[1/(z-L)]\,|n_k\rangle = \langle n_k \mid n_{kz}\rangle, \tag{1.12}$$

where n_{kz} is the Fourier–Laplace transform of $n(\boldsymbol{r}, t)$.

The simplest way to obtain a diffusion equation for $G_k^s(t)$ is to write its equation of motion in the desired form

$$\frac{\partial}{\partial t} G_k^s(t) = -k^2 D_k(t)\, G_k^s(t) \tag{1.13}$$

and consider it merely as a definition of a time- and wavenumber-dependent diffusion coefficient $D_k(t)$. Therefore,

$$D_k(t) = -[k^2 G_k^s(t)]^{-1} \frac{\partial}{\partial t} G_k^s(t). \tag{1.14}$$

By means of eq. (1.9) the function $G_k^s(t)$ can be related immediately to the current–current correlation function $C_k(t)$ as

$$\frac{\partial}{\partial t} G_k^s(t) = -k^2 \int_0^t \mathrm{d}\tau\, C_k(\tau), \tag{1.15}$$

where

$$C_k(t) = \langle j_k | \, e^{tL} \, | j_k \rangle = \langle j_k^* j_k(t) \rangle. \tag{1.16}$$

Alternative expressions for $D_k(t)$ are therefore

$$D_k(t) = [G_k^s(t)]^{-1} \int_0^t d\tau \, C_k(\tau) \tag{1.17a}$$

$$= (\langle e^{-ik\Delta x_1(t)} \rangle)^{-1} \int_0^t d\tau \, \langle v_{1x} v_{1x}(\tau) \, e^{-ik\Delta x_1(\tau)} \rangle. \tag{1.17b}$$

In eq. (1.17b) $\boldsymbol{k}$ is taken parallel to the x axis. In order to obtain a diffusion equation of the standard form one assumes that $D_k(t)$ can be expanded in powers of k (or rather ik), and that each term converges for large times rather quickly to a constant value. One obtains, then, from (1.17b) and (1.8)

$$D_k(t) = D_0(t) - k^2 D_2(t) + \cdots, \tag{1.18}$$

where

$$D_0(t) = \int_0^t d\tau \, \langle v_{1x} v_{1x}(\tau) \rangle, \tag{1.19}$$

is the time-dependent diffusion coefficient, and

$$\begin{aligned} D_2(t) = \int_0^t dt_1 \int_{t_1}^t dt_2 \int_{t_2}^t dt_3 \, [&\langle v_{1x} v_{1x}(t_1) \, v_{1x}(t_2) \, v_{1x}(t_3) \rangle \\ &- \langle v_{1x} v_{1x}(t_1) \rangle \langle v_{1x}(t_2) \, v_{1x}(t_3) \rangle - \langle v_{1x} v_{1x}(t_2) \rangle \langle v_{1x}(t_1) \, v_{1x}(t_3) \rangle \\ &- \langle v_{1x} v_{1x}(t_3) \rangle \langle v_{1x}(t_1) \, v_{1x}(t_2) \rangle] \end{aligned} \tag{1.20}$$

is the time-dependent super-Burnett coefficient, which are expressed in cumulants of the two- and four-point velocity correlation function. An analogous procedure has been devised by McLennan[6]). In the sequel we will investigate the question if indeed the functions $D_0(t)$ and $D_2(t)$ converge fast enough to the linear diffusion coefficient D and the linear super-Burnett coefficient D_2, respectively, given by

$$D = \lim_{t \to \infty} D_0(t) = \int_0^\infty dt \, \langle v_{1x} v_{1x}(t) \rangle \tag{1.21}$$

and

$$D_2 = \lim_{t \to \infty} D_2(t), \tag{1.22}$$

where (1.21) is the familiar expression for the diffusion coefficient.

If the approach to these limiting values is sufficiently fast, we may replace (1.13) by the more physical higher-order linear diffusion equation

$$\frac{\partial}{\partial t} G_k^s(t) = (-Dk^2 + D_2k^4 + \cdots)\, G_k^s(t) \tag{1.23}$$

which should hold approximately for long times.

We have developed a kinetic theory, which enables us to study the long-time behaviour of $D_0(t)$ and $D_2(t)$ in the limit of low densities. Another method to study the long-time behaviour of these quantities is given by the mode–mode coupling theories, the result of which will be compared with the kinetic-theory results.

Since the results of the mode–mode coupling theory can be formulated most easily in Laplace language, we develop a formal description of the diffusion equation [compare (1.13)] in Laplace language, and obtain a quantity which we can formally identify as a k- and z-dependent diffusion coefficient [compare (1.14)], and which we will study in the limit for small values of k and z.

A formal derivation of the diffusion equation can be given with the help of Zwanzig's projection-operator technique[7]), applied to the Laplace transform of eq. (1.9) for n_{kz}. We introduce hermitean projection operators P and $P_\perp = 1 - P$, as

$$P = \sum_k |n_k\rangle \langle n_k| . \tag{1.24}$$

Equations of motion for Pn_{kz} and $P_\perp n_{kz}$ can be obtained in the standard way, with the result

$$G_{kz}^s = \langle n_k \mid Pn_{kz}\rangle = (z + k^2\hat{C}_{kz})^{-1}, \tag{1.25a}$$

or in time language

$$\frac{\partial}{\partial t} G_k^s(t) = -k^2 \int_0^t \mathrm{d}\tau\, \hat{C}_k(\tau)\, G_k^s\,(t - \tau), \tag{1.25b}$$

where the projected current–current correlation function $\hat{C}_{kz}$ is given by

$$\hat{C}_{kz} = \langle j_k|\, (z - \hat{L})^{-1}\, |j_k\rangle, \tag{1.26}$$

with $\hat{L} = P_\perp L P_\perp$. The Laplace transforms of the correlation functions $C_k(t)$, defined in (1.16), and $\hat{C}_k(t)$, defined in (1.26) are related by

$$C_{kz} = z\hat{C}_{kz}/(z + k^2\hat{C}_{kz}), \tag{1.27}$$

as can be shown from the operator identity

$$P_{\perp}(z-L)^{-1}P_{\perp} = P_{\perp}(z-\hat{L})^{-1}P_{\perp} + P_{\perp}(z-\hat{L})^{-1}P_{\perp}LP(z-L)^{-1}P_{\perp}. \tag{1.28}$$

From the fact that $\hat{C}_{kz}$ contains the operator $\hat{L} = P_{\perp}LP_{\perp}$ and $P_{\perp}$ projects orthogonally to the function n_k, which approaches an eigenfunction of L with eigenvalue zero as $k \to 0$, it is believed that $\hat{C}_{kz}$ is a well behaved continuous function around $k = 0$ and $z = 0$, although it need not be analytic at that point. Note first that according to (1.27)

$$\lim_{k\to 0} \hat{C}_{kz} = \lim_{k\to 0} C_{kz} \equiv C_{0_z}, \tag{1.29}$$

so that $D = \lim_{z\to 0} \lim_{k\to 0} \hat{C}_{kz}$, in agreement with (1.21). On the basis of the assumed continuity of $\hat{C}_{kz}$ at $k = 0$ and $z = 0$, we may expect

$$\hat{C}_{kz} = D + \delta\hat{C}_{kz}, \tag{1.30}$$

where $\delta\hat{C}_{kz}$ vanishes if k and z approach zero. Secondly, notice that if $\hat{C}_{kz}$ is continuous around $k = 0$ and $z = 0$, the function C_{kz} is clearly not, since it follows from (1.27) that

$$\lim_{z\to 0}\lim_{k\to 0} C_{kz} = D; \qquad \lim_{k\to 0}\lim_{z\to 0} C_{kz} = 0. \tag{1.31}$$

The phenomenological mode–mode coupling theory yields an approximate expression for $\hat{C}_{kz}$, which is supposed to apply for small values of k and z; it confirms the continuity property as expressed in (1.30), and it shows that $\hat{C}_{kz}$ is a nonanalytic function of k and z. Explicit expressions and calculations will be given in section 2.

In order to compare the mode–mode results for $\hat{C}_{kz}$, with the kinetic-theory results for $D_0(t)$ and $D_2(t)$ we have to relate these coefficients with the coefficients in the k expansion of $\hat{C}_{kz}$ at fixed z, or equivalently, with the coefficients in the k expansion of $\hat{C}_k(t)$ at fixed t, which are defined as

$$\hat{C}_k(t) = \hat{C}_0(t) - k^2\hat{C}_2(t) + \cdots. \tag{1.32}$$

This can be done directly by inserting (1.32) into (1.25b), expanding the resulting equation up to $\mathcal{O}(k^4)$ included, and comparing the coefficients with $D_0(t)$ and $D_2(t)$ by means of (1.13) and (1.18). The result for the time-dependent diffusion coefficient is

$$D_0(t) = \int_0^t \mathrm{d}\tau\, \hat{C}_0(\tau) \tag{1.33}$$

and for the time-dependent super-Burnett coefficient

$$D_2(t) = \int_0^t \mathrm{d}\tau\, \hat{C}_2(\tau) - \int_0^t \mathrm{d}t_1 \int_{t_1}^t \mathrm{d}t_2 \int_{t_2}^t \mathrm{d}t_3$$

$$\times\, [\hat{C}_0(t_2)\, \hat{C}_0\,(t_3 - t_1) + \hat{C}_0(t_3)\, \hat{C}_0\,(t_2 - t_1)]. \tag{1.34}$$

From (1.29) it is clear that $\hat{C}_0(t)$ equals the velocity autocorrelation function $C_0(t)$, and the expressions (1.19) and (1.33) are obviously the same. Of course, eq. (1.27) can also be used to relate the expansion coefficients $\hat{C}_0(t)$, $\hat{C}_2(t)$, ... of $\hat{C}_k(t)$ with the expansion coefficients $C_0(t)$, $C_2(t)$, ... of $C_k(t)$. The functions $C_0(t)$, $C_2(t)$ ... can be easily expressed in terms of two-point, four-point ... velocity correlation functions, and in this way one proves that also (1.34) and (1.20) are the same. This is, of course, no surprise, since we have merely transformed identities. The purpose for deriving eqs. (1.33) and (1.34) is that we can calculate their right-hand sides from the mode–mode coupling theory, and their left-hand sides from kinetic theory, and then compare the results. Since the mode–mode coupling theory is only an approximate theory, it is not *a priori* clear that $D_2(t)$ is correctly predicted by this theory. However, if the results from both theories agree, this serves as a test for the validity of the mode–mode theory for the dominant small z or large t dependence up to $\mathcal{O}(k^2)$ inclusive.

Section 2 is devoted to the calculation of the mode–mode results, section 3 deals with the kinetic theory, which is used in section 4 to calculate the super-Burnett coefficient.

2. *Diffusion process from the mode–mode coupling theory.* Thus far the relations derived are formal identities for the probability function $G_k^{\mathrm{s}}(t)$. One of the few theories which give an explicit prediction for the small k and large t dependence of the current–current correlation function $\hat{C}_k(t)$ for all densities and all reasonable intermolecular potentials is the phenomenological mode–mode coupling theory which gives a contribution to $\hat{C}_k(t)$ of the form[2,4,8]):

$$\hat{C}_k^{(\mathrm{mm})}(t) = \sum_i \frac{V}{(2\pi)^3} \int' \mathrm{d}\boldsymbol{q}\, |\langle j_k^* \varphi_{\boldsymbol{q}}^i \varphi_{k-\boldsymbol{q}}^{\mathrm{s}} \rangle|^2\, G_{\boldsymbol{q}}^i(t)\, G_{k-\boldsymbol{q}}^{\mathrm{s}}(t). \tag{2.1}$$

The prime on the integral sign indicates that $|\boldsymbol{q}| < q_0$, where q_0 is a cut-off wave number of the order of a reciprocal miscroscopic correlation length, such as the mean free path in a moderately dense gas.

The self-diffusion mode $\varphi_{k-\boldsymbol{q}}^{\mathrm{s}}$ is equal to the microscopic tagged-particle density function:

$$\varphi_{k-\boldsymbol{q}}^{\mathrm{s}} = n_{k-\boldsymbol{q}} = \mathrm{e}^{-\mathrm{i}(k-\boldsymbol{q})\cdot \boldsymbol{r}_1}. \tag{2.2}$$

The function $G^{s}_{k-q}(t)$ is the hydrodynamic correlation function (1.7), also referred to as the hydrodynamic propagator of the diffusive mode. Using the lowest-order approximation for $\hat{C}_{kz}$ as is described in (1.25a) and (1.30) one obtains for this propagator:

$$G^{s}_{k-q}(t) = \exp\left[-D\,(\boldsymbol{k} - \boldsymbol{q})^2\, t\right]. \tag{2.3}$$

The microscopic functions φ^{i}_{q} with $i = 1, \ldots, 5$ represent the five normalized orthogonal hydrodynamic modes (two opposite sound modes, two shear modes and the heat mode) given explicitly in ref. 8.

The functions $G^{i}_{q}(t)$ are the propagators of the hydrodynamic modes φ^{i}_{q}. Note that only contributions are taken into account which result from the coupling of the diffusion mode of the tagged particle with one hydrodynamic mode of the fluid. Two coupled diffusion modes give no contribution because the mode–mode amplitude $\langle j^{*}_{k}\varphi^{s}_{q}\varphi^{s}_{k-q}\rangle = 0$ as follows from (2.2) and (1.10). A combination of the diffusion mode and the heat mode does not contribute to (2.1) because the heat mode is a scalar quantity so that the corresponding amplitude $\langle j^{*}_{k}\varphi^{i}_{q}\varphi^{s}_{k-q}\rangle$ vanishes. The combination of the diffusion mode and a sound mode may be neglected since it is for large times of higher order in $1/t$, than a combination of the diffusion mode and a shear mode.

Finally we notice that a combination of two hydrodynamic modes of the fluid would give an amplitude proportional to the density of the tagged particle, which is vanishingly small, whereas the amplitudes considered above are independent of the tagged-particle density. So we are left with a combination of the diffusion mode and one of the two shear modes, which are given as:

$$\varphi^{\eta_j}_{q} = (\beta/\varrho V)^{\frac{1}{2}}\, \hat{\boldsymbol{q}}^{(j)}_{\perp} \cdot \sum_{l=1}^{N} m\boldsymbol{v}_l\, \mathrm{e}^{-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_l}, \tag{2.4}$$

where $\hat{\boldsymbol{q}}^{(j)}_{\perp}$ with $j = 1, 2$ are two orthogonal unit vectors perpendicular to $\hat{\boldsymbol{q}}$. Here the mass density $\varrho = mn$, where n is the equilibrium number density and $\beta = (k_{\mathrm{B}}T)^{-1}$, where T is the temperature and k_{B} Boltzmann's constant. The propagators of the shear modes are to lowest order given by:

$$G^{\eta_j}_{q}(t) = \mathrm{e}^{-\nu q^2 t} \qquad (j = 1, 2), \tag{2.5}$$

where the kinematic viscosity is $\nu = \eta/\varrho$ and η is the shear viscosity of the fluid. If we choose at fixed $\boldsymbol{k}$ the two perpendicular unit vectors $\hat{\boldsymbol{q}}^{(j)}_{\perp}$ as

$$\hat{\boldsymbol{q}}^{(1)}_{\perp} = \hat{\boldsymbol{q}} \times \hat{\boldsymbol{k}}/|\hat{\boldsymbol{q}} \times \hat{\boldsymbol{k}}|, \tag{2.6a}$$

$$\hat{\boldsymbol{q}}^{(2)}_{\perp} = [\hat{\boldsymbol{k}} - (\hat{\boldsymbol{k}} \cdot \hat{\boldsymbol{q}})\, \hat{\boldsymbol{q}}]/[1 - (\hat{\boldsymbol{k}} \cdot \hat{\boldsymbol{q}})^2]^{\frac{1}{2}}, \tag{2.6b}$$

the two amplitudes occurring in (2.1) become:

$$\langle j_k^* \varphi_q^{\eta_1} \varphi_{k-q}^s \rangle = 0, \tag{2.7a}$$

$$\langle j_k^* \varphi_q^{\eta_2} \varphi_{k-q}^s \rangle = \{[1 - (\hat{k} \cdot \hat{q})^2]/\beta \varrho V\}^{\frac{1}{2}}. \tag{2.7b}$$

From (2.1), (2.3), (2.5) and (2.7) one obtains for small k and large t:

$$\hat{C}_k^{(\mathrm{mm})}(t) = \frac{1}{\beta \varrho} \int' \frac{\mathrm{d}\boldsymbol{q}}{(2\pi)^3} [1 - (\hat{\boldsymbol{k}} \cdot \hat{\boldsymbol{q}})^2] \, \mathrm{e}^{-\nu q^2 t} \, \mathrm{e}^{-D(\boldsymbol{k}-\boldsymbol{q})^2 t}$$

or in Laplace language for small k and small z:

$$\hat{C}_{kz}^{(\mathrm{mm})} = \frac{1}{\beta \varrho} \int' \frac{\mathrm{d}\boldsymbol{q}}{(2\pi)^3} \frac{1 - (\hat{\boldsymbol{k}} \cdot \hat{\boldsymbol{q}})^2}{z + \nu q^2 + D(\boldsymbol{k} - \boldsymbol{q})^2}.$$

Defining the dimensionless frequency:

$$s(k, z) = \frac{D + \nu}{D} \frac{z + Dk^2}{Dk^2}, \tag{2.8}$$

and using the dimensionless variables $x = \hat{\boldsymbol{k}} \cdot \hat{\boldsymbol{q}}$ and $y = [(D + \nu)/D](q/k)$ one gets easily:

$$\hat{C}_{kz}^{(\mathrm{mm})} = \frac{Dk}{4\pi^2 \beta \varrho (D + \nu)^2} \int_{-1}^{+1} \mathrm{d}x \, (1 - x^2) \int_0^{y_0} \mathrm{d}y \frac{y^2}{y^2 - 2xy + s}, \tag{2.9}$$

where $y_0 = [(D + \nu)/D](q_0/k)$. The limit $k = 0$ and $z = 0$ of this expression contributes to the diffusion coefficient as is expressed in (1.30).

We are interested now in the mode–mode contribution to $\delta\hat{C}_{kz}$ which is by definition $\delta\hat{C}_{kz}^{(mm)} = \hat{C}_{kz}^{(mm)} - \hat{C}_{00}^{(mm)}$. The y integral in (2.9) can be performed exactly and we obtain:

$$\delta\hat{C}_{kz}^{(\mathrm{mm})} = \frac{Dk}{4\pi \beta \varrho (D + \nu)^2} \int_{-1}^{+1} \mathrm{d}x \frac{(1 - x^2)(x^2 - \frac{1}{2}s)}{(s - x^2)^{\frac{1}{2}}}. \tag{2.10}$$

Going from (2.9) to (2.10) we have omitted terms which are at least of order k^2 times an analytic function of z which do not affect our results. The remaining x integral can also be performed exactly, and by virtue of the definition (1.30) we arrive at the final result:

$$\hat{C}_{kz} = D + \frac{Dk}{16\pi \beta \varrho (D + \nu)^2} [(s - 2)(s - 1)^{\frac{1}{2}} - s^2 \operatorname{arctg}(s - 1)^{-\frac{1}{2}}]. \tag{2.11}$$

This should hold for small k and z, where the dimensionless frequency s is defined in (2.8). A similar result has also been obtained by several authors[9,25,26]. Note that the term $\delta\hat{C}_{kz}$ is indeed nonanalytic at the point $k = 0$ and $z = 0$.

The correlation function $\hat{C}_{kz}$ can easily be expanded in powers of k at fixed z: $\hat{C}_{kz} = \hat{C}_{0_z} - k^2\hat{C}_{2_z} + k^4\hat{C}_{4_z} - \cdots$ because for $k \to 0$, the frequency s is very large and so the arctangent in (2.11) may be expanded in odd powers of $(s-1)^{-\frac{1}{2}}$. The result either for small z or large t is:

$$\hat{C}_{0_z} = D - \frac{z^{\frac{1}{2}}}{6\pi\beta\varrho\,(D+\nu)^{3/2}}, \tag{2.12a}$$

$$\hat{C}_0(t) = \frac{1}{12\pi^{3/2}\beta\varrho\,(D+\nu)^{3/2}}\,\frac{1}{t^{3/2}}, \tag{2.12b}$$

which is the well-known long-time tail in the velocity autocorrelation function, and:

$$\hat{C}_{2_z} = \frac{D\,(5\nu + 2D)}{60\pi\beta\varrho\,(D+\nu)^{5/2}}\,\frac{1}{z^{\frac{1}{2}}} + \mathcal{O}(1), \tag{2.13a}$$

$$\hat{C}_2(t) = \frac{D\,(5\nu + 2D)}{60\pi\beta\varrho\,(D+\nu)^{5/2}}\,\frac{1}{t^{\frac{1}{2}}}. \tag{2.13b}$$

From the previous equations and (1.33) it is easy to calculate the time-dependent diffusion coefficient $D_0(t)$ defined in (1.18):

$$D_0(t) = D - \frac{1}{6\pi^{3/2}\beta\varrho\,(D+\nu)^{3/2}}\,\frac{1}{t^{\frac{1}{2}}} \tag{2.14}$$

and so indeed $D_0(t)$ converges to the diffusion coefficient D itself for long times.

To obtain the super-Burnett coefficient $D_2(t)$ from (1.34), one has to calculate the quantities:

$$E_1(t) = \int_0^t \mathrm{d}t_1 \int_{t_1}^t \mathrm{d}t_2 \int_{t_2}^t \mathrm{d}t_3\, \hat{C}_0(t_1)\,\hat{C}_0\,(t_3 - t_2), \tag{2.15a}$$

$$E_2(t) = \int_0^t \mathrm{d}t_1 \int_{t_1}^t \mathrm{d}t_2 \int_{t_2}^t \mathrm{d}t_3\, \hat{C}_0(t_2)\,\hat{C}_0\,(t_3 - t_1), \tag{2.15b}$$

$$E_3(t) = \int_0^t \mathrm{d}t_1 \int_{t_1}^t \mathrm{d}t_2 \int_{t_2}^t \mathrm{d}t_3\, \hat{C}_0(t_3)\,\hat{C}_0\,(t_2 - t_1), \tag{2.15c}$$

where $E_1(t)$ is added for later reference.

Noting that $\int_0^\infty \mathrm{d}t\, \hat{C}_0(t) = D$ and using the result (2.12b) for large times we get for large t:

$$E_1(t) = D^2 t - [2D/3\pi^{3/2}\beta\varrho\,(D+\nu)^{3/2}]\, t^{\frac{1}{2}} + \mathcal{O}(1), \tag{2.16a}$$

$$E_2(t) = \mathcal{O}\,(\log t), \tag{2.16b}$$

$$E_3(t) = [D/6\pi^{3/2}\beta\varrho\,(D+\nu)^{3/2}]\, t^{\frac{1}{2}} + \mathcal{O}\,(\log t). \tag{2.16c}$$

Now the time-dependent super-Burnett coefficient for large t follows from (1.34), (2.13b) and (2.16b), (2.16c):

$$D_2(t) = -[D^2/10\pi^{3/2}\beta\varrho\,(D+\nu)^{5/2}]\, t^{\frac{1}{2}} + \mathcal{O}(1). \tag{2.17}$$

Therefore the super-Burnett coefficient $D_2 = \lim_{t\to\infty} D_2(t)$ itself does not exist, but diverges proportional to $t^{\frac{1}{2}}$ as t approaches infinity, and we have found the coefficient of the divergent term. This result cannot be trusted without further justification. All quantities (modes and propagators) in our starting eq. (2.1) were taken to lowest order, while $\hat{C}_{kz}$ was expanded up to order k^2 to obtain the super-Burnett coefficient. The answer to the question whether (2.17) is right after all, will be obtained from the kinetic theory of hard spheres in the next sections. Results similar to (2.17) have been obtained in refs. 27 and 28.

3. *Kinetic theory of hard spheres.* In this and the next section we use the kinetic theory of hard spheres for low densities to calculate the functions $D_0(t)$ and $D_2(t)$ and compare them with the results of section 2. We will first introduce a diagrammatic method to study this kinetic theory[10–14]), in as far as we need it for the discussion of the long-time behaviour of the velocity autocorrelation function[3,16–20]). This method will be extended in section 4 to the calculation of the four point correlation function. It can be derived starting from the binary-collision expansion of the streaming operator $\exp tL$[10]), neglecting all statistical correlations, taking everywhere the limit $k \to 0$ for the Fourier transform of the binary collision operator $T_k\,(ij)$[17]) and applying straightforwardly diagrammatic techniques. In fact we will use the diagrammatic representation introduced by Kawasaki and Oppenheim[11]) for deriving kinetic equations.

We introduce the kinetic (self) propagator for the tagged particle, $\Gamma_k^{\mathrm{s}}\,(1, t)$, which is a one-particle operator acting on functions of $\boldsymbol{v}_1$ only, by means of the definition:

$$\langle f(\boldsymbol{v}_1)\, \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_1}\, \mathrm{e}^{tL}\, g(\boldsymbol{v}_1)\, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_1}\rangle = \langle f(\boldsymbol{v}_1)\, \Gamma_k^{\mathrm{s}}\,(1, t)\, g(\boldsymbol{v}_1)\rangle_1, \tag{3.1}$$

where f and g are arbitrary functions of $\boldsymbol{v}_1$ with the property $\langle f\rangle_1 = 0$ and $\langle g\rangle_1 = 0$ and the one-particle average is defined as

$$\langle f(\boldsymbol{v}_i)\rangle_i = \int \mathrm{d}\boldsymbol{v}_i\, \phi_0(v_i) f(\boldsymbol{v}_i). \tag{3.2}$$

The normalized maxwellian is given by:

$$\phi_0(v) = (\beta m/2\pi)^{3/2} \exp(-\tfrac{1}{2}\beta m v^2). \tag{3.3}$$

We introduce the kinetic propagator for a fluid particle $\Gamma_k(i, t)$, which is a one-particle operator acting on functions of v_i only, by means of the definition:

$$N^{-1} \left\langle \sum_{l=1}^{N} f(v_l)\, e^{ik\cdot r_l}\, e^{tL} \sum_{j=1}^{N} g(v_j)\, e^{-ik\cdot r_j} \right\rangle = \langle f(v_i)\, \Gamma_k(i, t)\, g(v_i) \rangle_i, \tag{3.4}$$

where i may be any number except 1, to avoid confusion with the tagged particle. Note that Γ describes the joint correlation functions between any fluid particle at time t and any fluid particle at the initial time, while Γ^s describes the autocorrelation functions of the tagged particle.

We will review the (modified) diagrammatic representation of Kawasaki and Oppenheim by listing the rules for drawing diagrams and for writing down the corresponding analytic expressions. Our diagrams differ from theirs, since they neither contain free-particle propagators, nor vertices corresponding to Boltzmann collision operators. This is due to the fact that we have carried out a further resummation, as will be explained below. The operators $\Gamma_k^s(1, t)$ and $\Gamma_k(i, t)$ are both represented by a double straight line, labelled $(1, k)$ and (i, k), respectively, as shown at the left-hand side of fig. 1, where the vertical axis is the time axis from the top ($t = 0$) to the bottom (t).

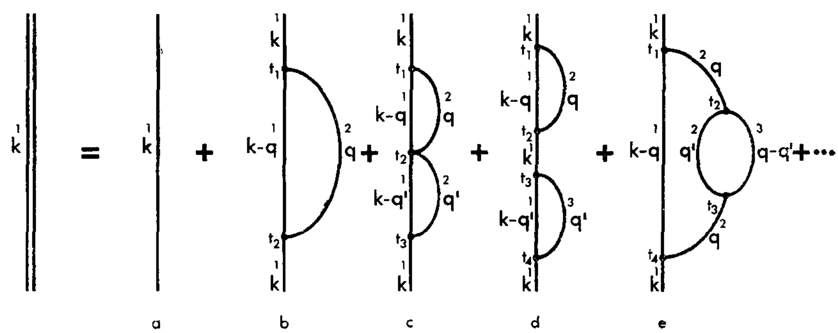

Fig. 1. Diagrammatic representation of the propagator $\Gamma_k^s(1, t)$. The representation of $\Gamma_k(i, t)$ is obtained by replacing 1 with i.

The kinetic theory mentioned above yields at low densities diagrammatic expansions of the same structure both for Γ^s and Γ drawn in fig. 1. The right-hand side of fig. 1 contains all diagrams which can be built up from dots and line segments such that: (i) each diagram can only contain vertices of type 1, 2 or 3 as is shown in fig. 2; (ii) no line segments, except one at the top and one at the bottom, have an open end; (iii) the dots are labelled as they occur from the top to the bottom by an ordered set of times t_1, t_2, ..., and ordered time integrations are performed from $t = 0$ up to t; (iv) each line segment is labelled by a wave number and a particle label; (v) the first and the last line segments occurring in each diagram have the same wave number and particle label as $\boldsymbol{\Gamma}^{\mathrm{s}}$ or $\boldsymbol{\Gamma}$; (vi) at each dot the sum of incoming and outgoing wave numbers is the same and one integrates over all wave vectors except $\boldsymbol{k}$, each with a weight factor $(2\pi)^{-3}$, (vii) at each dot the particle labels of the left incoming and left outgoing line segments are the sa me; (viii) at each dot with two incoming and two outgoing line segments also the right incoming and outgoing line segments have the same particle label; (ix) at each dot with one incoming and two outgoing line segments a new particle label j has to be introduced for the right outgoing line segment, and one integrates over the velocity $\boldsymbol{v}_j$ with a weight function $n\phi_0\,(v_j)$.

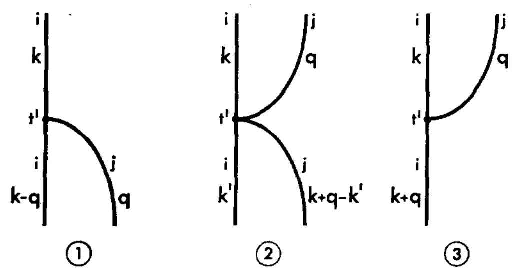

Fig. 2. Types of vertices which may occur in the diagrams representing $\boldsymbol{\Gamma}_k^{\mathrm{s}}$ and $\boldsymbol{\Gamma}_k$.

The rules how to read the diagrams are slightly different in the cases where fig. 1 represents the expansion of $\boldsymbol{\Gamma}^{\mathrm{s}}$ or $\boldsymbol{\Gamma}$. Let us first discuss the case that fig. 1 stands for the diagram expansion of $\boldsymbol{\Gamma}_k^{\mathrm{s}}(1, t)$: (a) reading a diagram from the bottom to the top one has to write down the corresponding expression from the right to the left; (b) each dot appearing at a vertex of type 1 or 2 represents the binary-collision operator T_0 defined as:

$$T_0\,(ij) = \sigma^2 \int_{\boldsymbol{v}_{ij}\cdot\hat{\boldsymbol{\sigma}}<0} \mathrm{d}\hat{\boldsymbol{\sigma}}\, |\boldsymbol{v}_{ij}\cdot\hat{\boldsymbol{\sigma}}|\, [b_{\hat{\sigma}}\,(ij) - 1], \tag{3.5}$$

where i and j are the particle labels occurring in the vertex, $\boldsymbol{v}_{ij} = \boldsymbol{v}_i - \boldsymbol{v}_j$, σ is the hard-sphere diameter, $\hat{\boldsymbol{\sigma}}$ is a unit vector and the operator $b_{\hat{\sigma}}\,(ij)$ replaces the velocities $\boldsymbol{v}_i$ and $\boldsymbol{v}_j$ by their values after a collision of the particles i and j, in which their centres are separated by the vector $\sigma\hat{\boldsymbol{\sigma}}$; (c) each dot appearing at a vertex of type 3 represents $T_0\,(ij)$ if i or j equals 1 (the label of the tagged particle) and represents $T_0\,(ij)\,(1 + P_{ij})$ in all other cases, where i and j are the particle labels occurring in the vertex and the permutation operator P_{ij} interchanges the labels of particles i and j; (d) each line segment labelled with wave number $\boldsymbol{q}$ and particle label i between dots labelled with times t_1 and t_2, respectively, represents either the Boltzmann propagator for the tagged particle $\Gamma_q^s(1, t_2 - t_1)$ if $i = 1$, or the Boltzmann propagator for a fluid particle $\Gamma_q(i, t_2 - t_1)$ in all other cases.

The Boltzmann propagators are defined as:

$$\Gamma_q^s(1, t) = \exp L_q^s(1)\, t, \tag{3.6a}$$

$$\Gamma_q(i, t) = \exp L_q(i)\, t, \tag{3.6b}$$

where:

$$L_q^s(1) = -\mathrm{i}\boldsymbol{q} \cdot \boldsymbol{v}_1 + n\Lambda^s(1), \tag{3.7a}$$

$$L_q(i) = -\mathrm{i}\boldsymbol{q} \cdot \boldsymbol{v}_i + n\Lambda(i). \tag{3.7b}$$

The Lorentz–Boltzmann operator for the self-motion of a tagged particle is defined as:

$$\Lambda^s(1) = \int \mathrm{d}\boldsymbol{v}_2\, \phi_0(v_2)\, T_0\,(1\,2). \tag{3.8a}$$

The Boltzmann operator describing the motion of the fluid is given by:

$$\Lambda(i) = \int \mathrm{d}\boldsymbol{v}_j\, \phi_0(v_j)\, T_0\,(i\,j)\,(1 + P_{ij}). \tag{3.8b}$$

Moreover if fig. 1 stands for the diagram expansion of $\boldsymbol{\Gamma}_k(i, t)$ with $i \neq 1$, the same four rules (a), (b), (c) and (d) are applicable except for the fact that the tagged-particle label 1 is forbidden everywhere in the diagrams.

In the diagrams used by Kawasaki and Oppenheim a fourth type of vertex [see (i) and fig. 2] is allowed, namely a single dot with one incoming line labelled $(i, \boldsymbol{k})$ and one outgoing line labelled $(i, \boldsymbol{k})$, representing the Lorentz–Boltzmann operator $\Lambda^s(1)$ if $i = 1$ or the Boltzmann operator $\Lambda(i)$ if $i \neq 1$. Furthermore, in Kawasaki and Oppenheim's paper, diagram rule (d) is changed in the sense that each line segment labelled $(i, \boldsymbol{q})$ represents a free-particle propagator

$$\exp\,[-\mathrm{i}\boldsymbol{q} \cdot \boldsymbol{v}_i\,(t_2 - t_1)].$$

The diagrams of Kawasaki and Oppenheim are immediately recovered from ours by expanding the Boltzmann propagators (3.6) in powers of Boltzmann collision operators (3.8) and free-particle propagators. Hence, our diagrams represent a further resummation of theirs.

The diagram expansion of fig. 1 can now explicitly be written down as:

$$\boldsymbol{\Gamma}_k^s(1, t) = \Gamma_k^s(1, t) + R_k^s(1, t) + \cdots, \tag{3.9a}$$

$$\boldsymbol{\Gamma}_k(i, t) = \Gamma_k(i, t) + R_k(i, t) + \cdots. \tag{3.9b}$$

The first term on the right-hand side is the translation of diagram 1a. The so-called ring propagator R^s (or R) is the translation of diagram 1b and is equal to:

$$R_k^s(1, t) = \int_0^t dt_1 \int_{t_1}^t dt_2 \int d\boldsymbol{q}\,(2\pi)^{-3} \int d\boldsymbol{v}_2\, n\phi_0(v_2)$$
$$\times\, \Gamma_k^s(1, t_1)\, T_0(1\,2)\, \Gamma_{k-q}^s(1, t_2 - t_1)\, \Gamma_q(2, t_2 - t_1)\, T_0(1\,2)\, \Gamma_k^s(1, t - t_2). \quad (3.10)$$

An analogous expression holds for $R_k(i, t)$. The operator corresponding to the diagram 1c is referred to as the repeated ring propagator.

Let us now study the propagators Γ^s and Γ, defined in (3.6), in more detail. If we define an inner product in the one-particle velocity space for any two functions of $\boldsymbol{v}_i$ as:

$$\langle f \mid g\rangle_i = \langle f^* g\rangle_i, \quad (3.11)$$

where the average is defined in (3.2) and where $i = 1$ refers to the tagged particle and $i \neq 1$ to a fluid particle, then $L_0^s(1) = n\Lambda^s(1)$ and $L_0(i) = n\Lambda(i)$ are hermitean operators, but $L_q^s(1)$ and $L_q(i)$ are clearly not for $q \neq 0$. We assume that in some q-region around $q = 0$ the operators L_q^s and L_q have a complete set of eigenfunctions labelled with λ and denoted by:

$$L_q^s(1)\, \varphi_q^{s,\lambda}(\boldsymbol{v}_1) = z_q^{s,\lambda} \varphi_q^{s,\lambda}(\boldsymbol{v}_1), \quad (3.12a)$$

$$L_q(i)\, \varphi_q^{\lambda}(\boldsymbol{v}_i) = z_q^{\lambda} \varphi_q^{\lambda}(\boldsymbol{v}_i), \quad (3.12b)$$

where the eigenvalues are denoted by z^λ and have a nonpositive real part. If $q = 0$ both spectra are real and nonpositive, some eigenvalues are zero and the gap between the zero eigenvalues and the first nonvanishing eigenvalue is of the order of the inverse mean free time (t_0^{-1})[21]. The operator $L_0^s(1)$ has only one eigenfunction with zero eigenvalue, the unit function; the operator $L_0(i)$ has five eigenfunctions with zero eigenvalue. They are the summational invariants 1, $\boldsymbol{v}_i$ and v_i^2.

Using ordinary perturbation theory, where q is used as the expansion parameter, one finds one eigenfunction of $L_q^s(1)$ with vanishing eigenvalue as q approaches zero. This eigenfunction is called the diffusion mode:

$$\varphi_q^s = 1 + iq\,(1/n\Lambda^s)\, \hat{\boldsymbol{q}} \cdot \boldsymbol{v}_1 + \mathcal{O}(q^2) \quad (3.13)$$

and the corresponding eigenvalue is

$$z_q^s = -Dq^2 + \mathcal{O}(q^4), \quad (3.14)$$

where the Boltzmann diffusion coefficient is given by:

$$D = \langle v_{1x}\,(-1/n\Lambda^s)\, v_{1x}\rangle_1. \quad (3.15)$$

From the fact that there is a gap of order t_0^{-1} in the spectrum of L_0^s it is clear that the concept of "diffusion mode" may only be used if $Dq^2t_0 \ll 1$, which will be sufficient for our purposes.

Using perturbation theory for degenerate eigenvalues one obtains five eigenfunctions of $L_q(i)$ with eigenvalues approaching zero as q goes to zero. These are the five hydrodynamic modes and corresponding hydrodynamic frequencies denoted by φ_q^j and z_q^j, respectively, where $j = 1, \dots, 5$. They are given in ref. 15.

We will need explicitly the two normalized shear modes ($j = 1, 2$) to first order in q:

$$\varphi_q^{\eta_j}(\boldsymbol{v}_i) = (\beta m)^{\frac{1}{2}} [\hat{\boldsymbol{q}}_\perp^{(j)} \cdot \boldsymbol{v}_i + \mathrm{i}q\,(1/n\Lambda)\,\hat{\boldsymbol{q}} \cdot \boldsymbol{v}_i \hat{\boldsymbol{q}}_\perp^{(j)} \cdot \boldsymbol{v}_i], \tag{3.16}$$

with the corresponding eigenvalue:

$$z_q^{\eta_j} = -\nu q^2 + \mathcal{O}(q^4) \qquad (j = 1, 2), \tag{3.17}$$

where $\hat{\boldsymbol{q}}_\perp^{(j)}$ are two orthogonal unit vectors perpendicular to $\boldsymbol{q}$, and the kinematic viscosity is $\nu = \eta/\varrho$, where η is the low-density limit of the shear viscosity (Boltzmann value). The hermitean-conjugate operators of L^s and L are given by:

$$L_q^{s\dagger}(1) = +\mathrm{i}\boldsymbol{q} \cdot \boldsymbol{v}_1 + n\Lambda^s(1), \tag{3.18a}$$

$$L_q^\dagger(i) = +\mathrm{i}\boldsymbol{q} \cdot \boldsymbol{v}_i + n\Lambda(i). \tag{3.18b}$$

They have eigenfunctions and eigenvalues denoted by $\tilde{\varphi}_q^{s,\lambda}$, $\tilde{z}_q^{s,\lambda}$ and $\tilde{\varphi}_q^\lambda$, $\tilde{z}_q^\lambda$, respectively.

Due to the fact that Λ^s and Λ are real and symmetric operators we have the properties:

$$\tilde{\varphi}_q^{s,\lambda} = \varphi_q^{s,\lambda*}, \qquad \tilde{z}_q^{s,\lambda} = z_q^{s,\lambda*}, \tag{3.19a}$$

$$\tilde{\varphi}_q^\lambda = \varphi_q^{\lambda*}, \qquad \tilde{z}_q^\lambda = z_q^{\lambda*}. \tag{3.19b}$$

Due to the fact that Λ^s and Λ are isotropic operators in $\boldsymbol{v}$ space $z_q^{s,\lambda*}$ and $z_q^{\lambda*}$ are eigenvalues of L_q^s and L_q, respectively, with eigenfunctions $\varphi_q^{s,\lambda*}(-\boldsymbol{v}_1)$ and $\varphi_q^{\lambda*}(-\boldsymbol{v}_i)$. The functions $\tilde{\varphi}_q^{s,\lambda}$ and $\varphi_q^{s,\lambda}$ form a biorthonormal set, *i.e.*, $\langle\tilde{\varphi}_q^{s,\lambda} \mid \varphi_q^{s,\lambda'}\rangle = \delta_{\lambda,\lambda'}$ and similarly for the functions $\tilde{\varphi}^\lambda$ and φ^λ. These biorthonormal sets can be used to decompose the propagators Γ^s and Γ into:

$$\Gamma_q^s(1, t) = |\varphi_q^s\rangle_1\, \mathrm{e}^{z_q^s t}\, \langle\tilde{\varphi}_q^s| + \sum_\lambda{}' |\varphi_q^{s,\lambda}\rangle_1\, \mathrm{e}^{z_q^{s,\lambda} t}\, \langle\tilde{\varphi}_q^{s,\lambda}|, \tag{3.20a}$$

$$\Gamma_q(i, t) = \sum_j |\varphi_q^j\rangle_i\, \mathrm{e}^{z_q^j t}\, \langle\tilde{\varphi}_q^j| + \sum_\lambda{}' |\varphi_q^\lambda\rangle_i\, \mathrm{e}^{z_q^\lambda t}\, \langle\tilde{\varphi}_q^\lambda|, \tag{3.20b}$$

where $j = 1, \ldots, 5$ and the prime on the summation sign indicates that λ runs over all eigenfunctions except the diffusion mode (3.20a) or the hydrodynamic modes (3.20b). On a time scale where t is measured in units t_0 and q is such that $Dq^2t_0 \ll 1$, the first term on the right-hand side of (3.20a) and (3.20b) is slowly decaying in time while the second term is fast damped. Therefore we define the projection operator on the diffusion mode as

$$P_q^s(1) = |\varphi_q^s\rangle_1 \langle\tilde{\varphi}_q^s| \tag{3.21a}$$

and the projection operator on the hydrodynamic modes as

$$P_q(i) = \sum_j |\varphi_q^j\rangle_i \langle\tilde{\varphi}_q^j|, \tag{3.21b}$$

where $j = 1, \ldots, 5$. These projection operators can be used to divide the propagators into a slowly decaying part ($P_q^s\Gamma_q^s$ and $P_q\Gamma_q$) and a fast decaying part [$(1 - P_q^s) \times \Gamma_q^s$ and $(1 - P_q)\,\Gamma_q$, respectively].

The operators $P^s\Gamma^s$ and $P\Gamma$ will be denoted in diagrammatic form as a dashed single straight vertical line (slow decay); the operators $(1 - P^s)\,\Gamma^s$ and $(1 - P)\,\Gamma$ are denoted by a dotted line (fast decay). Fig. 3 represents eq. (3.20) in diagrammatic form.

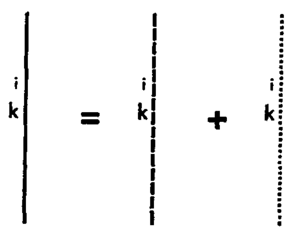

Fig. 3. Decomposition of the Boltzmann propagators into a slowly and a fast decaying part.

Since we are interested in long times it is sufficient for our purposes to replace the fast decaying parts of Γ^s and Γ by properly normalized δ functions in time, and so eq. (3.20a) may approximately be written as:

$$\Gamma_q^s(1, t) \simeq P_q^s(1)\,\mathrm{e}^{-Dq^2t} + [1 - P_q^s(1)]\,[\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{v}_1 - n\Lambda^s(1)]^{-1}\,\delta(t). \tag{3.22}$$

This becomes an exact relation if the limit $q \to 0$ is taken while Dq^2t is kept fixed [*i.e.*, time is measured in units $(Dq^2)^{-1}$].

As can be subsequently verified we only need the slowly decaying part of Γ and of this slow part we in fact need only the two shear modes to first order in q:

$$P_q(i)\,\Gamma_q(i, t) \simeq \sum_{j=1,2} |\varphi_q^{\eta_j}(\boldsymbol{v}_i)\rangle_i\,\mathrm{e}^{-\nu q^2 t}\,\langle\tilde{\varphi}_q^{\eta_j}(\boldsymbol{v}_i)|. \tag{3.23}$$

Because of the fact that the five hydrodynamic modes to zeroth order in q are linear combinations of the summational invariants 1, $\boldsymbol{v}$ and v^2 one has the useful property:

$$T_0\,(1\,2)\,[\varphi^j_{\boldsymbol{q}}(\boldsymbol{v}_1) + \varphi^j_{\boldsymbol{q}}(\boldsymbol{v}_2)] = 0. \tag{3.24}$$

From the definition of the Lorentz–Boltzmann operator given in (3.8a) and the fact that the diffusion mode equals 1 to lowest order in q it follows that:

$$\begin{aligned}\langle T_0\,(1\,2)\,\varphi^j_{\boldsymbol{q}}(\boldsymbol{v}_2)\,\varphi^{\mathrm{s}}_{-\boldsymbol{q}}(\boldsymbol{v}_1)\rangle_2 &= -\Lambda^{\mathrm{s}}(1)\,\varphi^j_{\boldsymbol{q}}(\boldsymbol{v}_1)\,\varphi^{\mathrm{s}}_{-\boldsymbol{q}}(\boldsymbol{v}_1),\\ \langle \varphi^j_{\boldsymbol{q}}(\boldsymbol{v}_2)\,\varphi^{\mathrm{s}}_{-\boldsymbol{q}}(\boldsymbol{v}_1)\,T_0\,(1\,2)\rangle_2 &= -\varphi^j_{\boldsymbol{q}}(\boldsymbol{v}_1)\,\varphi^{\mathrm{s}}_{-\boldsymbol{q}}(\boldsymbol{v}_1)\,\Lambda^{\mathrm{s}}(1),\end{aligned} \tag{3.25}$$

which holds if the modes are taken to lowest order in q. Let us now apply these results to the velocity autocorrelation function which, according to (1.16), (1.26), (1.29) and (3.1), can be written as

$$C_0(t) = \hat{C}_0(t) = \langle v_{1x}\boldsymbol{\Gamma}^{\mathrm{s}}_0\,(1, t)\,v_{1x}\rangle_1. \tag{3.26}$$

This function is represented in diagrammatic form by the left-hand side of fig. 4, where the two crosses stand for the two velocities and the double vertical line for $\boldsymbol{\Gamma}^{\mathrm{s}}_0$, according to fig. 1.

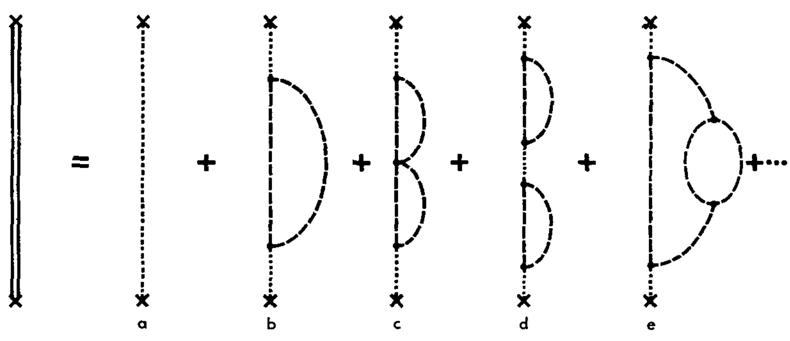

Fig. 4. Various contributions to the velocity autocorrelation function.

Following the expansion of fig. 1 or equivalently relation (3.9a) we obtain:

$$C_0(t) = C^{(\mathrm{B})}_0(t) + C^{(\mathrm{R})}_0(t) + \cdots, \tag{3.27}$$

where the Boltzmann contribution is given by:

$$C^{(\mathrm{B})}_0(t) = \langle v_{1x}\Gamma^{\mathrm{s}}_0\,(1, t)\,v_{1x}\rangle_1.$$

Using the fact that

$$P_0^s(1)\,|v_{1x}\rangle = 0, \qquad \langle v_{1x}|\,P_0^s(1) = 0, \tag{3.28}$$

it is seen directly that only the fast decaying part of $\Gamma_0^s(1, t)$ contributes. This is indicated in term (a) of fig. 4, where the decomposition of fig. 3 is applied. Using the approximation (3.22) and the definition for the diffusion coefficient (3.15) we obtain:

$$C_0^{(B)}(t) = D\delta(t). \tag{3.29}$$

The ring contribution to the velocity autocorrelation function is equal to:

$$C_0^{(R)}(t) = \langle v_{1x} R_0^s(1, t)\, v_{1x}\rangle_1,$$

where the ring propagator is given in (3.10). From the property (3.28) it is seen that only the fast decaying parts of $\Gamma_0^s(1, t_1)$ and $\Gamma_0^s(1, t - t_2)$ in (3.10) enter into the ring contribution. The long-time behaviour of $C_0^{(R)}(t)$ is obtained by inserting for $\Gamma_{-q}^s(1, t_2 - t_1)$ and $\Gamma_q(2, t_2 - t_1)$ their slowly decaying parts as is indicated in diagram (b) of fig. 4.

For $t \gg t_0$ one finds with the help of (3.22) and (3.23):

$$\begin{aligned} C_0^{(R)}(t) = \sum_{j=1,2} \int_0^t \mathrm{d}t_1 \int_{t_1}^t \mathrm{d}t_2 \int \mathrm{d}\boldsymbol{q}\, (2\pi)^{-3}\, \mathrm{e}^{-(D+\nu)q^2(t_2-t_1)} \\ \times \langle v_{1x}(1 - P_0^s)(-n\Lambda^s)^{-1}\,\delta(t_1)\, n\,\langle T_0(1\,2)\,\varphi_q^{\eta_j}(v_2)\,\varphi_{-q}^s(v_1)\rangle_2\rangle_1 \\ \times \langle\langle \varphi_q^{\eta_j}(v_2)\,\varphi_{-q}^s(v_1)\,T_0(1\,2)\rangle_2\,(1 - P_0^s)(-n\Lambda^s)^{-1}\,\delta(t - t_2)\,v_{1x}\rangle_1 . \end{aligned}$$

In this expression the functions $\tilde{\varphi}_q^\lambda$ do not appear since we have expressed the inner products directly in terms of averages using (3.11) and (3.19).

The modes may be taken to lowest order in q and so we can apply (3.25) to eliminate the T_0 and Λ^s operators.

By performing the time integrals we arrive at the relation:

$$C_0^{(R)}(t) = \sum_{j=1,2} n^{-1} \int \mathrm{d}\boldsymbol{q}\,(2\pi)^{-3}\,[\langle v_{1x}\varphi_q^{\eta_j}(v_1)\,\varphi_{-q}^s(v_1)\rangle_1]^2\,\mathrm{e}^{-(\nu+D)q^2t},$$

which is just the mode–mode coupling formula for $k = 0$ used in section 2, now obtained from kinetic theory. This derivation was first given by Dorfman and Cohen[3]).

From (3.13) and (3.16) the amplitude can be calculated in the $q \to 0$ limit:

$$\sum_{j=1,2} (\langle v_{1x}\varphi_q^{\eta_j}\varphi_{-q}^s\rangle_1)^2 = (\beta m)^{-1}(1 - \hat{q}_x^2), \tag{3.30}$$

where $\hat{q}_x$ is the x component of the unit vector $\hat{\boldsymbol{q}}$. By performing the q integration one finds for the dominant long-time tail in the velocity autocorrelation function for $t \gg t_0$:

$$C_0^{(\mathrm{R})}(t) = \frac{1}{12\pi^{3/2}\beta\varrho\,(D + \nu)^{3/2}}\,\frac{1}{t^{3/2}}, \tag{3.31}$$

which is the same result as (2.12b), but here D and ν are the Boltzmann (low-density) values of the diffusion- and kinematic-viscosity coefficients.

The contributions of diagrams c and d of fig. 4 to the velocity autocorrelation function are of the same order in time as the ring contribution ($t^{-3/2}$) but the coefficients are of higher order in the density and so they may consistently be neglected within the framework of this low-density kinetic theory.

The contribution to $C_0(t)$ describing the next order in time arises from diagram e in fig. 4, and reads

$$\begin{aligned} C_0^{(\mathrm{e})}(t) &= \int_0^t \mathrm{d}t_1 \int_{t_1}^t \mathrm{d}t_2 \int \mathrm{d}\boldsymbol{k}\,(2\pi)^{-3}\, n \\ &\times \langle v_{1x}\delta(t_1)\,(-n\Lambda^{\mathrm{s}})^{-1}\,\langle T_0\,(1\,2)|\,\varphi^{\mathrm{s}}_{-k}(\boldsymbol{v}_1)\rangle_1\, \mathrm{e}^{-Dk^2(t_2-t_1)} \\ &\times \langle\tilde{\varphi}^{\mathrm{s}}_{-k}(v_1)\,|\,\bar{\Gamma}_k\,(2, t_2 - t_1)\,T_0\,(1\,2)\rangle_2 \\ &\times \delta(t - t_2)\,(-n\Lambda^{\mathrm{s}})^{-1}\,v_{1x}\rangle_1. \end{aligned} \tag{3.32}$$

The slow propagator $\bar{\Gamma}_k\,(2, t)$ is given in Laplace language as

$$\begin{aligned} \bar{\Gamma}_{kz}(2) &= \sum_i |\varphi_k^{\eta_i}(\boldsymbol{v}_2)\rangle_2\,(z + \nu k^2)^{-1}\,\langle\tilde{\varphi}_k^{\eta_i}(\boldsymbol{v}_2)| \\ &\times \sum_{\lambda,\mu}\int \mathrm{d}\boldsymbol{q}\,(2\pi)^{-3}\,(z - z_q^\lambda - z_l^\mu)^{-1}\, n \\ &\times \langle T_0\,(2\,3)\,\varphi_q^\lambda(\boldsymbol{v}_2)\,\varphi_l^\mu(\boldsymbol{v}_3)\rangle_2\rangle_3 \\ &\times \langle\langle\varphi_q^\lambda(\boldsymbol{v}_2)\,\varphi_l^\mu(\boldsymbol{v}_3)\,T_0\,(2\,3)\,(1 + P_{23})\rangle_3 \\ &\times \sum_j |\varphi_k^{\eta_j}(v_2)\rangle_2\,(z + \nu k^2)^{-1}\,\langle\tilde{\varphi}_k^{\eta_j}(v_2)|, \end{aligned} \tag{3.33}$$

where $\boldsymbol{l} = \boldsymbol{k} - \boldsymbol{q}$, the indices i and j run over the shear modes and λ and μ run over all five hydrodynamic modes of (3.12b). By using relations similar to (3.25), for the full Boltzmann operator, as given by Ernst and Dorfman[17]), eq. (3.33) can be written as

$$\begin{aligned} \bar{\Gamma}_{kz}(2) &= \sum_{i,j} |\varphi_k^{\eta_i}(\boldsymbol{v}_2)\rangle_2\,(z + \nu k^2)^{-1}\,\tfrac{1}{2}n\sum_{\lambda,\mu}\int \mathrm{d}\boldsymbol{q}\,(2\pi)^{-3}\,(z - z_q^\lambda - z_l^\mu)^{-1} \\ &\times \langle\varphi_k^{\eta_i}\Lambda\varphi_q^\lambda\varphi_l^\mu\rangle_2\,\langle\varphi_q^\lambda\varphi_l^\mu\Lambda\varphi_k^{\eta_j}\rangle_2\,(z + \nu k^2)^{-1}\,\langle\tilde{\varphi}_k^{\eta_j}(\boldsymbol{v}_2)|. \end{aligned} \tag{3.34}$$

The averages in (3.34) can be evaluated directly by means of (3.16), yielding

$$\langle \varphi_q^\lambda \varphi_l^\mu A \varphi_k^{\eta_j} \rangle_2 = ikn^{-1} A_{\eta_j}^{\lambda\mu}(\hat{q}, \hat{l}), \tag{3.35}$$

where $A_{\eta_j}^{\lambda\mu}(\hat{q}, \hat{l})$ is a two-mode amplitude introduced by Ernst and Dorfman as

$$A_{\eta_j}^{\lambda\mu}(\hat{q}, \hat{l}) = (\beta m)^{\frac{1}{2}} \langle \varphi_q^\lambda \varphi_l^\mu \hat{k} \cdot v_2 \hat{k}_\perp^{(j)} \cdot v_2 \rangle_2 . \tag{3.36}$$

Eq. (3.34) reduces now to

$$\bar{\Gamma}_{kz}(2) = -k^2 \sum_i |\varphi_k^{\eta_i}(v_2)\rangle_2 (z + \nu k^2)^{-2} \langle \tilde{\varphi}_k^{\eta_i}(v_2)| \times \left((1/2n) \sum_{\lambda,\mu} \int \mathrm{d}q\, (2\pi)^{-3} \,|\, A_{\eta_i}^{\lambda\mu}(\hat{q}, \hat{l}) \,|^2 (z - z_q^\lambda - z_l^\mu)^{-1}\right). \tag{3.37}$$

The contributions to $\bar{\Gamma}_k(2, t)$ come mainly from z values around $z \approx -\nu k^2$. In the factor in large parentheses $(\cdots)$ on the second line of (3.37) we may therefore replace z by $-\nu k^2$. The resulting expression has been calculated by Ernst and Dorfman, who have shown that only two opposite sound modes contribute. The result is

$$(\cdots) = a - \Delta_\eta(1)\, k^{\frac{1}{2}}, \tag{3.38}$$

where a is some constant, and

$$\Delta_\eta(1) = (1/77\pi\, 2^{\frac{1}{2}})\, (c^{\frac{1}{2}}/\beta\varrho \Gamma_s^{3/2}). \tag{3.39}$$

Here, c is the adiabatic sound velocity and Γ_s the sound-damping constant in the low-density limit. The constant a appearing on the right-hand side of (3.38) is a higher-density correction to the ring diagram in fig. 4b, which replaces ν in (3.31) by $\nu + a$, and it should be neglected since we restrict ourselves consistently to lowest order in the density.

Inversion of the Laplace transform in (3.37) yields

$$\bar{\Gamma}_k(2, t) \simeq \mathrm{e}^{-\nu k^2 t} \Delta_\eta(1)\, k^2 t \sum_i |\varphi_k^{\eta_i}\rangle_2 \langle \tilde{\varphi}_k^{\eta_i}| . \tag{3.40}$$

Inserting this result in (3.32) and carrying out the remaining integrations yields finally

$$C_0^{(e)}(t) \simeq \frac{\Delta_\eta(1)\, \Gamma(11/4)}{6\pi^2 \beta\varrho\, (D + \nu)^{11/4}} \frac{1}{t^{7/4}}, \tag{3.41}$$

where $\Gamma(x)$ is the gamma function.

As the next order terms one finds contributions proportional to $t^{-2+2^{-n}}$ with $n = 3, 4, \ldots$. This result was first obtained by Pomeau[22]), from hydrodynamic considerations. The time-dependent diffusion coefficient $D_0(t)$ defined in (1.19) can be calculated from the results obtained so far: (3.29), (3.31) and (3.41).

The limiting value $\lim_{t\to\infty} D_0(t)$ may be approximated by the Boltzmann diffusion coefficient obtained as the time integral over $C_0^{(B)}(t)$; all other contributions may be neglected since they are of higher order in the density. The leading deviation from that limiting value for long times arises from the contribution $C_0^{(R)}(t)$, and so one finds the same long-time behaviour for $D_0(t)$ as followed from the phenomenological mode–mode coupling theory, given in (2.14), provided one replaces D and ν by their low-density values.

In the next section the behaviour of the super-Burnett coefficient $D_2(t)$ will be derived from the kinetic theory of hard spheres in the low-density limit. The main reason for doing this is that we want to check the predictions from the mode–mode theory against the results of kinetic theory. Of course Dorfman and Cohen[3]) have already shown that the result (2.12b) for the long-time tail of the velocity correlation function obtained from the mode–mode theory agrees with the result (3.31) from kinetic theory. Their comparison deals only with the mode–mode formula (2.1) in the limit as $k \to 0$. Here, however, we have calculated eq. (2.1) to $\mathcal{O}(k^2)$, and in section 4 we will show that this result agrees with the result from kinetic theory.

4. *Super-Burnett coefficient from kinetic theory.* Our main goal is now to find the super-Burnett coefficient $D_2(t)$, defined in (1.20) from kinetic theory. In order to do so we have to adapt the kinetic theory of section 3 to the calculation of the 4-point correlation function which contributes to $D_2(t)$ a term $E(t)$ defined by

$$E(t) = \int_0^t \mathrm{d}t_1 \int_{t_1}^t \mathrm{d}t_2 \int_{t_2}^t \mathrm{d}t_3 \, \langle v_{1x} v_{1x}(t_1)\, v_{1x}(t_2)\, v_{1x}(t_3)\rangle, \tag{4.1}$$

so that:

$$D_2(t) = E(t) - E_1(t) - E_2(t) - E_3(t). \tag{4.2}$$

The functions $E_i(t)$ $(i = 1, 2, 3)$ are defined in (2.15) and have in fact been calculated in (2.16), provided one replaces D and ν by their low-density values. In fact one should add terms of order $t^{\frac{1}{4}}$, $t^{1/8}$, ... to $E_1(t)$ and $E_3(t)$ which arise from $C_0^{(e)}(t)$ in (3.41) and higher-order contributions to the velocity autocorrelation function.

The function $E(t)$ can be calculated from the same kinetic theory as used in section 3 with some modifications. They can simply be stated as follows. 1) $E(t)$ is represented by the set of all labelled diagrams which can be obtained by attaching four crosses to the tagged-particle line of each diagram occurring in the expansion of $\Gamma_0^{s}(1, t_3)$ drawn in fig. 1: one cross at the top, $t = 0$, one cross at the bottom, t_3, and two crosses at intermediate levels, labelled with times t_1 and t_2.

2) One has to perform time-ordered integrations from 0 to t over t_1, t_2, t_3 and the times corresponding to the dots. 3) Each cross represents the tagged-particle velocity v_{1x} and one integrates over $\boldsymbol{v}_1$ with a weight function $\phi_0(v_1)$. 4) Furthermore the diagrams have to be read according to the rules (a), (b), (c) and (d) given in section 3, where a cross is equivalent to a dot as far as rule (d) is concerned.

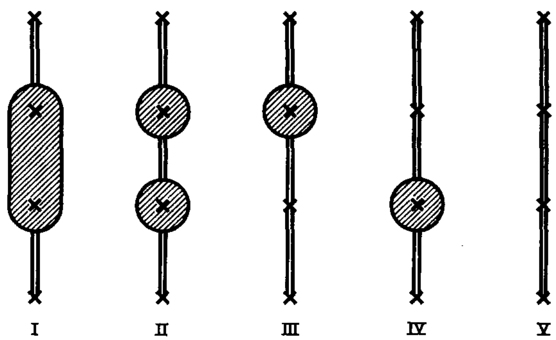

Fig. 5. Classes of diagrams contributing to the super-Burnett coefficient.

Eventually one may resum diagrams according to the expansion of fig. 1. The diagrams contributing to $E(t)$ are divided into five classes (I, ..., V), drawn schematically in fig. 5. The double straight line is the full propagator $\Gamma_0^s(1, t')$ and the bubbles stand for the sum of all diagrams with one or two crosses in their interior, as indicated. All diagrams of class V together give a contribution to $E(t)$ equal to:

$$E_{(\mathrm{V})}(t) = \int_0^t \mathrm{d}t_1 \int_{t_1}^t \mathrm{d}t_2 \int_{t_2}^t \mathrm{d}t_3$$
$$\langle v_{1x}\Gamma_0^s(1, t_1)\, v_{1x}\Gamma_0^s(1, t_2 - t_1)\, v_{1x}\Gamma_0^s(1, t_3 - t_2)\, v_{1x}\rangle_1 . \tag{4.3}$$

Let us first derive some useful properties of the full propagator Γ_0^s from the kinetic theory of section 3. From the fact that the operator $T_0\,(ij)$ acting on the unit function gives zero we find from (3.6a), (3.7a), (3.8a), (3.13) and (3.21a):

$$P_0^s(1)\, \Gamma_0^s(1, t') = P_0^s(1); \qquad \Gamma_0^s(1, t')\, P_0^s(1) = P_0^s(1). \tag{4.4}$$

If we apply this property to the ring propagator we find from (3.10):

$$P_0^s(1)\, R_0^s(1, t') = 0; \qquad R_0^s(1, t')\, P_0^s(1) = 0. \tag{4.5}$$

The orthogonal part of the Boltzmann propagator, $(1 - P_0^s)\,\Gamma_0^s$, decays exponentially in time as is indicated in (3.20a). The orthogonal part of the ring propagator can be estimated from the result (3.31) to be of the order of

$$R_0^s(1, t') \approx f(t')\,(1 - P_0^s)\, U(1)\,(1 - P_0^s), \tag{4.6}$$

where $f(t)$ is some bounded function of time with a leading asymptotic behaviour for large t proportional to $t^{-3/2}$ and $U(1)$ is some regular time-independent operator in one-particle space. All the other operators occurring in the expansion of Γ_0^s have the same property (4.5) and decay also at least proportional to $t^{-3/2}$ as follows from the result (3.41).

Clearly the unit function is an exact eigenfunction of the full propagator with eigenvalue 1 and we can find a decomposition of Γ_0^s into a projected and an orthogonal part:

$$\Gamma_0^s = P_0^s\Gamma_0^s + (1 - P_0^s)\,\Gamma_0^s\,(1 - P_0^s), \tag{4.7}$$

$$P_0^s\Gamma_0^s = P_0^s; \qquad \Gamma_0^s P_0^s = P_0^s. \tag{4.8}$$

The orthogonal part of Γ_0^s may be estimated by:

$$(1 - P_0^s)\,\Gamma_0^s\,(1, t') \approx f(t')\,(1 - P_0^s)\,U(1)\,(1 - P_0^s), \tag{4.9}$$

where $f(t)$ and $U(1)$ have the same meaning as in (4.6). Applying the decomposition (4.7) to the full propagators occurring in the expression (4.3) for $E_{(V)}(t)$, and using the property (3.28), one finds that the first and the last propagator may be replaced by their orthogonal parts. If one takes the projected part of $\Gamma_0^s\,(1, t_2 - t_1)$ one finds a contribution to $E_{(V)}(t)$ equal to:

$$E_{(V,1)}(t) = \int_0^t dt_1 \int_{t_1}^t dt_2 \int_{t_2}^t dt_3\; C_0(t_1)\,C_0\,(t_3 - t_2), \tag{4.10}$$

which is by itself the most important contribution to $E(t)$, but in the calculation of $D_2(t)$, according to (4.2), it is just cancelled by $E_1(t)$ as follows from the definition (2.15a). If one takes the orthogonal part of $\Gamma_0^s\,(1, t_2 - t_1)$ and uses (4.9) one finds a contribution to $E_{(V)}(t)$ of the order of

$$E_{(V,2)}(t) \approx \int_0^t dt_1 \int_{t_1}^t dt_2 \int_{t_2}^t dt_3\, f(t_1) f(t_2 - t_1) f(t_3 - t_2), \tag{4.11}$$

which is finite as t approaches infinity, as can be seen easily by taking the Laplace transform of this expression. We conclude therefore that only those diagrams of class V which are contained in subclass (V, 1) give a divergent contribution to $E(t)$ equal to (4.10).

Let us now pass on to class IV. The sum of all diagrams of class IV is equal to:

$$E_{(IV)}(t) = \int_0^t dt_1 \int_{t_1}^t dt_2 \int_{t_2}^t dt_3 \int_{t_3}^t dt_4$$

$$\langle v_{1x}\Gamma_0^s\,(t_1)\, v_{1x}\,\Gamma_0^s\,(t_2 - t_1)\, B_0^s\,(t_3 - t_2)\,\Gamma_0^s\,(t_4 - t_3)\, v_{1x}\rangle_1, \tag{4.12}$$

where the operator $\boldsymbol{B}_0^s$, acting on functions of $\boldsymbol{v}_1$ only, represents the bubble containing one cross in fig. 5 IV. The series expansion of this bubble operator gives a decomposition of class IV into subclasses IVA, IVB, ... as drawn in fig. 6. Note that all external propagators and $\boldsymbol{B}_0^s$ in the expression (4.12) may be replaced by

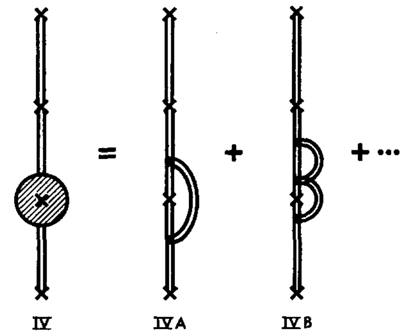

Fig. 6. Decomposition of class IV into subclasses.

their orthogonal parts because of the property (3.28) and the fact that $\boldsymbol{B}_0^s$ always starts and ends with the operator T_0 (1 2). The sum of all diagrams of subclass IVA is equal to $E_{(\mathrm{IV\,A})}(t)$ given by the same expression as (4.12) if $\boldsymbol{B}_0^s\,(t_3 - t_2)$ is replaced by:

$$\boldsymbol{B}_{(\mathrm{A})}^s\,(t_3 - t_2) = \int_{t_2}^{t_3} \mathrm{d}t_2' \int \mathrm{d}\boldsymbol{q}\,(2\pi)^{-3}\, n\, \langle T_0\,(1\,2)\,\boldsymbol{\Gamma}_{-\boldsymbol{q}}\,(2, t_3 - t_2)$$

$$\times\, \boldsymbol{\Gamma}_{\boldsymbol{q}}^s\,(1, t_2' - t_2)\, v_{1x} \boldsymbol{\Gamma}_{\boldsymbol{q}}^s\,(1, t_3 - t_2')\, T_0\,(1\,2)\rangle_2 . \qquad (4.13)$$

If we insert in this expression the Boltzmann propagators Γ_{-q} and Γ_q^s instead of the full propagators we obtain the kinetic operator $B_{(A)}^s\,(t_3 - t_2)$ drawn in fig. 7. The self propagators occurring in $B_{(\mathrm{A})}^s$ can be decomposed into a slowly and a fast decaying part, following fig. 3, as indicated in fig. 7, so that $B_{(\mathrm{A})}^s$ falls apart into 4 terms, which are now estimated.

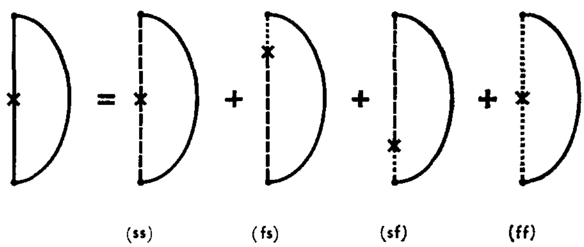

Fig. 7. Decomposition of the operator $B_{(A)}^s(t)$ occurring in diagrams of subclass IV A.

If for both self propagators the slow decay is taken and the lowest-order result (3.23) is used for the propagator of the fluid particle, we find:

$$B^{\mathrm{s}}_{(\mathrm{A},\,\mathrm{ss})}(t_3 - t_2) = \int_{t_2}^{t_3} \mathrm{d}t_2' \int \mathrm{d}\boldsymbol{q}\,(2\pi)^{-3}$$
$$\times \sum_{j=1,2} \mathrm{e}^{-(\nu+D)q^2(t_3-t_2)}\, n\,\langle T_0(1\,2)\,\varphi^{\mathrm{s}}_{\boldsymbol{q}}(\boldsymbol{v}_1)\,\varphi^{\eta_j}_{-\boldsymbol{q}}(\boldsymbol{v}_2)\rangle_1\rangle_2$$
$$\times \langle \varphi^{\mathrm{s}}_{\boldsymbol{q}}(\boldsymbol{v}_1)\, v_{1x}\varphi^{\mathrm{s}}_{\boldsymbol{q}}(\boldsymbol{v}_1)\rangle_1 \,\langle\langle \varphi^{\mathrm{s}}_{\boldsymbol{q}}(\boldsymbol{v}_1)\,\varphi^{\eta_j}_{-\boldsymbol{q}}(\boldsymbol{v}_2)\, T_0(1\,2)\rangle_2, \quad (4.14)$$

where from (3.13), (3.15) and (3.19a) it follows that

$$\langle \varphi^{\mathrm{s}}_{\boldsymbol{q}}(\boldsymbol{v}_1)\, v_{1x}\varphi^{\mathrm{s}}_{\boldsymbol{q}}(\boldsymbol{v}_1)\rangle_1 = -2\mathrm{i}q_x D + \mathcal{O}(q^2). \quad (4.15)$$

So, at least one extra factor of order q enters the $\boldsymbol{q}$ integration, which will give an extra factor $(t_3 - t_2)^{-\frac{1}{2}}$ if the q integral is performed.

The other matrix elements of (4.14) are at most equal to a constant if $\boldsymbol{q}$ approaches zero, and so we estimate the kinetic operator $B^{\mathrm{s}}_{(\mathrm{A},\,\mathrm{ss})}$ by performing the integrals over t_2' and $\boldsymbol{q}$ with the result:

$$B^{\mathrm{s}}_{(\mathrm{A},\,\mathrm{ss})}(t_3 - t_2) \approx g\,(t_3 - t_2)\,(1 - P^{\mathrm{s}}_0)\,U'(1)\,(1 - P^{\mathrm{s}}_0), \quad (4.16)$$

where $g(t)$ is a bounded function of time with a leading asymptotic behaviour for large t at most proportional to t^{-1}, and $U'(1)$ is some regular time-independent operator in one particle space.

The same arguments can be applied to the operator $B^{\mathrm{s}}_{(\mathrm{A},\,\mathrm{fs})}(t_3 - t_2)$ occurring in fig. 7. In that case no extra factor q enters the $\boldsymbol{q}$ integration but there is a $\delta(t_2' - t_2)$ involved in the t_2' integral, and therefore we may estimate:

$$B^{\mathrm{s}}_{(\mathrm{A},\,\mathrm{fs})}(t_3 - t_2) \approx f(t_3 - t_2)\,(1 - P^{\mathrm{s}}_0)\,U''(1)\,(1 - P^{\mathrm{s}}_0), \quad (4.17)$$

where $f(t)$ and $U''(1)$ are taken in the sense of (4.6). It is clear that the same estimate holds for the operator $B^{\mathrm{s}}_{(\mathrm{A},\,\mathrm{sf})}(t_3 - t_2)$ occurring in fig. 7.

The last operator of this set of four satisfies:

$$B^{\mathrm{s}}_{(\mathrm{A},\,\mathrm{ff})}(t_3 - t_2) \approx \delta\,(t_3 - t_2)\,(1 - P^{\mathrm{s}}_0)\,U''(1)\,(1 - P^{\mathrm{s}}_0)$$

and therefore we conclude that the leading behaviour for long times of the operator $B^{\mathrm{s}}_{(\mathrm{A})}$ arises from the contribution $B^{\mathrm{s}}_{(\mathrm{A},\,\mathrm{ss})}$ given in (4.14) and (4.16).

We can dress the Boltzmann propagators in fig. 7 with ring propagators, repeated ring propagators and so on, according to fig. 1, to obtain an estimate of the full $\boldsymbol{B}^{\mathrm{s}}_{(\mathrm{A})}$ operator and we find that $B^{\mathrm{s}}_{(\mathrm{A},\,\mathrm{ss})}$ still describes the leading time behaviour of $\boldsymbol{B}^{s}_{(A)}$. Applying the same procedure to the operators $\boldsymbol{B}^{s}_{(B)}$, ... occurring in fig. 6, one finds an estimate for the complete bubble operator with one cross:

$$\boldsymbol{B}^{s}_{0}(t_3 - t_2) \approx g(t_3 - t_2)(1 - P^{s}_{0})\, U'(1)(1 - P^{s}_{0}), \tag{4.18}$$

where $g(t)$ and $U'(1)$ are taken in the sense of (4.16). The leading time behaviour of the bubble operator arises completely from the operator $B^{s}_{(A,\,ss)}$ given in (4.14). From this result we can estimate the sum of all diagrams of class IV. Using (4.9), (4.12) and (4.18) we obtain:

$$E_{(IV)}(t) \approx \int_0^t \mathrm{d}t_1 \cdots \int_{t_3}^t \mathrm{d}t_4 f(t_1) f(t_2 - t_1)\, g(t_3 - t_2) f(t_4 - t_3).$$

From the Laplace transform of this expression one derives immediately that the dominant behaviour is at most

$$E_{(IV)}(t) \approx \log t, \tag{4.19}$$

which is our final result for class IV.
It is clear from fig. 5 that the same estimate holds for the sum of all diagrams of class III:

$$E_{(III)}(t) \approx \log t. \tag{4.20}$$

The sum of all diagrams of class II give a contribution to $E(t)$ equal to:

$$E_{(II)}(t) = \int_0^t \mathrm{d}t_1 \cdots \int_{t_4}^t \mathrm{d}t_5 \langle v_{1x} \boldsymbol{\Gamma}^{s}_{0}(t_1) \boldsymbol{B}^{s}_{0}(t_2 - t_1)$$

$$\times\, \boldsymbol{\Gamma}^{s}_{0}(t_3 - t_2) \boldsymbol{B}^{s}_{0}(t_4 - t_3) \boldsymbol{\Gamma}^{s}_{0}(t_5 - t_4)\, v_{1x} \rangle_1 .$$

All operators occurring in this expression may be replaced by their orthogonal parts and the estimates (4.9) and (4.18) may be applied:

$$E_{(II)}(t) \approx \int_0^t \mathrm{d}t_1 \cdots \int_{t_4}^t \mathrm{d}t_5 f(t_1)\, g(t_2 - t_1) f(t_3 - t_2)\, g(t_4 - t_3) f(t_5 - t_4),$$

and we obtain the final result for class II:

$$E_{(II)}(t) \approx (\log t)^2. \tag{4.21}$$

The set of diagrams belonging to class I may be decomposed into subclasses IA, IB, ... according to fig. 8. Let us first consider diagram IA.1 of class IA given in fig. 9 where all full propagators are replaced by their Boltzmann equivalents. Diagram IA.1 gives a contribution to $E(t)$ equal to:

$$E_{(\mathrm{IA.1})}(t) = \int_0^t \mathrm{d}t_1 \cdots \int_{t_4}^t \mathrm{d}t_5 \int \mathrm{d}\boldsymbol{q}\,(2\pi)^{-3}\,n$$

$$\times \langle v_{1x} \Gamma_0^{\mathrm{s}}(t_1) \langle T_0(1\,2)\,\Gamma_{-q}(2, t_4 - t_1)\,\Gamma_q^{\mathrm{s}}(t_2 - t_1)\,v_{1x}$$

$$\times \Gamma_q^{\mathrm{s}}(t_3 - t_2)\,v_{1x}\Gamma_q^{\mathrm{s}}(t_4 - t_3)\,T_0(1\,2)\rangle_2\,\Gamma_0^{\mathrm{s}}(t_5 - t_4)\,v_{1x}\rangle_1\,. \tag{4.22}$$

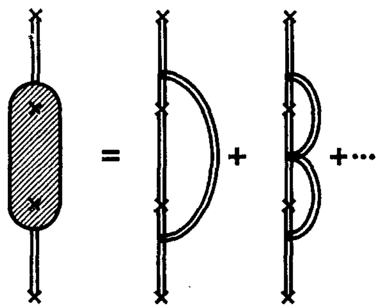

Fig. 8. Decomposition of class I into subclasses.

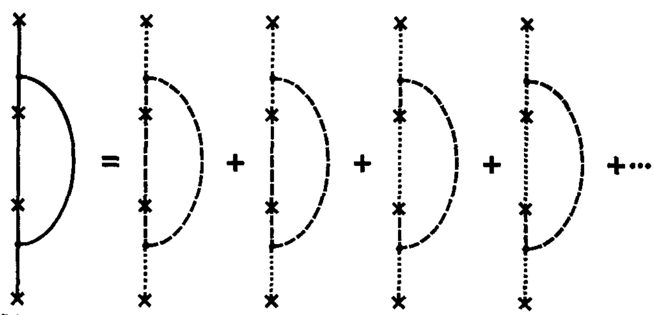

Fig. 9. Decomposition of the diagram IA.1, belonging to subclass IA and defined in (4.22).

The Boltzmann self propagators are again decomposed into a slow and a fast part and we obtain 8 contributions to $E_{(\mathrm{IA.1})}(t)$ as indicated in fig. 9. Note that the first and last propagators in each diagram are always fast decaying. Since we are interested in long times, the slow part of the propagator of the fluid particle is taken according to (3.23). Let us calculate the first of those 8 contributions using (3.22):

$$E_{(\mathrm{IA.\,1sss})}(t) = \int_0^t \mathrm{d}t_1 \cdots \int_{t_4}^t \mathrm{d}t_5 \int \mathrm{d}\boldsymbol{q}\,(2\pi)^{-3}$$

$$\times \sum_{j=1,2} \mathrm{e}^{-(\nu+D)q^2(t_4-t_1)}\, n\,\langle v_{1x}\delta(t_1)\,(-n\Lambda^{\mathrm{s}})^{-1}$$

$$\times \langle T_0(1\,2)\,\varphi^{\eta_j}_{-\boldsymbol{q}}(\boldsymbol{v}_2)\,\varphi^{\mathrm{s}}_{\boldsymbol{q}}(\boldsymbol{v}_1)\rangle_2\rangle_1\,(\langle\varphi^{\mathrm{s}}_{\boldsymbol{q}} v_{1x}\varphi^{\mathrm{s}}_{\boldsymbol{q}}\rangle_1)^2$$

$$\times \langle\langle\varphi^{\eta_j}_{-\boldsymbol{q}}(\boldsymbol{v}_2)\,\varphi^{\mathrm{s}}_{\boldsymbol{q}}(\boldsymbol{v}_1)\,T_0(1\,2)\rangle_2\,(-n\Lambda^{\mathrm{s}})^{-1}\,\delta(t_5-t_4)\,v_{1x}\rangle_1\,. \tag{4.23}$$

All matrix elements are known to their lowest nonvanishing order in q from (3.25), (3.30) and (4.15), and after performing all integrals we find for large times the result:

$$E_{(\mathrm{IA.\,1sss})}(t) = [-D^2/10\beta\varrho\pi^{3/2}(\nu + D)^{5/2}]\,t^{\frac{1}{2}} + \mathcal{O}(1). \tag{4.24}$$

In order to obtain this expression we needed $(\langle\varphi^{\mathrm{s}}_{\boldsymbol{q}} v_{1x}\varphi^{\mathrm{s}}_{\boldsymbol{q}}\rangle)^2$ as calculated in (4.15). Note that this square has a negative sign. Eq. (4.24) is the only contribution to the dominant long-time behaviour of the super-Burnett coefficient involving the first correction term to the diffusive mode (3.13). The matrix elements in (4.23) need not be taken to higher order in q, since extra factors q in the q integral give rise to extra factors $t^{-\frac{1}{2}}$ in the result.

Next we estimate the contribution (fss) to the diagram IA.1 occurring in fig. 9. In that case three δ functions of time are present and an extra factor q_x enters the q integral, coming from the matrix element $\langle\varphi^{\mathrm{s}}_{\boldsymbol{q}} v_{1x}\varphi^{\mathrm{s}}_{\boldsymbol{q}}\rangle_1$, and therefore:

$$E_{(\mathrm{IA.\,1fss})}(t) \approx \int_0^t \mathrm{d}t_1 \cdots \int_{t_4}^t \mathrm{d}t_5\,\delta(t_1)\,\delta(t_2-t_1)\,h(t_4-t_1)\,\delta(t_5-t_4),$$

where $h(t)$ is some bounded function of time with a leading asymptotic behaviour smaller than t^{-2} for large t. A straightforward estimate would lead to an asymptotic behaviour proportional to t^{-2}, but the coefficient of this term vanishes on performing the angular $\hat{\boldsymbol{q}}$ integration. Consequently

$$E_{(\mathrm{IA.\,1fss})}(t) = \mathcal{O}(1). \tag{4.25}$$

The same arguments may be applied to the contribution (ssf) yielding the same result. The contributions (ffs), (fsf), (sff) and (fff) drawn in fig. 9 involve at least four δ functions of time in the fivefold time integration given in (4.22) and are hence easily estimated to be finite for large t.

So we are left with the contribution (sfs) which reads

$$E_{(\mathrm{IA.\,1sfs})}(t) = \int_0^t \mathrm{d}t_1 \cdots \int_{t_4}^t \mathrm{d}t_5 \sum_{j=1,2} \int \mathrm{d}\boldsymbol{q}\,(2\pi)^{-3}$$

$$\times\, n^{-1}\, \mathrm{e}^{-(\nu+D)q^2(t_4-t_1)}\, \delta(t_1)\, \delta(t_3-t_2)\, \delta(t_5-t_4)$$

$$\times\, [\langle v_{1x}\varphi^{\mathrm{s}}_{\boldsymbol{q}}(\boldsymbol{v}_1)\, \varphi^{\eta_j}_{-\boldsymbol{q}}(\boldsymbol{v}_1)\rangle_1]^2\, \langle \varphi^{\mathrm{s}}_{\boldsymbol{q}} v_{1x}(1-P^{\mathrm{s}}_{\boldsymbol{q}})(-n\Lambda^{\mathrm{s}})^{-1}\, v_{1x}\varphi^{\mathrm{s}}_{\boldsymbol{q}}\rangle_1 .$$

The last matrix element equals D in the limit $q \to 0$, as follows from (3.15), the remaining one is given in (3.30), and so we find:

$$E_{(\mathrm{IA.1sfs})}(t) = [D/6\pi^{3/2}\beta\varrho\,(D+\nu)^{3/2}]\, t^{\frac{1}{2}} + \mathcal{O}(1). \tag{4.26}$$

This contribution to $D_2(t)$ in (4.2) cancels exactly the leading divergence in $E_3(t)$, as can be seen from the expression (2.16c) for $E_3(t)$.

So far we have studied completely the first diagram of class IA, drawn in fig. 9 and we have found two leading contributions to $E(t)$, which diverge as $t^{\frac{1}{2}}$. Further diagrams of class IA can be obtained by replacing the Γ^{s} operators in (4.22) by ring propagators, R^{s}, according to fig. 1. This will give no contributions to $E(t)$ of orders larger then log t.

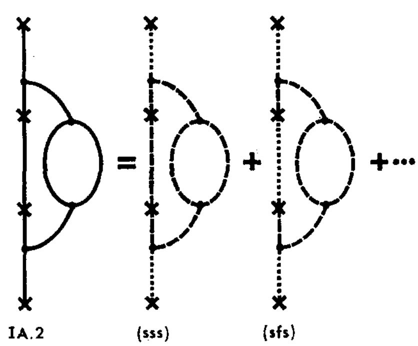

Fig. 10. Decomposition of the diagram IA.2, belonging to subclass IA.

More important contributions are obtained from diagram IA.2 drawn in fig. 10. The calculation of $E_{(\mathrm{IA.2sss})}(t)$, where in the side branch one shear mode, two opposite sound modes and one shear mode have to be taken from top to bottom, is rather lengthy but very similar to the calculation of $C_0^{(\mathrm{e})}(t)$ indicated in section 3.

Here we give only the result:

$$E_{(\mathrm{IA.2sss})}(t) = -\frac{4}{15}\,\frac{D^2 \Delta_\eta (1)\, \Gamma(15/4)}{\pi^2 \beta \varrho\, (D+\nu)^{15/4}}\, t^{\frac{1}{4}} + \mathcal{O}(1). \tag{4.27}$$

The calculation of $E_{(\mathrm{IA.2sfs})}(t)$ yields a term proportional to $t^{\frac{1}{4}}$ cancelling in (4.2) the contribution to $E_3(t)$ of order $t^{\frac{1}{4}}$ which originates from $C_0^{(e)}(t)$ [see the discussion below (4.2)]. All this is very similar to the treatment of diagram IA.1 in (4.26). Next contributions to diagram IA.2 are at most proportional to $\log t$. One may continue, finding diagrams belonging to subclass IA which give terms of order $t^{1/8}$, $t^{1/16}$, ... in the super-Burnett coefficient.

Finally we consider the subclass IB drawn in fig. 8. By the same straightforward estimation techniques and by first replacing all full propagators by their Boltzmann equivalents, one finds for the sum of all diagrams belonging to subclass IB at most a divergence like

$$E_{(\mathrm{IB})}(t) \approx (\log t)^2. \tag{4.28}$$

Similar estimates can be made for other subclasses of class I. Summarizing we find that the super-Burnett coefficient, $D_2(t)$, diverges as

$$\begin{aligned} D_2(t) = &-\frac{D^2}{10\pi^{3/2}\beta\varrho\,(\nu+D)^{5/2}}\, t^{\frac{1}{2}} \\ &-\frac{4}{15}\,\frac{D^2 \Delta_\eta (1)\, \Gamma(15/4)}{\pi^2 \beta \varrho\, (D+\nu)^{15/4}}\, t^{\frac{1}{4}} + \mathcal{O}(t^{1/8}), \end{aligned} \tag{4.29}$$

as t approaches infinity. The contributions to $D_2(t)$ arise from:

$E_{(\mathrm{V},1)}(t)$ [see (4.10)] which cancels $E_1(t)$ [see (2.15a)]; the diagrams IA.1sfs and IA.2sfs [see (4.26)] which cancel the terms of order $t^{\frac{1}{2}}$ and $t^{\frac{1}{4}}$ of $E_3(t)$ [see (2.16c) and the discussion following (4.2)]; and the diagrams IA.1sss and IA.2sss [see (4.24) and (4.27)] the contributions of which survive and give the coefficients in (4.29). The coefficients involve the low-density values of the transport coefficients D, ν and Γ_s and the sound velocity c. If one compares (4.29) with (2.17), one sees that the kinetic theory for a dilute gas of hard spheres confirms the result for $D_2(t)$ obtained from the phenomenological mode–mode coupling theory, if the latter result is restricted to low densities.

5. *Discussion and conclusions.* In section 4 we have used the kinetic theory of a dilute gas of hard spheres to calculate the super-Burnett coefficient and by a systematic investigation of all possible diagrams we have found the most singular behaviour of $D_2(t)$ as t goes to infinity. This result allows us to make some state-

ments about the four-point correlation function $\langle v_{1x}v_{1x}(t_1)\, v_{1x}(t_2)\, v_{1x}(t_3)\rangle$, when the difference between two time arguments becomes large. If, for instance, the time arguments are pairwise close together, say $(0, t_1)$ and (t_2, t_3), the four-point correlation function factorizes into $\langle v_{1x}(0)\, v_{1x}(t_1)\rangle \langle v_{1x}(t_2)\, v_{1x}(t_3)\rangle$ if (t_2, t_3) becomes large compared to $(0, t_1)$. This follows directly from eqs. (4.10) and (4.11), since the arguments used there apply also if we leave out the time integrals over t_1, t_2 and t_3.

Similar factorizations occur if we group the time arguments in other sets of two pairs, and if we let the time interval between the pairs become large. Even if we take *one* pair of times close together, say (t_1, t_2) and t_3 arbitrarily large, the four-point correlation function factorizes into $\langle v_{1x}(0)\, v_{1x}(t_3)\rangle \langle v_{1x}(t_1)\, v_{1x}(t_2)\rangle$ as follows from the result (4.26).

One might therefore hope that the four-point cumulant [*i.e.*, the integrand in eq. (1.20)], which is constructed from the four-point correlation function by subtracting all possible products of two-point correlation functions, would decay sufficiently rapidly, so that the super-Burnett coefficient, which is a threefold-ordered time integral over the four-point cumulant, would exist[6]). In that case we would have a generalized diffusion equation of the form (1.13), reducing for large times to (1.23). However, we have found persistent correlations from the diagrams IA.1sss and IA.2sss (figs. 9 and 10) which do not obey this decoupling scheme; taking t_3 large and t_1 and t_2 *arbitrary* at intermediate times, the four-point correlation function decays *independently* of t_1 and t_2, and proportionally to $t_3^{-5/2}$, which causes the divergence of the super-Burnett coefficient.

Van Kampen[23]) has recently given a systematic approximation scheme for deriving macroscopic equations (such as the generalized diffusion equation) based on the theory of stochastic linear differential equations, which can be applied if there exist two well separated time scales. This method, however, is not applicable to the linear diffusion equation for a tagged particle in a classical fluid. This has become clear from the existence of the hydrodynamic tails proportional to $t^{-3/2}$ occurring in the velocity autocorrelation function, showing that the two time scales relevant for the motion of a tagged particle in a classical fluid, namely the hydrodynamic time scale $\tau_m \approx (Dk^2)^{-1}$ and the time scale τ_c determined by the velocity autocorrelation function, are not well separated. A second important point is the comparison between the results obtained from kinetic theory and from the mode–mode coupling theory. Kinetic theory gives, at least for low densities, a relatively simple and systematic prescription how to calculate the most important contributions and how to estimate the neglected terms. On the other hand there are the mode–mode formulae. Although they are relatively simple and not limited to low densities, it is hard to assess the limits of validity of these formulae, because their derivation is based on phenomenological arguments. Since the calculations of the super-Burnett coefficient from both theories lead in the low-density limit to exactly the same result for the dominant divergent long-time behaviour, it gives some support to the conclusion that the $\mathcal{O}(k^2)$ contributions from the mode–mode formula for large times (*i.e.*, first k small, then t large) or for small values of the Laplace variable z (*i.e.*, first k small, then z small) can still be trusted.

Until now the mode–mode formulae for classical fluids, away from critical points, have been used in the literature for k exactly equal to zero, and then one has studied the large-t or small-z behaviour[2,4,5]) (see section 2). The results agree with kinetic theory[3]) (see section 3). Another application of the mode–mode formula, for values of z proportional to k or k^2 taking k small, has been made by several authors for determining the hydrodynamic dispersion relations in fluids[17,22,24]), the k expansion of which involves terms proportional to $k^{3-2^{-n}}$ ($n = 1, 2, \ldots$); *e.g.*, for the shear-mode frequency one finds[24]):

$$z_k^\eta = -\nu k^2 + \Delta_\eta(1)\, k^{5/2} + \cdots + \Delta_\eta(n)\, k^{3-2^{-n}} + \cdots, \tag{5.1}$$

with explicit expressions for the coefficients $\Delta_\eta(n)$, *e.g.*:

$$\Delta_\eta(1) = c^{\frac{1}{2}}/77\pi\, 2^{\frac{1}{2}}\beta\varrho\Gamma_s^{3/2}, \tag{5.2}$$

where c is the adiabatic sound velocity and Γ_s the sound damping constant. It has also been shown[22]) that the frequency z_k^s of the self-diffusion mode does not contain such rational powers. Ernst and Dorfman[17]) have also obtained the first two terms in the dispersion relations, which are of the general form (5.1), from kinetic theory, and they have shown that the results agree in the low-density limit.

An interesting implication of the dispersion relations (5.1) are higher asymptotic corrections to the $t^{-3/2}$ long-time tails, proportional to $t^{-2+2^{-n}}$ ($n = 2, 3, \ldots$). They arise immediately from the mode–mode formula (2.1) in the limit as $k \to 0$, in which the propagator $G_q^{\eta j}(t)$ in (2.5) is replaced by $\exp\left[-\nu q^2 t + \Delta_\eta(1)\, q^{5/2} t\right]$, while the propagator $G_{-q}^s(t) = \exp(-Dq^2 t)$ of the self-diffusion mode is not changed due to the absence of these rational powers in z_k^s. Straightforward calculations yield directly for large times

$$C_0(t) \simeq \frac{1}{12\pi^{3/2}\beta\varrho\,(D+\nu)^{3/2}}\,\frac{1}{t^{3/2}} + \frac{\Delta_\eta(1)\,\Gamma(11/4)}{6\pi^2\beta\varrho\,(D+\nu)^{11/4}}\,\frac{1}{t^{7/4}} + \cdots, \tag{5.3}$$

where $\Gamma(x)$ is the gamma function. In section 3 we obtained eq. (5.3) directly from kinetic theory in the low-density limit; the first term of (5.3) was given in (3.31) and the second term in (3.41). The second term is the contribution of the diagram (e) in fig. 4, which represents the dynamical processes responsible for the asymptotic correction proportional to $t^{-7/4}$. This independent calculation of the $t^{-2+2^{-n}}$ corrections on the basis of kinetic theory again supports the conclusion that the mode–mode theory may be trusted beyond its lowest-order predictions, at least in as far as they concern the effects discussed here.

We further came to the conclusion that the ordinary linear diffusion equation (*i.e.*, Fick's law) cannot be extended in an *analytic* way to higher order in the gradients (*i.e.*, higher orders in $\boldsymbol{k}$). In other words eq. (1.13) does not reduce to the form (1.23) for long times. One could ask if it would be possible to obtain a *nonanalytic* expansion in k, or in general a diffusion equation of the form:

$$\frac{\partial}{\partial t} G_k^{\mathrm{s}}(t) = -p(k)\, G_k^{\mathrm{s}}(t), \tag{5.4}$$

valid for large times at fixed values of k. If $p(k)$ exists, it should satisfy

$$p(k) = \lim_{t\to\infty} \left(-\frac{\partial}{\partial t} \log G_k^{\mathrm{s}}(t) \right). \tag{5.5a}$$

or alternatively:

$$p(k) = \lim_{t\to 0} \left(-(1/t) \log G_k^{\mathrm{s}}(t) \right). \tag{5.5b}$$

Then it follows from simple mathematical considerations that $-p(k)$ should be the first nonanalyticity of the Laplace transform G_{kz}^{s} seen from right to left in the complex z plane at fixed k. Furthermore if $p(k)$ exists, this first nonanalytic point is located on the real z axis, but it does not have to be a pole. From relation (1.25) and the mode–mode result (2.11) for $\hat{C}_{kz}$ is it clear that this point is situated at $s = 1$ or equivalently at $z = -[\nu D/(\nu + D)]\, k^2$, and so we find:

$$p(k) = [\nu D/(\nu + D)]\, k^2. \tag{5.6}$$

This is an unexpected result, because it predicts to lowest order in k a "diffusion coefficient" equal to $\nu D/(\nu + D)$, which is smaller than D. This is in complete contradiction with phenomenological experience as expressed by Fick's law. One might think that a refined mode-coupling theory could improve the situation, by cancelling all singularities of G_{kz}^{s} in the complex z plane, which are to the right of $z = -Dk^2$. In order to investigate this point we have considered the n-mode contributions, as given by the mode coupling theory of Kadanoff and Swift[8]), which gives a contribution to $\hat{C}_{kz}$ of the structure

$$\hat{C}_{kz}^{(n)} = \int' \mathrm{d}\boldsymbol{q}_1 \cdots \int' \mathrm{d}\boldsymbol{q}_n\, S(\boldsymbol{q}_1, \ldots, \boldsymbol{q}_n) \Big/ \left(z + \sum_{i=1}^{n} D_i q_i^2 \right), \tag{5.7}$$

where the $\boldsymbol{q}_i$ integrations are restricted by the condition $\sum_{i=1}^{n} \boldsymbol{q}_i = \boldsymbol{k}$, where S is some analytic function of its arguments and D_i is equal to ν, D or the heat diffusion constant D_T, according to the modes which are taken into account. The condition on the integration variables in (5.7) can be eliminated by transforming the n $\boldsymbol{q}$ variables to centre-of-mass- and relative coordinates, to obtain:

$$\hat{C}^{(n)}_{kz} = \int \mathrm{d}\boldsymbol{q}'_2 \cdots \int \mathrm{d}\boldsymbol{q}'_n\, S'(\boldsymbol{k}, \boldsymbol{q}'_2, \ldots, \boldsymbol{q}'_n) \Big/ \left(z + d_1 k^2 + \sum_{i=2}^{n} d_i q'^2_i \right). \tag{5.8}$$

The constants d_i are all positive and only d_1 is needed explicitly

$$d_1 = (D_1^{-1} + \cdots + D_n^{-1})^{-1}. \tag{5.9}$$

The first nonanalyticity of the function $\hat{C}^{(n)}_{kz}$ in the complex z plane is in general reached for $z = -d_1 k^2$ which is the largest real value of z for which the denominator in (5.8) vanishes. Hence it follows that $p(k)$ in this approximation has the form

$$p(k) = (D_1^{-1} + \cdots + D_n^{-1})^{-1}\, k^2. \tag{5.10}$$

If more and more modes are taken into account, the value of $p(k)$ approaches zero at any given value of k, so that also its lowest-order contribution in k which one would like to interprete as the "diffusion coefficient" would vanish. This result shows firstly that the difficulty posed by eq. (5.6) cannot be resolved by taking more and more modes into account, and secondly it shows, granting the validity of the mode-coupling theory, that a nonanalytic diffusion equation of the form (5.4) could not exist, since $p(k)$ would vanish. The reason for the unphysical results (5.6) and (5.10) is a question of limits. We are studying in (5.4) the limit of $G^{\mathrm{s}}_k(t)$ for *large* t at *fixed values* of k. What one should do is to search for an improved diffusion equation which only holds in a finite physical time regime, or alternatively, one should measure the time in units of $(Dk^2)^{-1}$, use k as a small parameter and let t become large while $\tau = Dk^2 t$ is kept finite. This will be the subject of a subsequent paper.

Acknowledgement. We want to thank Drs. J.W. Dufty and T. Keyes for stimulating discussions.

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