Low-Frequency Behavior of Transport Coefficients in Fluids

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It was recently shown that the kinetic-kinetic part of the Kubo integrands for shear viscosity and heat conductivity behaves as $t^{-d/2}$(d = dimensionality) for $t\rightarrow\infty$. We generalize this result to the complete (kinetic-kinetic + kinetic-potential + potential-potential) Kubo integrands for bulk and shear viscosity and heat conductivity and find explicitly the leading-order term for these autocorrelation functions for $t\rightarrow\infty$. The method is very similar to that used in the Landau-Placzeck calculation of the light-scattering cross section of simple fluids. This $t^{-d/2}$ behavior has two consequences that are examined: In two-dimensional fluids it leads to a divergence of Kubo integrals and in three dimensions it yields a nonanalytical low-frequency behavior of the frequency-dependent transport coefficients.

I. INTRODUCTION

Since the discovery[1] of a "long tail" in the long-time behavior of the velocity autocorrelation function $\langle \vec{v}_i(0)\cdot\vec{v}_i(t)\rangle$ in a fluid of hard discs, a number of investigators[2,3] have studied the asymptotic behavior of autocorrelation functions in a fluid.

As explained in Sec. II, one may study this problem according to the ideas of Landau and Placzeck[4] on the hydrodynamical regression of fluctuations. Consider an autocorrelation function of the form $\langle\langle X(\vec{r},0)Y(t)\rangle\rangle$, where $X(\vec{r},0)$ depends on the initial dynamical state of the many-body system *around* $\vec{r}$ and $Y(t)$ on the dynamical state of the system at time t. The system may be divided into large cells that are statistically independent, so that $X(\vec{r},0)$ only depends on the initial situation in a given cell. One may replace $Y(t)$ by its average value over a nonequilibrium ensemble initially in a given nonequilibrium situation around $\vec{r}$ and at equilibrium at large distances from $\vec{r}$. Assuming now that, for long times, this nonequilibrium ensemble goes to equilibrium according to the laws of hydrodynamics, we replace $Y(t)$ in this limit by its value over the corresponding local-equilibrium ensemble.

As explained in Sec. III, this gives means of computing the asymptotic value of the Green-Kubo integrands for shear viscosity, heat conductivity, and bulk viscosity. These autocorrelation functions behave as $t^{-d/2}$ (d = dimensionality) for large times.

This leads to a divergence of the Green-Kubo integrals in two-dimensional fluids and corroborates a previous result,[5] which proceeds from an analysis of the renormalized virial expansion for the collision operator. This divergence is examined in Sec. IV.

In Secs. V–VII, we examine the situation of three-dimensional fluids. We deduce from the $t^{-3/2}$ decay of the Green-Kubo integrands that the first term in the low-frequency expansion of transport coefficients is of order $\omega^{1/2}$. This result is extended at the low-frequency *long-wavelength* expansion of transport coefficients and leads to a $\beta^{5/2}$ term in the long-wavelength dependence of frequencies of hydrodynamical modes (β = wave number). We deduce from this long-wavelength expansion a first-perturbation value of the Green function for these modes beyond their usual Navier-Stokes value.

In Sec. VII it is shown that after the $t^{-3/2}$ term appears a $t^{-7/4}$ term in the asymptotic expansion of Green-Kubo integrands, which seems to be the second term of an infinite expansion of general order $t^{-(2-2^{-n})}$ (n is an integer ≥ 1).

II. LANDAU AND PLACZECK METHOD

The method of Landau and Placzeck[4] is well known and provides a powerful tool in the analysis of autocorrelation functions. However, its application to the Green-Kubo integrands has been criticized[6] and it is useful to recall its main features.

Let Ω_N be a point in phase space of a classical system of N identical particles of mass m:

$$\Omega_N=\{\vec{r}_1,\vec{v}_1;\ldots\vec{r}_N,\vec{v}_N\}. \tag{2.1}$$

Let further $\Omega_N^*(t,\Omega_N^0)$ be the point of phase space reached at time t by the system starting from Ω_N^0 at $t=0$. An autocorrelation function is defined by

$$\psi(t)=1/V\langle\textstyle\sum_i X_i(\Omega_N^0)\sum_j X_j\{\Omega_N^*(t,\Omega_N^0)\}\rangle\ , \tag{2.2}$$

where V is the volume of the box containing the particles, or the volume of a large part of an infinite system (in this case the sum $\sum_i$ is restricted by the condition $\vec{r}_i^{\,0}\in V$) and $X_i(\Omega_N^0)$ is a function of Ω_N^0 and depends in a particular way on dynamical variables of the particle i. Furthermore, X_i defines a fluctuating quantity such that the equilibrium fluctuation $\psi(t=0)$ remains constant in the thermodynamical limit. In (2.2) the average is performed over an equilibrium ensemble. The choice of this ensemble will be examined further. Restricting now our study to those functions X_i that do not depend on the location of the system with respect to the origin of coordinates, we may replace the definition (2.2) by

$$\psi(t) = \langle \sum_i \delta(\vec{r} - \vec{r}_i) X_i(\Omega_N^0) \sum_j X_j \{\Omega_N^*(t, \Omega_N^0)\} \rangle \ . \tag{2.3}$$

The equivalence of (2.2) and (2.3) is checked by noticing that the right-hand side of (2.3) does not depend on $\vec{r}$ and then integrating this quantity over $\vec{r}$ (in finite systems this translational invariance is rigorous for periodic systems only; however, we may admit that it remains valid almost everywhere in any large system).

Starting from (2.3) we shall explain how to compute the asymptotic value of $\Psi(t)$ by means of the method of Landau and Placzeck (of course, that explanation does not pretend to be original). Let us divide the box containing the system into cells with a size much larger than any correlation length and small with respect to the size of the box. Let ΔV^0 be the cell including $\vec{r}$ and let $\{\Delta V^I\}$ be the other cells. The equilibrium ensemble filling the box may be considered as a superposition of *statistically independent* grand canonical ensembles lying in each cell (these ensembles are independent since we may neglect interactions between cells when their size becomes large enough). Another important assumption is that $\sum_i X_i(\Omega_N^0)\, \delta(\vec{r} - \vec{r}_i^{\,0})$ only depends on the set of positions and momenta of particles lying in ΔV^0. This set will be denoted $\Omega_N^0 \cap \Delta V^0$.

Since the cells are statistically independent, we may perform independently the average over the grand canonical ensembles occupying ΔV^0 and the other cells. Thus (2.3) may be equivalently written

$$\psi(t) = \langle \sum_i \delta(\vec{r}_i - \vec{r}_i^{\,0}) X_i(\Omega_N^0) \times \langle \sum_j X_j [\Omega_N^*(t, \Omega_N^0)] \rangle_{\{\Delta V^I\}} \rangle_{\Delta V^0} \ , \tag{2.4}$$

where $\langle\ \rangle_{\Delta V^0}$ and $\langle\ \rangle_{\{\Delta V^I\}}$ stand for the average over the equilibrium ensemble located in ΔV^0 and $\{\Delta V^I\}$. The quantity $\langle \sum_j X_j [\Omega_N^*(t, \Omega_N^0)] \rangle_{\{\Delta V^I\}}$ is the value of $\sum_j X_j$, at time t in a nonequilibrium ensemble initially at equilibrium in $\{\Delta V^I\}$ and in a given dynamical state in ΔV^0.

Let us now assume that this nonequilibrium ensemble evolves for long times according to the laws of hydrodynamics. In this limit, we may then replace $\langle \sum_j X_j [\Omega_N^*(t, \Omega_N^0)] \rangle_{\{\Delta V^I\}}$ by the value of $\sum_j X_j$, in the local equilibrium ensemble describing this hydrodynamical stage in the decay of the initial fluctuation in ΔV^0. Let $Z(t, \Omega_N^0 \cap \Delta V^0)$ be this local equilibrium value of $\sum_j X_j$. Then we have for large times

$$\psi(t) \underset{t\to\infty}{\simeq} \langle \sum_i \delta(\vec{r} - \vec{r}_i^{\,0}) X_i(\Omega_N^0)\, Z(t, \Omega_N^0 \cap \Delta V^0) \rangle_{\Delta V^0} \ . \tag{2.5}$$

This constitutes the Landau-Placzeck approximation for an autocorrelation function. The problem of the choice of the equilibrium ensemble filling the box has disappeared and $\psi(t)$ is obtained for long times through a grand canonical average, as a consequence of the theory.[7]

The local equilibrium ensemble, over which Z is calculated, is defined by a set of $(d+2)$ functions of $\vec{r}$, t and $\Omega_N^0 \cap \Delta V^0$. This set of functions will be called a hydrodynamical field and is defined by

$$f(\vec{r}, t) \equiv \{S(\vec{r}, t), p(\vec{r}, t), \vec{u}(\vec{r}, t)\} \ ,$$

where $S(\vec{r}, t)$ is the local entropy per unit mass, $p(\vec{r}, t)$ the local pressure, and $\vec{u}(\vec{r}, t)$ the local fluid velocity. Further, $\delta f(\vec{r}, t)$ will be the perturbation of $f(\vec{r}, t)$ defined by $\delta f(\vec{r}, t) = f(\vec{r}, t) - f$, f being the equilibrium value of $f(\vec{r}, t)$. We shall assume that $f(\vec{r}, t)$ varies in space as smoothly as desired and that its amplitude goes to zero for large times. Then, in this limit, the $\vec{r}$-dependent thermodynamical quantities are related through the equilibrium equations of state, which gives, for example,

$$\delta\rho(\vec{r}, t) \underset{t\to\infty}{\simeq} \left.\frac{\partial\rho}{\partial S}\right|_p \delta S(\vec{r}, t) + \left.\frac{\partial\rho}{\partial p}\right|_S \delta p(\vec{r}, t) \ , \tag{2.6}$$

where $\delta\rho$ is the perturbation of the mass density.

Furthermore, since $\delta f(\vec{r}, t) \underset{t\to\infty}{\to} 0$, the motion of δf is described for long times by the *linearized* equations of hydrodynamics. These equations take a simple form if we use the Fourier transform of δf defined by

$$\delta f(\vec{\alpha}, t) \equiv \int d\vec{r}\, e^{2i\pi\vec{\alpha}\cdot\vec{r}}\, \delta f(\vec{r}, t) \ .$$

Then, because of the translational invariance of the laws of hydrodynamics,

$$\delta f(\vec{\alpha}, t) \underset{t\to\infty}{=} \phi(\vec{\alpha}, t - t_1)\, \delta f(\vec{\alpha}, t_1) \ , \tag{2.7}$$

when ϕ is a $(d+2)\times(d+2)$ matrix and $t > t_1$, t_1 being a large time such that when $t > t_1$, $\delta f(t)$ is small enough to evolve according to the *linearized* equations of hydrodynamics. The matrix $\phi(\vec{\alpha}, t - t_1)$ is known near $\alpha \to 0$ from elementary hydrodynamics. In this limit it is convenient to write $\delta f(\vec{\alpha})$ as a linear superposition of three modes[8]: (1) the mode of vorticity diffusion describing the motion of the $(d-1)$ independent components of $\vec{u}_T = (\overleftrightarrow{1} - \vec{\alpha}\,\vec{\alpha}/\alpha^2)\cdot\vec{u}$; (2) the two sound waves that propagate in the direction of $\vec{\alpha}$ and of $(-\vec{\alpha})$ and describe the motion of the pressure field and of $\vec{u}_L = \vec{u} - \vec{u}_T$; and (3) the mode of entropy diffusion at constant pressure or "heat diffusion." The corresponding elements of the matrix ϕ are given in Table I.

The second factor on the right-hand side ot (2.7) may also be computed near $\alpha = 0$ from the conservation laws. Let δM, $\delta\vec{P}$, and δE be the fluctuations of mass, momentum, and energy defined by $\Omega_N^0 \cap \Delta V^0$. From the usual conservations rules

$$\int d\vec{r}\, \delta\rho(\vec{r}, t) = \delta M \ , \qquad (2.8)$$

$$\int d\vec{r}\, \rho(\vec{r}, t)\, \vec{u}(\vec{r}, t) = \delta\vec{P} \ , \qquad (2.9a)$$

and

$$\tfrac{1}{2}\int \rho(\vec{r}, t) u^2(\vec{r}, t)\, d\vec{r} + \int d\vec{r}\, \delta\epsilon(\vec{r}, t) = \delta E \ , \qquad (2.10a)$$

where $\delta\rho$ and $\delta\epsilon$ are respectively the perturbations of the densities of mass and of internal energy. For large times $\rho(\vec{r}, t) \to \rho$ and $\int d\vec{r}\, u^2(\vec{r}, t) \sim t^{-d/2}$, as shown below. Then (2.9a) and (2.10a) take the asymptotic form

$$\int d\vec{r}\, \vec{u}(\vec{r}, t) \underset{t\to\infty}{\simeq} \delta\vec{P}/\rho \qquad (2.9b)$$

and

$$\int d\vec{r}\, \delta\epsilon(\vec{r}, t) \underset{t\to\infty}{\simeq} \delta E \ . \qquad (2.10b)$$

Using now (2.6) and a similar relation for $\delta\epsilon$, we deduce from the conservation relations

$$\delta\vec{u}(0, t_1) \underset{t_1\to\infty}{\simeq} \delta\vec{P}/\rho \ , \qquad (2.11a)$$

$$\delta S(0, t_1) \underset{t_1\to\infty}{\simeq} (1/\rho T)(\delta E - h\delta M) \ , \qquad (2.11b)$$

and

$$\delta\vec{p}(0, t_1) \underset{t_1\to\infty}{\simeq} \left.\frac{\partial p}{\partial \epsilon}\right|_\rho \left[\delta E - \left.\frac{\partial \epsilon}{\partial \rho}\right|_p \delta M\right] \ , \qquad (2.11c)$$

where h is the equilibrium enthalpy per unit mass:

$$h = (\epsilon + p)/\rho \ .$$

From (2.7) and (2.11) we have an explicit value of $\delta f(\vec{\alpha}, t)$ in the limit $\alpha \to 0$, $t \to \infty$. This knowledge of δf will be sufficient for our purpose. Recall that we are looking for the local equilibrium value of $\sum_j X_j$, namely, $Z(t, \Omega_N^0 \cap \Delta V^0)$, which is a function of δf. In the original work of Landau and Placzeck, Z is the fluctuation of mass density at time t and distance $\vec{R}$ of the cell ΔV^0, a linear function of δf. In this paper we shall study the Green-Kubo autocorrelation functions, and it will be shown in Sec. III that in this case Z is equal to some linear combination of the $\frac{1}{2}(d+2)(d+3)$ quantities $\int \delta f^2(\vec{r}, t)\, d\vec{r}$, and this quadratic function of δf depends for long times on the value of $\delta f(\vec{\alpha}, t)$ near $\alpha = 0$.

Consider, for example, the quantity

$$\int d\vec{r}\, \delta S^2(\vec{r}, t) = \int d\vec{\alpha}\, |\delta S(\vec{\alpha}, t)|^2 \ .$$

Taking $\vec{\alpha}' = \vec{\alpha}\, t^{1/2}$ as the integration variable in this last expression, we obtain from (2.7) and (2.11b)

TABLE I. Components of $\phi(\vec{\alpha}, \tau)$ near $\alpha = 0$. η is the shear viscosity, ρ is the mass density, $C \equiv \{\partial p/\partial\rho \mid s\}^{1/2}$ = sound velocity, $\eta_\theta = \kappa/C_p$, $\eta_s = \frac{1}{2}\{[(2d - 2/d)]\eta + \zeta + \kappa(1/C_v - 1/C_p)\}$, κ is the heat conductivity, ζ is the bulk viscosity, and C_V and C_p are the heat capacities per unit mass at constant volume and pressure.

	S	p	u_L	$\vec{u}_T$
S	$\phi_{S,S} = \exp[-(4\pi^2\alpha^2/\rho)\eta_\theta\tau]$	$\phi_{S,p} = 0$	$\phi_{S,u_L} = 0$	$\phi_{S,\vec{u}_T} = 0$
P	$\phi_{p,S} = 0$	$\phi_{p,p} = \exp[-(4\pi^2\alpha^2/\rho)\eta_s\tau]\cos 2\pi\alpha C\tau$	$\phi_{u_L,u_L} = i\rho C(\vec{\alpha}/\alpha)\, \sin(2\pi\alpha C\tau)\exp[-(4\pi^2\alpha^2/\rho)\eta_s\tau]$	$\phi_{p,\vec{u}_T} = 0$
u_L	$\phi_{u_L,S} = 0$	$\phi_{u_L,p} = \frac{1}{(\rho C)^2}\, \phi_{p,u_L}$	$\phi_{u_L,u_L} = \phi_{p,p}$	$\phi_{u_L,\vec{u}_T} = 0$
$\vec{u}_T$	$\phi_{\vec{u}_T,S} = 0$	$\phi_{\vec{u}_T,p} = 0$	$\phi_{\vec{u}_T,u_L} = 0$	$\phi_{\vec{u}_T,\vec{u}_T} = \exp[-(4\pi^2\alpha^2/\rho)\eta]\tau$

$$\int d\vec{r}\,\delta S^2(\vec{r},t) \underset{t\to\infty}{\simeq} t^{-d/2}\int d\vec{\alpha}' \lim_{t\to\infty} |\delta S(\vec{\alpha}' t^{-1/2},t)|^2$$

$$\underset{t\to\infty}{\simeq} \left(\frac{\rho}{4\pi\eta_\theta t}\right)^{d/2} \frac{(\delta E - h\delta M)^2}{\rho^2 T^2} . \quad (2.12)$$

Along similar lines it could be shown that $\int d\vec{r}\,\delta f^2(\vec{r},t) \underset{t\to\infty}{\simeq} t^{-d/2}$ for those components of δf that behave according to a diffusion law. Consider now the components of $\int d\vec{r}\,\delta f^2(\vec{r},t)$ that are quadratic in the amplitude of the sound wave generated by the initial fluctuation. One of these quantities is $\int d\vec{r}\,\delta p^2(\vec{r},t)$, which is given by

$$\int \delta p^2(\vec{r},t)\,d\vec{r} = t^{-d/2}\int d\vec{\alpha}' \,|\delta p(\vec{\alpha}'\, t^{-1/2},t)|^2 . \quad (2.13)$$

From (2.7) and Table I,

$$|\delta p(\vec{\alpha}' t^{-1/2},t)|^2$$

$$\underset{t\to\infty}{\simeq} \tfrac{1}{2} e^{-8\pi^2\alpha'^2\eta_s/\rho}\{|\delta p(0,t_1)|^2 + \rho^2 C^2 |\vec{u}_L(0,t_1)|^2 + [\text{terms in cos, sin } (4\pi\alpha' C t^{1/2})]\} . \quad (2.14)$$

Terms in cos, sin $(4\pi\alpha' C t^{1/2})$ on the right-hand side of (2.14) give exponentially damped contributions to $\int d\vec{r}\,\delta p^2(\vec{r},t)$ and the other ones give contributions in $t^{-d/2}$, which yields

$$\int d\vec{r}\,\delta p^2(\vec{r},t) \underset{t\to\infty}{\simeq} \tfrac{1}{2}\left(\frac{\rho}{8\pi\eta_s t}\right)^{d/2} \times\left\{\frac{C^2\delta\vec{P}^2}{d} + \left.\frac{\partial p}{\partial\epsilon}\right|_\rho^2 \left[\delta E - \left.\frac{\partial\epsilon}{\partial\rho}\right|_p \delta M\right]^2\right\} . \quad (2.15)$$

Similarly,

$$\int d\vec{r}\,u_L^2(\vec{r},t) \underset{t\to\infty}{\simeq} \frac{1}{\rho^2 C^2}\int d\vec{r}\,\delta p^2(\vec{r},t)$$

and

$$\int d\vec{r}\,\vec{u}(\vec{r},t)\,\delta p(\vec{r},t)$$

$$\underset{t\to\infty}{\simeq} \left(\frac{\rho}{8\pi\eta_s t}\right)^{d/2} \frac{\delta\vec{P}}{\rho d}\left.\frac{\partial p}{\partial\epsilon}\right|_\rho \left[\delta E - \left.\frac{\partial\epsilon}{\partial\rho}\right|_p \delta M\right] .$$

To conclude, we have shown that $\int d\vec{r}\,\delta f^2(\vec{r},t)$ is asymptotically equal to $t^{-d/2}$ multiplied by the square of some linear combination of δM, $\delta\vec{P}$, and δE whenever δf^2 is the product of two diffusion components or of two sound-wave components of δf. The other components of $\int d\vec{r}\,\delta f^2(\vec{r},t)$, namely, the crossed quantities like $\int d\vec{r}\,\delta p(\vec{r},t)\,\delta S(\vec{r},t)$, decrease exponentially and may be neglected with respect to the elements of $\int d\vec{r}\,\delta f^2(\vec{r},t)$ considered above. In Sec. III we shall apply these remarks to the case of the Green-Kubo integrands.

III. ASYMPTOTIC VALUE OF GREEN-KUBO INTEGRANDS FOR η, κ, AND ζ

Using the method of Landau and Placzeck we shall calculate in this section the asymptotic values of the Green-Kubo integrands for η, κ, and ζ (η = shear viscosity, κ = heat conductivity, and ζ = bulk viscosity). The calculations will proceed as follows: The Green-Kubo integrands $\psi_{\eta,\kappa,\zeta}(t)$ are put into a form equivalent to (2.3). Then, according to the Landau-Placzeck theory, their asymptotic values are given by (2.5). For these autocorrelation functions the local equilibrium value of $\sum_j X_j$, namely, $Z_{\eta,\kappa,\zeta}$, is equal to some linear combinations of the $\frac{1}{2}(d+2)(d+3)$ quantities $\int \delta f^2(\vec{r},t)\,d\vec{r}$; then, as was shown at the end of Sec. II, the asymptotic value of $Z_{\eta,\kappa,\zeta}(t, \Omega_N^0 \cap \Delta V^0)$ depends on time and on initial fluctuations inside ΔV^0 as

$$Z_{\eta,\kappa,\zeta} \sim t^{-d/2}[\delta(M,\vec{P},E)]^2 , \quad (3.1)$$

where $[\delta(M,\vec{P},E)]^2$ stands for some linear combination of the quantities δM^2, $\delta M\delta\vec{P}$, $\delta M\delta E$, $\delta\vec{P}^2, \ldots$. Inserting into (2.5) the value of Z given in (3.1), and accounting for the translational invariance of equilibrium, we have

$$\psi_{\eta,\kappa,\zeta}(t) \underset{t\to\infty}{\sim} t^{-d/2}(1/\Delta V_0)\langle\!\langle[\delta(M,\vec{P},E)]^2 \times \sum_{j,\vec{r}_j^{\,0}\in\Delta V^0} X_j(\Omega_N^0)\rangle\!\rangle_{\Delta V^0} . \quad (3.2)$$

The equilibrium fluctuation on the right-hand side of (3.2) is calculated by the standard methods, which gives explicitly the asymptotic value of $\psi_{\eta,\kappa,\zeta}(t)$.

This method can be applied straightforwardly to the cases of the shear viscosity and heat conductivity, the asymptotic value of $\psi_{\eta,\kappa}(t)$ will be obtained in Sec. III A.

The case of the bulk viscosity is more complicated and will be handled in Sec. III B.

A. Asymptotic Value of $\psi_{\eta,\kappa}(t)$

The Green-Kubo formulas for shear viscosity and heat conductivity read[9]

$$\eta = (1/kT)\int_0^\infty dt\,\psi_\eta(t) \quad (3.3a)$$

and

$$\kappa = (1/kT)\int_0^\infty dt\,\psi_\kappa(t) , \quad (3.3b)$$

where ψ_η and ψ_κ are two autocorrelation functions defined by the general formula (2.2) and the functions X_η and X_κ are given by

$$X_{i,\eta} = \vec{P}_i : \vec{e}_x \vec{e}_y \quad (3.4a)$$

and

$$X_{i,\kappa} = \frac{\vec{e}_x}{T^{1/2}} \cdot \left(\vec{v}_i (E_i - mh) - \tfrac{1}{2}\sum_j \vec{r}_{ij}\frac{\partial V_{ij}}{\partial \vec{r}_i} \cdot \vec{v}_i\right), \quad (3.4b)$$

where $\vec{e}_{x,y}$ are two perpendicular unit vectors,

$$E_i = \tfrac{1}{2} m \vec{v}_i^2 + \tfrac{1}{2} \sum_y V_{ij} ,$$

V_{ij} is the two-body potential energy, and where

$$\overleftrightarrow{P}_i = m\vec{v}_i\vec{v}_i - \tfrac{1}{2}\sum_j \vec{r}_{ij} \frac{\partial V_{ij}}{\partial \vec{r}_i} . \tag{3.5}$$

We shall verify at first that the local equilibrium values of $\sum_j X_{j;\eta,\kappa}$ are given, for long times, by expressions of the form

$$Z_{\eta,\kappa} \sim \int \delta f^2(\vec{r}, t) d\vec{r} .$$

From (3.4) we have

$$Z_\eta = \rho \int d\vec{\alpha} u_x^*(\vec{\alpha}, t) u_y(\vec{\alpha}, t) - \tfrac{1}{2}\langle \vec{e}_x \vec{e}_y : \textstyle\sum_j \vec{r}_{ij} \partial V_{ij}/\partial \vec{r}_i \rangle^{\mathrm{LE}} , \tag{3.6a}$$

where $\langle\ \rangle^{\mathrm{LE}}$ stands for the local equilibrium average, and

$$Z_\kappa = \frac{\rho}{T^{1/2}} \int d\vec{\alpha} u_x^*(\vec{\alpha}, t) \delta h(\vec{\alpha}, t) , \tag{3.6b}$$

where δh is perturbed enthalpy per unit mass, which is the local average value of the microscopic quantity

$$m^{-1}\left(E_i + \frac{m\vec{v}_i^2}{2d} - \frac{1}{2d} \sum_j \vec{r}_{ij} \cdot \frac{\partial V_{ij}}{\partial \vec{r}_i}\right) - h .$$

To derive (3.6b) we have dropped terms of order $\int \delta f^3(\vec{r}, t) d\vec{r}$, which are negligible in the asymptotic limit with respect to $\int \delta f^2(\vec{r}, t) d\vec{r}$, since $\delta f(\vec{r}, t) \to 0$ at $t \to \infty$.

Before proceeding any further, let us determine the asymptotic order of the last term on the right-hand side of (3.6a). For an homogeneous equilibrium system, $\langle \vec{e}_x \vec{e}_y : \sum_j \vec{r}_{ij} \partial V_{ij}/\partial \vec{r}_i \rangle$ is equal to zero. Then this local equilibrium average is calculated through an expansion in powers of $\partial f(\vec{r}, t)/\partial \vec{r}$, which yields

$$\langle \vec{e}_x \vec{e}_y : \textstyle\sum_j \vec{r}_{ij} \partial V_{ij}/\partial \vec{r}_i \rangle^{\mathrm{LE}} \underset{t\to\infty}{\sim} \int d\vec{r} \frac{\partial \delta f(\vec{r}, t)}{\partial r_x} \frac{\partial \delta f(\vec{r}, t)}{\partial r_y} . \tag{3.7}$$

Using the method that succeeded in calculating $\int d\vec{r}\, \delta f^2(\vec{r}, t)$, we obtain

$$\int d\vec{r} \frac{\partial \delta f(\vec{r}, t)}{\partial r_x} \frac{\partial \delta f(\vec{r}, t)}{\partial r_y} \underset{t\to\infty}{\sim} t^{-1} \int \delta f^2(\vec{r}, t) d\vec{r} . \tag{3.8}$$

The first term on the right-hand side of (3.6a) being of order $\int \delta f^2(\vec{r}, t) d\vec{r}$ at $t \to \infty$, we have from (3.6a), (3.7), and (3.8)

$$Z_\eta \underset{t\to\infty}{\simeq} \rho \int d\vec{\alpha} u_x^*(\vec{\alpha}, t) u_y(\vec{\alpha}, t) . \tag{3.9}$$

Once we have expressed $Z_{\eta,\kappa}$ in the general form $\int d\vec{\alpha} |\delta f(\vec{\alpha}, t)|^2$, we may obtain their asymptotic value as explained in Sec. II. For that purpose, we replace in (3.6b) δh by a linear combination of δS and δp which evolve, respectively, according to the laws of entropy diffusion and of sound propagation. This can be done from

$$\delta h = T\delta S + \delta p/\rho ,$$

and we obtain

$$Z_\kappa(t, \Omega_N^0 \cap \Delta V^0) \underset{t\to\infty}{\simeq} \frac{\delta P_x}{\rho T^{1/2}} \left(\frac{\rho}{4\pi t}\right)^{d/2} \times \left[\frac{(\delta E - h\delta M)(d-1)}{(\eta_\theta + \eta)^{d/2}} - \frac{1}{(2\eta_s)^{d/2}} \frac{\partial p}{\partial \epsilon}\bigg|_\rho \times \left(\delta E - \frac{\partial \epsilon}{\partial \rho}\bigg|_p \delta M\right)\right] \tag{3.10a}$$

and

$$Z_\eta(t, \Omega_N^0 \cap \Delta V^0) \underset{t\to\infty}{\simeq} \frac{\delta P_x \delta P_y}{d(d+2)\rho} \left(\frac{\rho}{8\pi t}\right)^{d/2} \left(\frac{d^2-2}{\eta^{d/2}} + \frac{1}{\eta_s^{d/2}}\right). \tag{3.10b}$$

In (3.10b) terms involving δM have been omitted, since their final contributions to $\psi_\eta(t)$ vanish, δM being a fluctuation independent of $\delta\vec{P}$.

From the Landau-Placzeck theory, the asymptotic value of $\psi_\eta(t)$ is given by

$$\psi_\eta(t) \underset{t\to\infty}{\simeq} (1/\Delta V^0) \langle \sum_{i, \vec{r}_i \in \Delta V^0} X_{i,\eta} Z_\eta(t, \Omega_N^0 \cap \Delta V^0) \rangle_{\Delta V^0} . \tag{3.11}$$

Then from (3.4a) and (3.10b)

$$\psi_\eta(t) \underset{t\to\infty}{\simeq} \frac{(kT)^2}{d(d+2)} \left(\frac{\rho}{8\pi t}\right)^{d/2} \left(\frac{d^2-2}{\eta^{d/2}} + \frac{1}{\eta_s^{d/2}}\right) . \tag{3.12}$$

The asymptotic value of $\psi_\kappa(t)$ is obtained in a very similar manner. From (3.4b) and (3.10a)

$$\psi_\kappa(t) \underset{t\to\infty}{\simeq} \frac{1}{\rho T}\left(\frac{\rho}{4\pi t}\right)^{d/2} \left[\frac{d-1}{(\eta_\theta + \eta)^{d/2}} \Phi_\kappa^1 - \frac{\partial p}{\partial \epsilon}\bigg|_\rho \frac{1}{(2\eta_s)^{d/2}} \left(\Phi_\kappa^1 - \rho T \frac{\partial S}{\partial \rho}\bigg|_p \Phi_\kappa^2\right)\right] , \tag{3.13}$$

where we have used

$$\frac{\partial \epsilon}{\partial \rho}\bigg|_p = h + \rho T \frac{\partial S}{\partial \rho}\bigg|_p$$

and where $\Phi_\kappa^{1,2}$ are two equilibrium fluctuations defined as

$$\Phi_\kappa^1 = (1/\Delta V^0) \langle (\sum_{i, \vec{r}_i \in \Delta V^0} X_{i,\kappa}) \delta P_x (\delta E - h\delta M) \rangle_{\Delta V^0} \tag{3.14a}$$

and

$$\Phi_\kappa^2 = (1/\Delta V^0) \langle (\sum_{i, \vec{r}_i \in \Delta V^0} X_{i,\kappa}) \delta P_x \delta M \rangle_{\Delta V^0} . \tag{3.14b}$$

These fluctuations are computed in Appendix A.

Inserting their values into (3.13), we obtain

$$\psi_\kappa(t) \underset{t\to\infty}{\simeq} \frac{(kT)^2}{d} C_p \left(\frac{\rho}{4\pi t}\right)^{d/2} \times\left(\frac{d-1}{(\eta_\theta+\eta)^{d/2}} + \frac{\chi^2(\gamma-1)}{(2\eta_s)^{d/2}}\right), \quad (3.15)$$

where

$$\gamma = \frac{C_p}{C_v} \text{ and } \chi = \frac{\rho}{T}\frac{\partial T}{\partial\rho}\bigg|_p .$$

Recently a particular case of formulas (3.12) and (3.15) was published[2] that concerned the kinetic-kinetic contribution to ψ_η and ψ_κ. Since we have shown [Eqs. (3.8), (3.9)] that the asymptotic contribution to ψ_η is of a purely kinetic origin, our formula (3.12) coincides with the long-time kinetic kinetic contribution to $\psi_\eta(t)$.

But the situation is different for $\psi_\kappa(t)$. In the previously cited work,[2] Ernst *et al.* calculated the asymptotic value of the kinetic-kinetic part of $\psi_\kappa(t)$. Let $\psi_\kappa^k(t)$ be this kinetic-kinetic part of ψ_κ. It is defined as $\psi_\kappa(t)$, except that $X_{i,\kappa}$ is replaced by

$$X_{i,\kappa}^k = (v_{ix}/T^{1/2})\left[\tfrac{1}{2}mv_i^2 - (d+2)\tfrac{1}{2}kT\right] . \quad (3.16)$$

Then the kinetic-kinetic contribution to Z_κ reads

$$Z_\kappa^k(t) \underset{t\to\infty}{\simeq} \frac{(d+2)\rho}{2m}\int d\vec{\alpha}\, u_x^*(\vec{\alpha},t)\,\delta T(\vec{\alpha},t) , \quad (3.17)$$

where δT is the perturbed temperature. In the limit of smooth perturbation with a weak amplitude, δT is related to δS and δp as

$$\delta T = T\frac{\delta S}{C_p} - \frac{1}{\rho C_p \chi}\,\delta p .$$

Applying now the method outlined in Sec. II, we may calculate Z_κ^k in terms of δE, δM, and $\delta\vec{P}$. Terms proportional to δM may be omitted, since they give zero when inserted into $\langle X_\kappa^k Z_\kappa^k\rangle$, and we have

$$Z_\kappa^k(t) \underset{t\to\infty}{\simeq} \frac{\delta P_x\,\delta E}{d\rho T^{1/2}}\left(\frac{\rho}{4\pi t}\right)^{d/2}\left(\frac{d-1}{(\eta+\eta_\theta)^{d/2}} + \frac{\gamma-1}{(2\eta_s)^{d/2}}\right). \quad (3.18)$$

The asymptotic value of $\psi_\kappa^k(t)$ follows immediately and reads

$$\psi_\kappa^k(t) \simeq (kT)^2 C_p^0\left(\frac{\rho}{4\pi t}\right)^{d/2}\left(\frac{d-1}{(\eta+\eta_\theta)^{d/2}} + \frac{\gamma-1}{(2\eta_s)^{d/2}}\right), \quad (3.19)$$

where $C_p^0 = (k/m)\frac{1}{2}(d+2)$ is the heat capacity at constant pressure in the perfect-gas limit.

This formula agrees perfectly well with that which has been given Ernst *et al.*,[2] and its low-density limit coincides with that of $\psi_\kappa(t)$, since

$$\chi(\rho=0) = -1 .$$

Recently Ernst *et al.* presented the result of a computation of $\psi_\kappa(t)$ for long times.[10] In our notation, their formula reads

$$\psi_\kappa(t) \underset{t\to\infty}{\simeq} \frac{(kT)^2}{dT}\left(\frac{\rho}{4\pi t}\right)\frac{d}{2}\left(\frac{C_p T(d-1)}{(\eta_\theta+\eta)^{\nu/2}} + \frac{C_p}{C_V}\frac{\partial p}{\partial\rho}\bigg|_T \frac{1}{(2\eta_s)^{d/2}}\right) . \quad (3.20)$$

The identity of (3.15) and (3.20) can be shown from the Mayer relation:

$$C_p - C_V = \frac{1}{T\chi^2}\frac{\partial p}{\partial\rho}\bigg|_T .$$

A similar calculation has been recently done by Wainwright *et al.*[11] for two-dimensional fluids. We agree with their result concerning the kinetic-kinetic contributions to ψ_η and ψ_κ. However these authors claim that the long-time behavior of ψ_κ is identical to the long-time behavior of ψ_κ^k, whereas a comparison between $\psi_\kappa(t)$ given by (3.15) and $\psi_\kappa^k(t)$, given by (3.19), clearly shows that $\psi_\kappa(t) \simeq \psi_\kappa^k(t)$ at $t\to\infty$ does not hold, except in the low-density limit, although ψ_κ and ψ_κ^k are of the same order in t at $t\to\infty$.

We do not think that the arguments based on the symmetry of the pressure field (and more generally of the scalar components of δf) given by these authors are sufficient to eliminate the kinetic-potential and potential-potential contribution to $\psi_\kappa(t)$ in comparison to $\psi_\kappa^k(t)$. Let us consider, for example, that contribution to Z_κ which is proportional to the product $\vec{u}_T\,\delta S$:

$$Z_\kappa^{V,\theta}(t) \underset{t\to\infty}{\simeq} \rho T^{1/2}\int d\vec{\alpha} \times \delta S^*(\vec{\alpha},t)\,\vec{e}_x\cdot(\vec{1} - \vec{\alpha}\,\vec{\alpha}/\alpha^2)\cdot\vec{u}(\vec{\alpha},t) . \quad (3.21)$$

In the limit $\vec{\alpha}=0$, $\delta S(\vec{\alpha},t)$ evolves according to

$$\delta S(\vec{\alpha},t) = \exp\{-[(2\pi\alpha)^2/\rho]\,\eta_\theta(t-t_1)\}\,\delta S(\vec{\alpha},t_1) . \quad (3.22)$$

From (3.22) and

$$\delta S(\vec{\alpha},t_1) \underset{\alpha\to 0,\, t_1\to\infty}{\simeq} \frac{\delta E - h\delta M}{\rho T}$$

it may seem that, near $\alpha=0$, $\delta S(\vec{\alpha},t)$ is a scalar quantity from the geometrical point of view; thus the action of geometrical transformations on $Z_\kappa^{V,\theta}$ is completely determined by $\vec{u}$. From (3.21) and the conservation relations,

$$Z_\kappa^{V,\theta}(t) \underset{t\to\infty}{\simeq} \frac{d-1}{d}\frac{\delta P_x}{T^{1/2}}(\delta E - h\delta M)\left(\frac{\rho}{4\pi(\eta+\eta_\theta)}\right)^{d/2},$$

in which the potential contributions to δE, invariant under geometrical transformation, cannot be eliminated from simple arguments of spatial symmetry. The same sort of consideration remains valid when one explains the contribution to Z_κ and ψ_κ, which is quadratic in the amplitude of the sound wave generated by the initial fluctuation in ΔV^0: The potential terms occur in scalar quantities and cannot be eliminated by geometrical considerations.

B. Long-Time Behavior of $\psi_\xi(t)$

It will be shown that the Green-Kubo integrand for the bulk viscosity has the same qualitative behavior as $\psi_{\eta,\kappa}(t)$ at $t\to\infty$. The Green-Kubo formula for the bulk viscosity reads

$$\zeta=(1/kT)\int_0^\infty dt\,\psi_\xi(t)\ . \qquad (3.23)$$

In order to deal with an infinite system, we shall use the grand-canonical form of the autocorrelation function $\psi_\xi(t)$. It is defined from the fluctuations occurring in a large part, say ΔV^0, of an infinite system and reads[9]

$$\psi_\xi(t)=(1/\Delta V^0)\langle Y_\xi(\Omega_N^0\cap\Delta V^0) \times\langle Y_\xi[\Omega_N^*(t,\Omega_N^0)]\rangle_{\{\Delta V^I\}}\rangle_{\Delta V^0}\ , \qquad (3.24)$$

where

$$Y_\xi(\Omega_N)=\sum_i\frac{1}{d}\left(m\vec v_i^{\,2}-\frac{1}{2}\sum_j\vec r_{ij}\cdot\frac{\partial V_{ij}}{\partial\vec r_i}\right) -p\Delta V^0-\frac{\partial p}{\partial\epsilon}\bigg|_\rho\delta E-\frac{\partial p}{\partial\rho}\bigg|_\epsilon\delta M\ , \qquad (3.25)$$

δM and δE being the initial fluctuations of mass and energy *inside* ΔV^0 (namely, those fluctuations that are defined by $\Omega_N^0\cap\Delta V^0$), and where $Y_\xi(\Omega_N^0\cap\Delta V^0)$ is equal to $Y_\xi(\Omega_N^0)$, except that the sum $\sum_i$ runs over particles i lying in ΔV^0. The autocorrelation function $\psi_\xi(t)$ may be put into a form very close to (2.4), which reads

$$\psi_\xi(t)=\langle Y_\xi'(\Omega_N^0)\langle Y_\xi\{\Omega_N^*(t,\Omega_N^0)\}\rangle_{\{\Delta V^I\}}\rangle_{\Delta V^0}\ , \qquad (3.26)$$

where

$$Y_\xi'(\Omega_N^0)=\sum_i\frac{\delta(\vec r-\vec r_i)}{d}\left(\frac{1}{2}m\vec v_i^{\,2}-\frac{1}{2}\vec r_{ij}\cdot\frac{\partial V_{ij}}{\partial\vec r_i}\right) -p-\frac{\partial p}{\partial\epsilon}\bigg|_\rho\left[\textstyle\sum_i\delta(\vec r-\vec r_i)-\epsilon\right] -\frac{\partial p}{\partial\rho}\bigg|_\epsilon\left[\textstyle\sum_i m\delta(\vec r-\vec r_i)-\rho\right]\ . \qquad (3.27)$$

Now we may apply the Landau-Placzeck method to compute $\psi_\xi(t)$, since Y_ξ' depends on the dynamical situation around $\vec r$. For long times, we replace $\langle Y_\xi\{\Omega_N^*(t,\Omega_N^0)\}\rangle_{\{\Delta V^I\}}$ by its average value over the local-equilibrium ensemble describing the asymptotic decay of the initial fluctuation. From (3.27) this local-equilibrium value of $\langle Y_\xi\{\Omega_N^*(t,\Omega_N^0)\rangle\rangle_{\Delta V^0}$ reads

$$Z_\xi(t)\underset{t\to\infty}{\simeq}\delta p(\vec\alpha=0,t)+\frac{\rho}{d}\int d\vec r\,\vec u^2(\vec r,t) -\delta E\frac{\partial p}{\partial\epsilon}\bigg|_\rho-\delta M\frac{\partial p}{\partial\rho}\bigg|_\epsilon\ . \qquad (3.28)$$

This value of Z_ξ does not take at once the form $\int\delta f^2(\vec r,t)\,d\vec r$. However it may be reduced to this last form by means of equilibrium relations among p, ϵ, and ρ.

For that purpose we evaluate $\delta p(\vec\alpha=0,t)$ up to the second order in δM, δE, and $\delta\vec P$ by using (2.6)–(2.8). Let $\delta^1 f$ be the variation of hydrodynamical field linear in δM, δE, and $\delta\vec P$ and $\delta^2 f$ be the variation quadratic in these fluctuations. From (2.6) and (2.8): $\delta^1\rho(\vec\alpha=0,t)=\delta M$ and $\delta^2\rho(\vec\alpha=0,t)=0$. On the other hand, $\delta^1\epsilon(\vec\alpha=0,t)=\delta E$ and $\delta^2\epsilon(\vec\alpha=0,t)=-\frac{1}{2}\rho\int d\vec r\,\vec u^2(\vec r,t)$. Writing now $\delta^2\rho$ and $\delta^2\epsilon$ in terms of $\delta^{1,2}S$ and $\delta^{1,2}p$, accounting for $\delta^2\rho(\vec\alpha=0,t)=0$ and eliminating $\delta^2 S(\vec\alpha=0,t)$, we have

$$\delta^1 p(\vec\alpha=0,t)=\frac{\partial p}{\partial\epsilon}\bigg|_\rho\delta E+\frac{\partial p}{\partial\rho}\bigg|_\epsilon\delta M \qquad (3.29)$$

and

$$\delta^2 p=\frac{\partial p}{\partial\epsilon}\bigg|_\rho\Bigg[\delta^2\epsilon-\tfrac{1}{2}(\delta^1 p)^2\left(\frac{\partial^2\epsilon}{\partial p^2}\bigg|_S-\frac{\partial\epsilon}{\partial\rho}\bigg|_p\frac{\partial^2\rho}{\partial p^2}\bigg|_S\right) -\tfrac{1}{2}(\delta^1 S)^2\left(\frac{\partial^2\epsilon}{\partial S^2}\bigg|_p-\frac{\partial\epsilon}{\partial\rho}\bigg|_p\frac{\partial^2\rho}{\partial S^2}\bigg|_p\right) +(\text{terms in }\delta^1 S\,\delta^1 p)\Bigg]\ . \qquad (3.30\text{a})$$

Using

$$\frac{\partial^2\epsilon}{\partial S^2}\bigg|_p-\frac{\partial\epsilon}{\partial\rho}\bigg|_p\frac{\partial^2\rho}{\partial S^2}\bigg|_p=\frac{\partial\rho}{\partial S}\bigg|_p^2\frac{\partial^2\epsilon}{\partial\rho^2}\bigg|_p$$

and

$$\frac{\partial^2\epsilon}{\partial p^2}\bigg|_S-\frac{\partial\epsilon}{\partial\rho}\bigg|_p\frac{\partial^2\rho}{\partial p^2}\bigg|_S=\frac{1}{C^4}\left(\frac{C^2}{\rho}-\frac{\partial\epsilon}{\partial p}\bigg|_\rho\frac{\partial C^2}{\partial\rho}\bigg|_S\right)\ ,$$

we simplify (3.30a) as

$$\delta^2 p=\frac{\partial p}{\partial\epsilon}\bigg|_\rho\delta^2\epsilon-\frac{(\delta^1 p)^2}{2\rho C^2}\left(\frac{\partial p}{\partial\epsilon}\bigg|_\rho-\frac{\rho}{C^2}\frac{\partial C^2}{\partial\rho}\bigg|_S\right) -\frac{(\delta^1 S)^2}{2}\frac{\partial p}{\partial\epsilon}\bigg|_\rho\frac{\partial\rho}{\partial S}\bigg|_p^2\frac{\partial^2\epsilon}{\partial\rho^2}\bigg|_p+(\text{terms}\sim\delta^1 S\,\delta^1 p)\ . \qquad (3.30\text{b})$$

Terms proportional to the product $\delta^1 S\,\delta^1 p$ are not written explicitly in (3.30), since they contribute as $\int\delta S(\vec r,t)\delta p(\vec r,t)\,d\vec r$ to $\delta^2 p(\vec\alpha=0,t)$ and $Z_\xi(t,\Omega_N^0\cap\Delta V^0)$ and this contribution is negligible at $t\to\infty$ with respect to $\int\delta p^2(\vec r,t)\,d\vec r$ and $\int\delta S^2(\vec r,t)\,d\vec r$.

Using now (3.29) and (3.30b) to express $\delta p(\vec\alpha=0,t)$, we obtain from (3.28)

$$Z_\xi(t,\Omega_N^0\cap\Delta V^0)\underset{t\to\infty}{\simeq}\rho\left(\frac{1}{d}-\frac{1}{2}\frac{\partial p}{\partial\epsilon}\bigg|_\rho\right)\int\vec{u}^2(\vec{r},t)d\vec{r}$$
$$-\frac{1}{2\rho C^2}\left(\frac{\partial p}{\partial\epsilon}\bigg|_\rho-\frac{\rho}{C^2}\frac{\partial C^2}{\partial\rho}\right)\bigg|_S\bigg)\int\delta p^2(\vec{r},t)d\vec{r}$$
$$-\frac{1}{2}\frac{\partial p}{\partial\epsilon}\bigg|_\rho\frac{\partial\rho}{\partial S}\bigg|_p^2\frac{\partial^2\epsilon}{\partial\rho^2}\bigg|_p\int\delta S^2(\vec{r},t)d\vec{r}\;. \quad (3.31)$$

The various coefficients in front of the integrals on the right-hand side of (3.31) vanish in the perfect-gas limit. This may be verified from

$$\epsilon\underset{\rho\to0}{\simeq}\tfrac{1}{2}pd$$

and

$$\frac{\rho}{C^2}\frac{\partial C^2}{\partial\rho}\bigg|_S\underset{\rho\to0}{\simeq}\frac{\rho}{T}\frac{\partial T}{\partial\rho}\bigg|_S\underset{\rho\to0}{\simeq}\frac{2}{d}\;.$$

Using now the laws of hydrodynamics to compute the asymptotic values of $\int\vec{u}^2(\vec{r},t)d\vec{r}$, $\int\delta p^2(\vec{r},t)d\vec{r}$, and $\int\delta S^2(\vec{r},t)d\vec{r}$, we obtain from (3.31)

$$Z_\xi(t,\Omega_N^0\cap\Delta V^0)\underset{t\to\infty}{\simeq}Z_\xi^V(t,\Omega_N^0\cap\Delta V^0)+Z_\xi^\theta(t,\Omega_N^0\cap\Delta V^0)+Z_\xi^s(t,\Omega_N^0\cap\Delta V^0)\;, \quad (3.32)$$

where

$$Z_\xi^V(t,\Omega_N^0\cap\Delta V^0)=\frac{d-1}{d}\left(\frac{\rho}{8\pi\eta t}\right)^{d/2}\frac{(\delta\vec{P})^2}{\rho}\left(\frac{1}{d}-\frac{1}{2}\frac{\partial p}{\partial\epsilon}\bigg|_\rho\right), \quad (3.33a)$$

$$Z_\xi^\theta(t,\Omega_N^0\cap\Delta V^0)=-\frac{1}{2}\frac{\partial p}{\partial\epsilon}\bigg|_\rho\frac{\partial\rho}{\partial S}\bigg|_p^2\frac{\partial^2\epsilon}{\partial\rho^2}\bigg|_p\frac{(\delta E-h\delta M)^2}{\rho^2T^2}\left(\frac{\rho}{8\pi\eta_\theta t}\right)^{d/2}, \quad (3.33b)$$

and

$$Z_\xi^s(t,\Omega_N^0\,\Delta V^0)=\frac{1}{2\rho C^2}\left(\frac{1}{d}-\frac{\partial p}{\partial\epsilon}\bigg|_\rho-\frac{\rho}{C}\frac{\partial C}{\partial\rho}\bigg|_S\right)\left(\frac{\rho}{8\pi\eta_s t}\right)^{d/2}\times\left[\frac{C^2(\delta\vec{P})^2}{d}+\frac{\partial p}{\partial\epsilon}\bigg|_\rho^2\left(\delta E-\frac{\partial\epsilon}{\partial\rho}\bigg|_p\delta M\right)^2\right]. \quad (3.33c)$$

Replacing now in (3.26) $\langle Y_\xi\{\Omega_N^*(t,\Omega_N^0)\}\rangle_{\{\Delta V^t\}}$ by its asymptotic value $Z_\xi(t,\Omega_N^0\cap\Delta V^0)$, we obtain

$$\psi_\xi(t)\underset{t\to\infty}{\simeq}\psi_\xi^V(t)+\psi_\xi^\theta(t)+\psi_\xi^s(t)\;, \quad (3.34)$$

where

$$\psi_\xi^V(t)=\langle Y_\xi'(\Omega_N^0)Z_\xi^V(t,\Omega_N^0\cap\Delta V^0)\rangle_{\Delta V^0}=2(kT)^2(d-1)\left(\frac{\rho}{8\pi\eta t}\right)^{d/2}\left(\frac{1}{d}+\frac{\chi(\gamma-1)}{2}\right)^2, \quad (3.35a)$$

$$\psi_\xi^\theta(t)=\frac{(\gamma-1)^2\chi^2}{2}\left(\frac{\rho}{8\pi\eta_\theta t}\right)^{d/2}\left(\frac{T}{C_p}\frac{\partial C_p}{\partial T}\bigg|_p-\rho\chi T\frac{\partial C_p}{\partial p}\bigg|_T\right)^2(kT)^2 \quad (3.35b)$$

and where

$$\psi_\xi^s(t)=\frac{(kT)^2}{2}\left(\frac{\rho}{8\pi\eta_s t}\right)^{d/2}\left(\frac{1}{d}-\frac{\partial p}{\partial\epsilon}\bigg|_\rho-\frac{\rho}{C}\frac{\partial C}{\partial\rho}\bigg|_S\right)^2. \quad (3.35c)$$

These expressions have been obtained by using the fluctuation formulas derived in Appendix B, and the thermodynamical relations

$$\frac{\partial p}{\partial\epsilon}\bigg|_\rho=-\chi(\gamma-1),$$

$$\frac{\partial^2\epsilon}{\partial\rho^2}\bigg|_p=\rho\chi^2C_pT\left(\frac{T}{C_p}\frac{\partial C_p}{\partial T}\bigg|_p-\rho\chi T\frac{\partial C_p}{\partial p}\bigg|_T\right).$$

The coefficient

$$\frac{1}{d}-\frac{\partial p}{\partial\epsilon}\bigg|_\rho-\frac{\rho}{C}\frac{\partial C}{\partial\rho}\bigg|_S$$

can be expressed by means of χ, C_p, and C_V and their derivatives with respect to p and T as

$$\frac{1}{d}-\frac{\partial p}{\partial\epsilon}\bigg|_\rho-\frac{\rho}{C}\frac{\partial C}{\partial\rho}\bigg|_S=\frac{1}{d}+\frac{\chi(\gamma-1)}{2}+\frac{1}{2\chi C_p}\frac{\partial}{\partial T}\bigg|_p[C_p\gamma^2\chi^2(\gamma-1)]-\frac{\rho T}{2}\frac{\partial}{\partial p}\bigg|_T[\gamma\chi^2C_p(\gamma-1)]\;.$$

Our asymptotic value of $\psi_\xi(t)$ agrees with that which was recently published by Ernst *et al.*[10]

IV. DIVERGENCE OF GREEN-KUBO INTEGRALS IN TWO-DIMENSIONAL FLUIDS

Since we have shown that the Green-Kubo integrands for η, κ, and ζ decay as $t^{-d/2}$ at $t\to\infty$, we should conclude that the Green-Kubo integrals diverge logarithmically for two-dimensional systems. One may draw from this fact two different conclusions.

(a) One (or eventually more) of the assumptions that are necessary to obtain this result is wrong, but transport coefficients exist (and Green-Kubo integrals converge) in two-dimensional fluids.

(b) Transport coefficients do not exist in two-dimensional fluids.

Let us examine these two possibilities.

Conclusion (a) is rather difficult to discuss. However, it might be interesting to recall the main assumptions used to find the $t^{-d/2}$ behavior. For long times the motion of the many-body system is described by the laws of hydrodynamics, and these laws are linearized around the equilibrium state of the fluid. This use of hydrodynamics is justified by noticing that in the hydrodynamical limit (which is equal to the slowly varying hydrodynamical field) the Liouville equation may be expanded in powers of the derivatives of $\delta f(\vec{r}, t)$ and the usual equation of hydrodynamics are recovered. But with our knowledge, the precise manner in which the solution of the equations of hydrodynamics approximates the solution of the Liouville equation is yet unknown.

The second assumption (linearization of the laws of hydrodynamics) also poses a difficult question, since we do not know how the solution of the *nonlinearized* hydrodynamical equations approximate to the solution of these *linearized* equations.

Assuming that conclusion (b) is valid (that transport coefficients do not exist in two-dimensional fluids), we face two connected problems: How do Green-Kubo integrands behave asymptotically in two-dimensional fluids? And what sort of laws replace the laws of Fourier and Newton in two-dimensional fluids? In fact, we cannot assert at the same time that Green-Kubo integrands behave as t^{-1} at $t \to \infty$ and that the laws of Fourier and Newton are wrong, since this t^{-1} behavior was established by using the transport laws in their usual form. These transport laws can be modified in two different ways:

(i) The relation between a thermodynamical force (here "force" has the sense given by Onsager) and the corresponding flux is no longer local but remains linear. This has been investigated by Wainwright *et al.*[11] and leads to

$$\psi_{\eta,\kappa}(t) \underset{t\to\infty}{\sim} 1/t(\ln t)^{1/2} .$$

(ii) The relation between a thermodynamical force and the corresponding flux is no more linear, but remains local in space and time. This possibility of such nonlinear transport laws is exhibited in the following example.

The velocity of a given particle submitted in a fluid to a small external force $\vec{F}$ is usually given by the transport law[12]

$$\vec{u} \underset{\vec{F}\to 0}{\simeq} \frac{D}{kT}\vec{F} , \tag{4.1}$$

where D is the self-diffusion coefficient of the particle. In the Einstein limit, the particle is assumed to be a large rigid body and its interaction with the surrounding fluid is handled hydrodynamically. In the case of a large sphere, D is given by the well-known Stokes-Einstein formula. In two-dimensional fluids, the situation is different, since the viscous drag on a large circle moving with a constant velocity is given near $\vec{u} = 0$ (if we assume the existence of the shear viscosity) by[13]

$$\vec{F} \underset{\vec{u}\to 0}{\simeq} \frac{4\pi\vec{u}\eta}{\ln|\vec{u}|} . \tag{4.2}$$

[In fact the Oseen solution of this problem yields

$$\vec{F} = \frac{4\pi\vec{u}\eta}{\frac{1}{2} - c - \ln(u\rho\delta/8\eta)} ,$$

where δ is the diameter of the circle and c the Euler constant; (4.2) is recovered by taking the limit $\vec{u} \to 0$ in this expression of the drag.]

Expressing now $\vec{F}$ as a function of $\vec{u}$, we have from (4.2)

$$\vec{u} \underset{\vec{F}\to 0}{\simeq} \frac{-\vec{F}\ln|\vec{F}|}{4\pi\eta} . \tag{4.3}$$

In (4.3), $\vec{F}$ is the external force and is equal and opposite to the drag.

Using the Landau-Placzeck method, it can be shown[1,2] that the Green-Kubo integral for the self-diffusion coefficient diverges logarithmically in two-dimensional fluids. Thus it is worth emphasizing that, in a particular case, the linear transport relation (4.1) is replaced by the nonlinear transport law (4.2) when the Green-Kubo integral for the transport coefficient diverges. However this nonlinear transport law cannot take the form (4.3) if the shear viscosity does not exist.

The above statements (linear and nonlocal transport law versus nonlinear and local transport law) are not mutually exclusive.

Consider, for instance, the functional

$$\Gamma\{F(t)\} = \int_{-\infty}^{t} dt' \frac{e^{-t'F^2(t')}}{[(t-t')^2 + \tau^2]^{1/2}} F(t') , \tag{4.4}$$

which becomes in the limit $F \to 0$

$$\frac{\delta\Gamma}{\delta F}\bigg|_{F=0} F \equiv \int_{-\infty}^{t} dt' \frac{F(t')}{[(t-t')^2 + \tau^2]^{1/2}} \tag{4.5}$$

and in the static limit [$F(t)$ constant]

$$\Gamma\{\text{constant}\, F\} = \tfrac{1}{2}\pi[H_0(\tau F^2) - N_0(\tau F^2)] , \tag{4.6}$$

where H_0 and N_0 are, respectively, the Struve and Neumann's functions.[14] Near $F = 0$, (4.6) becomes

$$\Gamma\{\text{constant}\, F\} \underset{F\to 0}{\simeq} -2F\ln|F| . \tag{4.7}$$

Suppose now that in two-dimensional fluids the current is related to the thermodynamical force through a relation of the form (4.4). In the limits considered above, we may deduce from this unique functional relation either a linear (but nonlocal) transport law (4.5) or a local (but nonlinear) transport law [(4.6) and (4.7)] (obviously there is no claim that this particular functional is the actual form of transport laws in two-dimensional fluids.)

As a conclusion it should be emphasized that any attempt to find a nonlinear and nonlocal functional relation between forces and fluxes encounters great difficulties, since, in particular, equations of hydrodynamics cannot be linearized and simply solved if we give up the linearity of transport laws.

V. LOW-FREQUENCY LONG-WAVELENGTH BEHAVIOR OF TRANSPORT COEFFICIENTS IN THREE-DIMENSIONAL FLUIDS

In Sec. III, we were able to find the asymptotic value of the Green-Kubo integrands, provided that $d>2$.

In three dimensions this will allow us to find the first term in the low-frequency expansion of these transport coefficient. This result will be generalized to the low-frequency long-wavelength expansion of transport coefficients.

Define

$$\xi(\omega)=(1/kT)\int_0^\infty dt\, e^{-i\omega t}\psi_\xi(t) \qquad (5.1)$$

as a frequency-dependent transport coefficient ($\xi=\eta, \kappa$, or ζ). From (3.12)–(3.15) and (3.4)–(3.5), we know that in three-dimensional fluids

$$\psi_\xi(t) \underset{t\to\infty}{\simeq} kTA_\xi t^{-3/2}, \qquad (5.2)$$

where

$$A_\eta=A_\eta^s+A_\eta^V, \qquad (5.3a)$$

$$A_\kappa=A_\kappa^s+A_\kappa^{V,\theta}, \qquad (5.3b)$$

$$A_\zeta=A_\zeta^V+A_\zeta^\theta+A_\zeta^s, \qquad (5.3c)$$

and where

$$A_\eta^s=\frac{kT}{15}\left(\frac{\rho}{8\pi\eta_s}\right)^{3/2}, \qquad (5.4a)$$

$$A_\eta^V=\frac{7kT}{15}\left(\frac{\rho}{8\pi\eta}\right)^{3/2}, \qquad (5.4b)$$

$$A_\kappa^s=\frac{C_pkT\chi^2(\gamma-1)}{3}\left(\frac{\rho}{8\pi\eta_s}\right)^{3/2}, \qquad (5.5a)$$

$$A_\kappa^{V,\theta}=\frac{2C_pkT}{3}\left(\frac{\rho}{4\pi(\eta+\eta_\theta)}\right)^{3/2}, \qquad (5.5b)$$

$$A_\zeta^V=4kT\left(\frac{\rho}{8\pi\eta}\right)^{3/2}\left(\frac{1}{3}+\frac{\chi(\gamma-1)}{2}\right)^2, \qquad (5.6a)$$

$$A_\zeta=\frac{kT\chi^2(\gamma-1)^2}{2}\left(\frac{\rho}{8\pi\eta_\theta}\right)^{3/2}\left(\frac{T}{C_p}\frac{\partial C_p}{\partial p}\bigg|_p-\rho\chi T\frac{\partial C_p}{\partial p}\bigg|_T\right)^2, \qquad (5.6b)$$

$$A_\zeta^s=\frac{kT}{2}\left(\frac{\rho}{8\pi\eta_s}\right)^{3/2}\left(\tfrac{1}{3}+\chi(\gamma-1)-\frac{\rho}{C}\frac{\partial C}{\partial\rho}\bigg|_S\right)^2. \qquad (5.6c)$$

Consider now the quantity

$$\xi(\omega)-\xi=(1/kT)\int_0^\infty dt\,(e^{-i\omega t}-1)\,\zeta_\xi(t), \qquad (5.7)$$

where ξ stands for $\xi(\omega=0)$. Taking $|\omega|\ t=t'$ as the integration variable in (5.7), we deduce from (5.2)

$$\xi(\omega)-\xi \underset{\omega\to 0}{\simeq} -|2\pi\omega|^{1/2}A_\xi(1+i\,\mathrm{sgn}\omega), \qquad (5.8)$$

where $\mathrm{sgn}\omega=\omega/|\omega|$.

This $\omega^{1/2}$ shift in the low-frequency dependence of transport coefficients has been already found for the self-diffusion coefficient of a large sphere immersed in a fluid[15]; it is a simple consequence of the fact that the drag on a sphere executing small translatory oscillations with a frequency ω in an incompressible fluid is shifted by a quantity of order $\omega^{1/2}$ with respect to the usual stationary Stokes drag.[16]

The presence of a real and an imaginary part in terms of order $\omega^{1/2}$ follows immediately from causality, since $\xi(\omega)$ is a response function. Let $\xi'(\omega)$ and $\xi''(\omega)$ be the real and imaginary part of $\xi(\omega)$ (recall that $\xi=\eta$, κ, or ζ). The Krâmers-Kronig rules relate ξ' and ξ'' as

$$\xi'(\omega)-\xi'(\omega=0)=-\frac{1}{\pi}\,\mathcal{P}\int_{-\infty}^{+\infty}\frac{du\,\xi''(\omega u)}{u(1-u)}, \qquad (5.9)$$

where $\mathcal{P}$ means the Cauchy principal value. Expanding $\xi''(\omega u)$ near $\omega=0$, one deduces immediately from (5.9) that, if $\xi''(\omega)\underset{\omega\to 0}{\sim}|\omega|^{1/2}$, then

$$\xi'(\omega)-\xi'(\omega=0)\underset{\omega\to 0}{\sim}|\omega|^{1/2},$$

where the coefficients of the $\omega^{1/2}$ terms in ξ' and ξ'' are related in such a way that

$$\xi(\omega)-\xi(0)\underset{\omega\to 0}{\sim}|\omega|^{1/2}(1+i\,\mathrm{sgn}\omega)\,(\text{real coeff.}).$$

The factor $\mathrm{sgn}\omega$ after i is needed to satisfy

$$\xi^*(\omega)=\xi(-\omega).$$

The generalization of (5.8) at any dimensionality $d>2$ is carried out in Appendix C.

The low-frequency expansion of transport coefficient given in (5.8) is not directly useful in the study of hydrodynamical phenomena: Hydrodynamical perturbations that may be studied by means of transport coefficients have a frequency and a wave number, these two quantities being connected to each other. More precisely, in hydrodynamics one studies three classes of linear perturbations.

(i) Sound waves, where the frequency is related to the wave number through the expansion

$$\omega_s(\beta)\underset{\beta\to 0}{=}\pm 2\pi\beta C-4i(\pi^2/\rho)\beta^2\eta_s. \qquad (5.10)$$

(ii) Diffusion phenomena (of vorticity and entropy), where the frequency (actually a real decrement) is related to the wave number by

$$\omega_v(\beta)\underset{\beta\to 0}{\simeq}-4i(\pi^2/\rho)\beta^2\eta \qquad (5.11a)$$

or

$$\omega_\theta(\beta) \underset{\beta\to 0}{\simeq} -4i(\pi^2/\rho)\beta^2\eta_\theta \,. \qquad (5.11b)$$

(iii) Static diffusion phenomena such as, for example, the thermal conduction between two parallel plates at different temperatures and at a distance much larger than any microscopic scale of length. In this last case the frequency is equal to zero.

We shall extend (5.8) to find the shift of η, κ, and ζ near $\omega=\beta=0$ when ω and β are related according to one of the above relations. For that purpose we define frequency-wavelength-dependent transport coefficients by[17]

$$\xi(\beta,\omega)=\frac{1}{kT}\int d\vec{r}\int_0^\infty dt\, e^{-i(\omega t-2\pi\vec{\beta}\cdot\vec{r})}\,\psi_\xi(t,\vec{r}) \,, \qquad (5.12)$$

where

$$\psi_\xi(t,\vec{r})=\langle \textstyle\sum_i X_{i,\xi}\,\delta(\vec{r}_i^{\,0})\sum_j X_{j,\xi}[\Omega_N^*(t,\Omega_N^0)]\,\delta[\vec{r}_j(t)-\vec{r}]\rangle \,, \qquad (5.13)$$

where $\vec{r}_i^{\,0}$ and $\vec{r}_j(t)$ are, respectively, the positions of particles i and j at point Ω_N^0 and $\Omega_N^*(t,\Omega_N^0)$ of phase space.

Before considering situations where $\beta\neq 0$, let us recover the $|\omega|^{1/2}$ shift in the low-frequency expansions of $\xi(\omega)\equiv\xi(\omega,\beta=0)$. This method of calculation will be used afterwards to expand $\xi(\omega,\beta)$ near $\beta=0$. This $|\omega|^{1/2}$ shift originates from the hydrodynamical contribution to $\psi_\xi(t)$ given by (2.5). Since $Z_\xi(t,\Omega_N^0\cap\Delta V^0)\sim\int d\vec{\alpha}\,|\delta f(\vec{\alpha},t)|^2$ the hydrodynamical contribution from (5.1) to $\xi(\omega)$ is

$$\xi^H(\omega)=\sum_{\lambda,\nu}\xi^H_{\lambda,\nu}(\omega) \,, \qquad (5.14)$$

where

$$\xi^H_{\lambda,\nu}(\omega)\propto\int_{\alpha<\alpha_0}\frac{d\vec{\alpha}}{\omega+\omega_\lambda(\alpha)+\omega_\nu(\alpha)}\,\frac{1}{\Delta V^0}\times\langle\sum_{i,\vec{r}_i\in\Delta V^0}X_{i,\xi}\,\delta f_\lambda(\vec{\alpha},t_1)\,\delta f_\nu^*(\vec{\alpha},t_1)\rangle_{\Delta V^0} \,. \qquad (5.15)$$

In (5.15) $\omega_{\lambda,\nu}(\alpha)$ are the frequencies of the hydrodynamical modes ($\lambda,\nu=v,s,\theta$), $\delta f_{\lambda,\nu}$ are some linear combinations of the components of the hydrodynamical field, and the integration domain is a sphere of radius α_0, a fixed wave number, as small as wanted. In fact, hydrodynamics is an asymptotic theory that is valid for vanishingly small wavenumber.

Considering now cases where $\omega_\lambda(\alpha)+\omega_\nu(\alpha)$ is of order α^2 near $\alpha=0$, which implies from (5.10) and (5.11) that λ, $\nu=v,\theta$ or $\lambda,\nu=s$, and taking $\vec{\alpha}'=\vec{\alpha}\,|\omega|^{-1/2}$ as the integration variable, we deduce from (5.15)

$$\xi^H_{\lambda,\nu}(\omega)-\xi^H_{\lambda,\nu}(\omega=0)\underset{\omega\to 0,d=3}{\sim}|\omega|^{1/2}\int\frac{d\vec{\alpha}'}{\alpha'^2[1+(i\alpha'^2/\rho)(\eta_\lambda+\eta_\nu)]}\,\frac{1}{\Delta V^0}\times\langle\sum_{i,\vec{r}_i\in\Delta V^0}X_{i,\xi}\,\delta f_\lambda(0,t_1)\,\delta f_\nu(0,t_1)\rangle_{\Delta V^0} \,, \qquad (5.16)$$

which agrees with (5.8).

This calculation can be extended to frequency- and *wave-number*-dependent transport coefficients. For that purpose, let us define at first the hydrodynamical contribution to a transport coefficient $\xi(\beta,\omega)$. Let $\xi^H(\beta,\omega)$ be this contribution, which is the Fourier transform in space and time of the autocorrelation function $(1/kT)\psi_\xi^H(t,\vec{r})$, which itself is defined as

$$\psi_\xi^H(t,\vec{r})=\langle\textstyle\sum_i\delta(\vec{r}_i^{\,0})X_{i,\xi}(\Omega_N^0)\,Z_\xi(t,\vec{r}_i\,\Omega_N^0\cap\Delta V^0)\rangle \,, \qquad (5.17)$$

where $Z_\xi(t,\vec{r})$ is the local equilibrium value of $\sum_j X_{j,\xi}\,\delta(\vec{r}-\vec{r}_j(t))$. Reasoning very similar to that which led to (3.6b), (3.9), and (3.31) gives

$$Z_\eta(t,\vec{r})=\rho\,u_x(\vec{r},t)\,u_y(\vec{r},t) \,, \qquad (5.18)$$

$$Z_\kappa(t,\vec{r})=\rho T^{-1/2}u_x(\vec{r},t)\,\delta h(\vec{r},t) \,, \qquad (5.19)$$

and

$$Z_\zeta(t,\vec{r})=\rho\left(\frac{1}{3}-\frac{1}{2}\frac{\partial p}{\partial\epsilon}\bigg|_\rho\right)u^2(\vec{r},t)-\frac{1}{2}\frac{\partial p}{\partial\epsilon}\bigg|_\rho\,\frac{\partial p}{\partial S}\bigg|_p^2\times\frac{\partial^2\epsilon}{\partial\rho^2}\bigg|_p\,\delta S^2(\vec{r},t)-\frac{1}{2\rho C^2}\left(\frac{\partial p}{\partial\epsilon}\bigg|_\rho-\frac{\rho}{C^2}\,\frac{\partial C^2}{\partial\rho}\bigg|_S\right)\delta p^2(\vec{r},t), \quad d=3. \qquad (5.20)$$

In three-dimensional fluids, the low-frequency expansion of $\xi^H(\omega)$ and $\xi(\omega)$ give the same first-order term, namely

$$\xi^H(\omega)-\xi^H(\omega=0)\simeq\xi(\omega)-\xi\sim|\omega|^{1/2}, \quad \omega\to 0 \,.$$

Generalizing this property to the low-frequency long-wavelength expansion of $\xi(\beta,\omega)$, we shall assume that

$$\xi^H(\beta,\omega)-\xi^H(0,0)\simeq\xi(\beta,\omega)-\xi, \quad \omega,\beta\to 0 \,. \qquad (5.21)$$

Since $Z_\xi(t,\vec{r})\sim\delta f^2(t,\vec{r})$, the hydrodynamical contribution to $\xi^H(\beta,\omega)$ reads

$$\xi^H(\beta,\omega)=\sum_{\lambda,\nu}\xi^H_{\lambda,\nu}(\beta,\omega) \,,$$

where λ, $\nu=v,s,\theta$ and where

$$\xi^H_{\lambda,\nu}(\beta,\omega)\propto\int_{\alpha<\alpha_0}\frac{d\vec{\alpha}}{i[\omega+\omega_\lambda(\vec{\alpha}+\frac{1}{2}\vec{\beta})+\omega_\nu(\vec{\alpha}-\frac{1}{2}\vec{\beta})]}\,\frac{1}{\Delta V^0}\times\langle\sum_{i,\vec{r}_i\in\Delta V^0}X_{i,\xi}(\Omega_N^0)\,\delta f_\lambda(\vec{\alpha}+\tfrac{1}{2}\vec{\beta},t_1)\times\delta f_\nu(-\vec{\alpha}+\tfrac{1}{2}\vec{\beta},t_1)\rangle_{\Delta V^0} \,. \qquad (5.22)$$

Because we have deduced from (5.15) the $|\omega|^{1/2}$ shift in the expansion of $\xi^H(\omega)$ near $\omega=0$, we may derive from (5.22) the value of $\xi^H(\beta,\omega)-\xi^H$ near $\omega=\beta=0$ (1) in the static limit ($\omega=0$, $\beta\to 0$) and in the diffusion limit ($\omega,\beta\to 0$, $\omega\sim\beta^2$) (this will be done in Sec. VA) and (2) in the limit defined by Eq. (5.10) ($\omega,\beta\to 0$, $\omega\simeq\pm 2\pi\beta C$) (this will be done in Sec. VB).

A. Long-Wavelength Expansion of ξ^H in Static Limit and for Diffusion Phenomena

We shall prove that the long-wavelength expansion of $\xi^H(\beta)\equiv\xi^H(\beta,\omega=0)$ starts as

$$\xi^H(\beta)=\xi^H(\beta=0)+O(\beta^{1/2}) \ .$$

This term in $\beta^{1/2}$ correspondes to a large-distance behavior in $r^{-7/2}$ of

$$\psi_\xi(r)\equiv\int_0^\infty dt\ \psi_\xi(t,r) \ . \qquad (5.23)$$

Further, in the limit of diffusion phenomena ($\omega\sim\beta^2$ at $\beta\to 0$), it will be seen that

$$\xi^H(\beta,\omega)-\xi^H \underset{\beta\to 0,\,\omega\sim\beta^2}{\simeq} \xi^H(\beta)-\xi^H \ . \qquad (5.24)$$

According to (5.22), $\xi^H(\beta)$ is the sum of various terms $\xi^H_{\lambda,\nu}(\beta)$ (recall that $\lambda,\nu=v,\theta,s$). We shall demonstrate at first that, near $\beta=0$,

$$\xi^H_{s,s}(\beta)-\xi^H_{s,s}\sim\beta^{1/2} \ , \qquad (5.25)$$

while

$$\xi^H_{\lambda,\nu}(\beta)-\xi^H_{\lambda,\nu}\sim\beta \ , \qquad (5.26)$$

if $\lambda,\nu=v,\theta$.

In order to show (5.25), we start from (5.22), take $\vec{\alpha}'=\vec{\alpha}\beta^{-1/2}$ as the variable of integration, use (5.10), and

$$\omega_s(\vec{\alpha}+\tfrac{1}{2}\beta)+\omega_s(-\vec{\alpha}+\tfrac{1}{2}\beta) \simeq \pm 2\pi\beta C\,\vec{\alpha}'\cdot\vec{\beta}/\alpha'-(8i\pi^2/\rho)\,\alpha'^2\beta\eta_s \ ,$$
$$\times\ \vec{\alpha},\vec{\beta}\to 0,\ \vec{\alpha}'=\vec{\alpha}\,\beta^{-1/2}\times\text{const}$$

which is true, provided one considers the sum of two different determinations of $\omega_s(\beta)$, and obtain, by carrying the limit $\beta\to 0$ through the integrand,

$$\xi^H_{s,s}(\beta)-\xi^H_{s,s}\underset{\beta\to 0}{\simeq}-\tfrac{1}{3}\pi^{1/2}(2\pi\beta C)^{1/2}A^s_\xi \qquad (5.27)$$

where the coefficients $A^s_{\eta,\kappa,\xi}$ are defined in (5.4a), (5.5a), and (5.6c).

In order to expand $\xi^H_{\theta,\theta}(\beta)$ near $\beta=0$, we take $\vec{\alpha}'=\vec{\alpha}\beta^{-1}$ as the integration variable in (5.22), carry out the expansion at first order in β, and obtain

$$\xi^H_{\theta,\theta}(\beta)-\xi^H_{\theta,\theta}\sim\beta\int\frac{d\vec{\alpha}'}{\alpha'^2[1+(8\pi^2\alpha'^2/\rho)\eta_\theta]} \ ,$$

which proves (5.26), since this calculation is extended straightforwardly to any contribution $\xi^H_{\lambda,\nu}$ such that $\lambda,\nu=v,\theta$. Very similar calculations give

$$\xi^H(\beta,\omega)-\xi^H \underset{\beta\to 0,\,\omega\sim\beta^2}{\simeq} \xi^H(\beta)-\xi^H\sim\beta^{1/2} \ .$$

From (5.21) and (5.27)

$$\xi(\beta)-\xi\simeq-\tfrac{1}{3}\pi^{1/2}(2\pi\beta C)^{1/2}A^s_\xi \ . \qquad (5.28)$$

This long-wavelength behavior of $\xi(\beta)$ is related to the large-distance behavior of

$$\psi_\xi(\vec{r})\equiv\int_0^\infty dt\,\psi_\xi(\vec{r},t)=kT\int d\vec{\beta}\,e^{2i\pi\vec{\beta}\cdot\vec{r}}\ \xi(\beta) \ . \qquad (5.29)$$

In fact, inserting into (5.29) the long-wavelength expansion of $\xi(\beta)$ given by (5.28), one obtains contributions to $\psi_\xi(r)$ singular at $r=0$, plus the value of $\psi_\xi(r)$ at large r which reads[18,19]

$$\psi_\xi(r)\underset{r\to\infty}{\simeq}\frac{A^s_\xi}{2\pi}\ \frac{C^{1/2}}{(2r)^{7/2}} \ . \qquad (5.30)$$

It is not very surprising to see that the long-range behavior of $\psi_\xi(r)$ is defined by the part of δf that evolves as a sound wave. In fact, it is obvious that sound waves may propagate perturbations over larger distances than diffusion modes do. This statement may be confirmed by the following reasoning.

An obvious extension of the Landau-Placzeck theory shows that the behavior of $\langle\sum_i\delta(\vec{r}_i^0)X_i^{(0)}\sum_j\int_0^\infty dt X_j^{(t)}\times\delta[\vec{r}-\vec{r}_j(t)]\rangle$ at large r is equal to $\langle\sum_i\delta(\vec{r}_i^0)X_i^{(0)}\times\int_0^\infty dt\,Z(t,\vec{r},\Omega_N^0\cap\Delta V^0)\rangle_{\Delta V^0}$.

From (5.18)–(5.20) and $Z_\xi(t,\vec{r})\sim\delta f^2(\vec{r},t)$,

$$\psi_\xi(\vec{r})\underset{r\to\infty}{\sim}\int_0^\infty dt\,\delta f^2(\vec{r},t) \ . \qquad (5.31)$$

Furthermore, the value of $\delta f(\vec{r},t)$ at large r may be computed from the linearized equations of hydrodynamics, which give for the sound wave component of δf

$$\delta f_s(r,t)\underset{r\to\infty}{\sim}\frac{(r-Ct)}{rt^{3/2}}e^{-(r-Ct)^2\rho/4\eta_s t} \ . \qquad (5.32)$$

[The proof of (5.32) may be found in Sec. VI.] Then the contribution to $\psi_\xi(r)$ quadratic in δf_s reads

$$\psi_{\xi;s,s}\underset{r\to\infty}{\sim}\frac{1}{r^2}\int_0^\infty dt\frac{(r-Ct)^2}{t^3}e^{-(r-Ct)^2\rho/2\eta_s t} \ . \qquad (5.33)$$

For a given value of r this integral is concentrated around $t=r/c$ and extends over an interval of time of order $r^{1/2}$. Thus, $\psi_{\xi;s,s}\sim(\Delta t)^3/r^5\sim r^{-7/2}$, which agrees with (5.30). On the other hand, a diffusion component of $\delta f(r,t)$ evolves according to the usual Gaussian law, which yields $\delta f_v(r,t)\sim t^{-3/2}e^{-r^2\rho/4\eta t}$. The corresponding contribution to $\psi_{\xi;v,v}(r)$ reads

$$\psi_{\xi;v,v}(r)\underset{r\to\infty}{\sim}\int\frac{dt}{t^3}\,e^{-\rho r^2/2\eta t}\sim r^{-4}$$

and may be neglected with respect to $\psi_{\xi;s,s}(r)$ at

$r \to \infty$. In the above reasoning we have not directly used the assumption (5.20), whose validity is thus confirmed in the static limit.

B. Long-Wavelength Expansion of $\xi[\beta, \omega_s(\beta)]$

The transport coefficient $\xi(\beta, \omega_s(\beta))$ may be expanded near $\beta = 0$ in a manner very similar to that used in Sec. V A: From (5.22) $\xi^H_{\lambda,\nu}(\beta, \omega_s) - \xi^H_{\lambda,\nu}$ may be expressed as a single integral over $\vec{\alpha}$ and calculated near $\beta = 0$ by putting $\vec{\alpha}' = \vec{\alpha}\beta^{-1/2}$ as a variable of integration. One obtains in this way

$$\xi(\beta, \pm 2\pi\beta C) - \xi \underset{\beta \to 0}{\simeq} -(2\pi)^{1/2}(2\pi\beta C)^{1/2} A'_\xi(1 \pm i) , \tag{5.34}$$

where

$$A'_\eta = A^v_\eta + (2^{3/2}/3)A^s_\eta , \tag{5.35a}$$

$$A'_\kappa = A^{v,\theta}_\kappa + (2^{3/2}/3)A^s_\kappa , \tag{5.35b}$$

$$A'_\xi = A^v_\xi + A^\theta_\xi + (2^{3/2}/3)A^s_\xi , \tag{5.35c}$$

where the quantities on the right-hand side of (5.35) are defined in (5.4)–(5.6).

Starting from the low-frequency long-wavelength expansions of transport coefficients found in this section, we shall be able to derive some hydrodynamical properties beyond the Navier-Stokes order.

VI. HYDRODYNAMICS BEYOND NAVIER-STOKES ORDER

Previously we have used Navier-Stokes equations in their usual form, in particular, the hydrodynamical modes have been studied by means of transport coefficients at zero frequency and wave number. In order to work at smaller wavelengths (namely, beyond the Navier-Stokes order), we have to consider frequency- and wavelength-dependent transport coefficients. Accordingly, the relation that gives $\omega_s(\beta)$ becomes

$$\omega_s(\beta) = 2\pi\beta C - [i(2\pi\beta)^2/\rho]\eta_s(\beta, \omega) , \tag{6.1}$$

where

$$\eta_s(\beta, \omega) = \tfrac{1}{2}[\tfrac{4}{3}\eta(\beta, \omega) + \zeta(\beta, \omega) + \kappa(\beta, \omega)(\gamma - 1)/C_p] . \tag{6.2}$$

However, it is known that, beyond the Navier-Stokes order, all transport phenomena cannot be accounted for through frequency- and wave-number-dependent transport coefficients defined as in (5.12).[20] We shall admit that these new transport effects yield corrections to $\omega_{s,\theta,V}(\beta)$ that are of order β^3 near $\beta = 0$ and may thus be neglected with respect to corrections considered below.

Using (6.1) and similar relations for $\omega_{V,\theta}(\beta)$, together with the expansions of $\xi(\beta, \omega)$ near $\beta = \omega = 0$ given in Sec. V, we shall find those terms which follow the order β^2 in expansions of $\omega_{s,\theta,V}(\beta)$ near $\beta = 0$. These terms "beyond the Navier-Stokes order" will be shown to be of order $\beta^{5/2}$. A simple consequence of this result will then be discussed. Let us define

$$G_{V,\theta,s}(\vec{R}, t) = \int d\vec{\beta}\, e^{-2i\pi\vec{\beta}\cdot\vec{R}}\, e^{-i\omega_{V,\theta,s}(\beta)t} \tag{6.3}$$

as the Green functions of hydrodynamical modes (these functions describe the hydrodynamical field created at any positive time by an initially singular perturbation of δf). At the Navier-Stokes order (in fact, in some well-defined asymptotic limit), these Green functions are obtained by inserting into (6.3) the values of $\omega_{s,V,\theta}(\beta)$ given in (5.10) and (5.11). The following order in this expansion of $G_{S,\theta,V}$ is obtained in a similar manner from the $\beta^{5/2}$ term in the expansion of $\omega_{s,\theta,V}(\beta)$.

In Sec. VI A we shall expand near $\beta = 0$ the frequency of a sound wave and compare our results with some recent works. In Sec. VI B we shall study the case of the diffusion modes.

A. Sound Waves beyond Navier-Stokes Order

Using (6.1), we shall expand $\omega_s(\beta)$ beyond the Kirchhoff damping rate, then compare this result with the sound dispersion found in the low-density limit and near the liquid-gas critical point, both of which were the subject of recent investigations. Furthermore, we shall derive, as announced, the first correction to the Navier-Stokes value of the Green function for sound waves.

Equation (6.1) yields straightforwardly

$$\omega_s(\beta) \mp 2\pi\beta C + (4i\pi^2/\rho)\eta_s\beta^2 \underset{\beta \to 0}{\simeq} -(4i\pi^2/\rho)\beta^2[\eta_s(\beta, \pm 2\pi\beta C) - \eta_s] . \tag{6.4}$$

Accounting for (5.33) and (5.34), we have

$$\eta_s(\vec{\beta}, \omega_s) - \eta_s \underset{\beta \to 0}{\simeq} -(2\pi)^{1/2}(2\pi\beta C)^{1/2}(1 \pm i)A'_{\eta_s} , \tag{6.5}$$

where

$$2A'_{\eta_s} = \tfrac{4}{3}A^V_\eta + A^V_\xi + A^\theta_\xi + (A^{V,\theta}_\kappa/C_p)(\gamma - 1) + (2^{3/2}/3)[\tfrac{4}{3}A^s_\eta + A^s_\xi + (A^s_\kappa/C_p)(\gamma - 1)] . \tag{6.6}$$

Now we may deduce from (6.4) and (6.5)

$$\omega_s(\beta) \mp 2\pi\beta C + i\frac{(2\pi\beta)^2\eta_s}{\rho} \underset{\beta \to 0}{\simeq} \frac{(2\pi\beta C)^{5/2}}{\rho C^2} A'_{\eta_s}(i \mp 1)(2\pi)^{1/2} . \tag{6.7}$$

In order to compare this last expansion of $\omega_s(\beta)$ with that deduced from the Boltzmann kinetic theory, let us consider the low-density limit of (6.7) for a gas where $A_\xi \ll A_{\kappa,\eta}$ and where the Eucken formula relates κ and η as $\kappa = \frac{15}{4}k/m$. In this limit, (6.7) becomes

$$\omega_s(\beta) \mp 2\pi\beta C + \tfrac{7}{3}i(2\pi\beta)^2\eta/\rho \underset{\beta\to 0,\rho\to 0}{\simeq} \frac{(2\pi)^{3/2}}{72}\frac{kT}{\rho}(i\mp 1)C^{1/2}\left(\frac{\rho}{\eta}\right)^{3/2}\beta^{5/2} \times\left[\tfrac{2}{5}(\tfrac{1}{2})^{3/2}+(\tfrac{2}{7})^{3/2}+\tfrac{8}{15}(\tfrac{3}{7})^{3/2}\right], \quad (6.8)$$

while the Boltzmann kinetic theory gives[21]

$$\omega_s(\beta) \mp 2\pi\beta C + \tfrac{7}{3}i(2\pi\beta)^2\eta/\rho \underset{\rho\to 0,\beta\to 0}{\simeq} \tfrac{141}{72}(\eta/\rho C^2)(2\pi\beta C)^3. \quad (6.9)$$

If we consider ω_s as a function of β and ρ, we may conclude from (6.8) and (6.9) that the expansion of $\omega_s(\beta,\rho)$ near $\beta=\rho=0$ is not unique beyond the Navier-Stokes order.

It should be pointed out that the existence of this $\beta^{5/2}$ term in the long-wavelength expansion of $\omega_s(\vec\beta)$ has been shown in the study of the sound dispersion near the liquid-gas critical point.[22] Kawasaki has shown that the sound velocity expands near the frequency $\omega=0$ as

$$C(\omega)-C(\omega=0) \underset{\omega\to 0}{\sim} \omega^{3/2}.$$

This can also be written

$$C(\vec\beta)-C(\vec\beta=0) \underset{\beta\to 0}{\sim} \beta^{3/2}. \quad (6.10)$$

Writing now the general dispersion equation as

$$\omega_s(\vec\beta)=\pm 2\pi\beta C(\vec\beta)-(4i\pi^2/\rho)\eta_s\beta^2$$

and expanding near $\beta=0$ the sound velocity given in (6.10), one obtains

$$\omega_s(\beta)=\pm 2\pi\beta C-(4i\pi^2/\rho)\eta_s\beta^2+O(\beta^{5/2}). \quad (6.11)$$

Although the calculations of Kawasaki are performed in the critical region, the reasoning leading to (6.10) seems to remain valid for any state of the fluid, subcritical or not. A quantitative comparison between our work and that of Kawasaki is not easy, since this author drops many terms as being not singular in $(T-T_c)$ or less singular in $(T-T_c)$, although they contribute to the order $\beta^{5/2}$ in (6.11).

We shall now deduce from (6.7) an asymptotic expansion of the Green function for the mode of sound propagation. This Green function may be viewed as the pressure distribution initiated by a singular pressure field in the linear approximation. The general form of this Green function is

$$G_s(R,t)\equiv\int d\vec\beta\, e^{+2i\pi\vec\beta\cdot\vec R}\,\tfrac{1}{2}(e^{-i\omega_s(\beta)t}+\text{c.c.}) = (1/R)\int_0^\infty d\beta\,\beta\sin 2\pi\beta R\,(e^{-i\omega_s(\beta)t}+\text{c.c.}). \quad (6.12)$$

The quantity $\omega_s(\beta)$ is a double-valued function. However the following results are independent of the choice of one of these determinations, provided that $\omega_s(\beta)$ stands everywhere for the same thing, as tacitly assumed from now on. Chosing $\omega_s(\beta)\simeq 2\pi\beta C$ at $\beta\to 0$, we may write (6.12) as

$$G_s(R,t)=(1/R)\int_0^\infty d\beta\,\beta\sin 2\pi\beta R \times(e^{-2i\pi\beta Ct}\,e^{-i[\omega_s(\beta)-2\pi\beta C]t}+\text{c.c.}). \quad (6.13)$$

This Green function takes the usual hydrodynamical form for large times and at fixed $(R-Ct)t^{-1/2}$. In this limit the right-hand side of (6.13) is evaluated by taking $\vec\beta'=\vec\beta\,|R-Ct|$ as the integration variable; rapidly oscillating terms vanish and we obtain

$$G_s(R,t) \underset{t\to\infty}{\simeq} G_s^0(R,t), \quad (R-Ct)^2t^{-1}\text{ fixed}, \quad (6.14)$$

where

$$G_s^0(R,t)=\frac{R-Ct}{8R}\left(\frac{\rho}{8\pi\eta_s t}\right)^{3/2}e^{-[(R-C)^2/4\eta_s t]/\rho}. \quad (6.15)$$

The term after G_s^0 in the expansion of $G_s(R,t)$ at fixed $(R-Ct)^2t^{-1}$ and large t may be obtained from (6.7) and (6.13). In fact, (6.13) yields

$$G_s(R,t)-G_s^0(R,t)\equiv\frac{1}{R}\int_0^\infty d\beta\,\beta\sin 2\pi\beta R \times\left[e^{-2i\pi\beta Ct}\left(e^{-i[\omega_s(\beta)-2\pi\beta C]t}-e^{-(2\pi\beta)^2\eta_s t/\rho}\right)+\text{c.c.}\right]. \quad (6.16)$$

The asymptotic value of the right-hand side of (6.16) is evaluated by using $\vec\beta'=\vec\beta\,|R-Ct|$ as the integration variable, and we obtain from (6.7)

$$G_s(R,t)-G_s^0(R,t) \underset{t\to\infty}{\simeq} \frac{C^{1/2}}{(2\pi)^{3/2}}\left(\frac{\rho}{\eta_s t}\right)^{9/4}A'_{\eta_s} \times\left[\Gamma(\tfrac{9}{4})\,{}_1F_1\left(\frac{9}{4};\frac{1}{2};-\rho\frac{(R-Ct)^2}{4\eta_s t}\right)-(R-Ct) \times\left(\frac{\rho}{4\eta_s t}\right)^{1/2}\Gamma\left(\frac{11}{4}\right){}_1F_1\left(\frac{11}{4};\frac{3}{2};-\rho\frac{(R-Ct)^2}{4\eta_s t}\right)\right], \quad (6.17)$$

where Γ is the Euler's integral and ${}_1F_1$ the degenerate hypergeometric function.[14]

It is interesting to notice that

$$\frac{G_s(R,t)-G_s^0(R,t)}{G_s^0(R,t)}\sim t^{-1/4}, \quad t\to\infty,\ (R-Ct)^2t^{-1}\text{ fixed}. \quad (6.18)$$

In Sec. VI B, a result similar to (6.18) will be established for the Green functions of diffusion modes.

B. Diffusion Processes beyond Navier-Stokes Order

In this subsection we shall expand the frequency of a diffusion mode beyond the Navier-Stokes order and derive a correction to the Green function of this mode beyond its usual Navier-Stokes value.

Calculation will be performed in the case of the mode of entropy diffusion.

The starting point is the generalized relation between $\omega_\theta(\beta)$ and β, which reads

$$\omega_\theta(\beta) = -i[(2\pi\beta)^2/\rho C_p]\,\kappa(\beta,\omega) \quad . \tag{6.19}$$

From (6.19) and

$$\kappa(\beta,\omega) - \kappa \underset{\substack{\beta\to 0\\ \omega\sim\beta^2}}{\simeq} -\tfrac{1}{3}\pi^{1/2} A_\kappa^s (2\pi\beta C)^{1/2} \quad , \tag{6.20}$$

which was shown in Sec. V, we have

$$\omega_\theta(\beta) + i\,\frac{(2\pi\beta)^2}{\rho}\,\eta_\theta \underset{\beta\to 0}{\simeq} i\,\frac{(\pi C)^{1/2}}{3\rho\, C_p} A_\kappa^s (2\Pi\beta)^{5/2} \quad . \tag{6.21}$$

Consider now

$$G_\theta(R,t) \equiv (2/R)\int_0^\infty d\beta\,\beta \sin 2\pi\beta R\, e^{-i\omega_\theta(\beta)t} \quad , \tag{6.22}$$

which is the Green function of the mode of entropy diffusion. Taking $\vec{\beta}' = \vec{\beta}\,t^{1/2}$ as the integration variable in (6.22), we find in the limit $t\to\infty$, R^2t^{-1} fixed, the usual Gaussian form

$$G_\theta(R,t) \simeq G_\theta^0(R,t) \; , \tag{6.23}$$

where

$$G_\theta^0(R,t) = (\rho/4\pi\eta_\theta t)^{3/2} e^{-R^2\rho/4\eta_\theta t} \quad . \tag{6.24}$$

The asymptotic value of $G_\theta - G_\theta^0$ is calculated by starting from an expression similar to (6.16) and then using (6.21). This yields

$$G_\theta(R,t) - G_\theta^0(R,t) \underset{\substack{t\to\infty\\ R^2t^{-1}\text{fixed}}}{\simeq} -\frac{A_\kappa^s C^{1/2}}{12 C_p \eta_\theta}\,\pi^{-3/2}\,\Gamma\!\left(\frac{11}{4}\right) \times \left(\frac{\rho}{\eta_\theta t}\right)^{7/4} {}_1F_1\!\left(\frac{11}{4};\frac{3}{2};\frac{R^2\rho}{4\eta_\theta t}\right) \quad . \tag{6.25}$$

The properties of the Green function of the mode of vorticity diffusion are very similar to those of $G_\theta(R,t)$. They can be deduced from (6.24) and (6.25) by replacing G_θ by G_v, η_θ by η and A_κ^s/C_p by A_η^s.

As announced at the end of Sec. VI A, $G_\theta - G_\theta^0$ verify a relation similar to (6.18). From (6.24) and (6.25),

$$\frac{G_\theta - G_\theta^0}{G_\theta^0} \sim \frac{kTC^{1/2}}{\eta}\left(\frac{\rho}{\eta}\right)^{7/4} t^{-1/4} \quad . \tag{6.26}$$

By putting $\eta/\eta_\theta \sim \eta_s/\eta_\theta \sim 1$, we have given this last relation in a dimensionless form, in order to make apparent some characteristic time. The approximation G_θ^0 of G_θ breaks down when the right-hand side of (6.26) becomes of order 1. This occurs when $t \lesssim \tau = (kT)^4 C^2 \rho^7/\eta^{11}$.

In the low-density limit, $\eta \sim mC/\sigma$, where σ is some atomic cross section, and τ becomes of order

$$\left(\frac{\rho\sigma^{3/2}}{m}\right)^7 \frac{\sigma^{1/2}}{C} \quad .$$

However, the meaning of this characteristic time in gases must be considered carefully, since the value of $G_\theta - G_\theta^0$ at large t and small ρ probably depends on the order of the limits. In fact, taking at first the limit $\rho\to 0$, we are at the approximation of the Boltzmann kinetic theory and the characteristic time will be the mean free flight time

$$\left(\frac{m}{\rho}\sigma^{-3/2}\right)\frac{\sigma^{1/2}}{C} \;,$$

which is much larger than the time τ considered above, which was found by taking at first the limit $t\to\infty$ and then the limit $\rho\to 0$.

VII. ASYMPTOTIC EXPANSION OF GREEN-KUBO INTEGRANDS IN THREE-DIMENSIONAL FLUIDS

A striking analogy between calculations of Secs. III and VI may be noticed: To find the asymptotic value of $Z_{\eta,\kappa,\zeta}(t) \sim \int \delta f^2(\vec{r},t)d\vec{r}$, we replaced $\delta f(\vec{r},t)$ by its asymptotic value, which is actually some linear combination of the Green functions $G^0_{s,\theta,V}$ considered in Sec. VI. In Sec. VI we were able to expand $G_{s,\theta,V}$ beyond their Navier-Stokes value. Therefore one can suppose that a similar calculation will provide the asymptotic value of $\delta f(\vec{r},t)$, and then of $\int \delta f^2(\vec{r},t)d\vec{r}$, beyond the Navier-Stokes order, namely, after terms in $t^{-3/2}$ found in Sec. III.

This expansion of $\psi_{\eta,\kappa,\zeta}(t)$ beyond the Navier-Stokes order is meaningful only if we assume that the hydrodynamic approximation yields the asymptotic value of $\psi_{\eta,\kappa,\zeta}$ and its first correction [here "hydrodynamic approximation" means that we replace $\psi(t)$ by its value (2.5) and then calculate $\delta f(\vec{r},t)$ in a hydrodynamical theory not restricted at the Navier-Stokes order]. As emphasized in Sec. IV, it is difficult to justify rigorously the replacement of a nonequilibrium ensemble by a local-equilibrium ensemble. However, even in the frame of the hydrodynamical approximation, many corrections to the $t^{-3/2}$ behavior appear at the Navier-Stokes order and thus must be compared with the "non-Navier-Stokes" corrections considered below.

To obtain $Z_{\eta,\kappa,\zeta} \sim \int \delta f^2(\vec{r},t)d\vec{r}$, we neglected everywhere contributions cubic in δf. For example, the local equilibrium value of $\sum_j X_{j,\kappa}$ includes a term in $\frac{1}{2}\rho\int u_x(\vec{r},t)u^2(\vec{r},t)d\vec{r}$. Using the asymptotic value of $\vec{u}(\vec{r},t)$ provided by the linearized Navier-Stokes equation, which is a linear combination of G_S^0 and G_V^0, we obtain

$$\int u_x(\vec{r},t)\,u^2(\vec{r},t)\,d\vec{r} \underset{t\to\infty}{\sim} t^{-3} \; .$$

This result can be extended straightforwardly to any quantity of the form $\int \delta f^3(\vec{r}, t)d\vec{r}$ which is either of the order of, or negligible with respect to t^{-3}.

Another sort of correction arises from the linearization of the laws of hydrodynamics. It may be seen that the corresponding corrections are at least of order $\int \delta f^3(\vec{r}, t)d\vec{r}$. Furthermore, to compute $\delta f(\vec{r}, t)$ we replaced $\delta f(\vec{r}, t_1)$ by a singular perturbation at time $t=0$; that is, we took $t^{-3/2}$ instead of $(t-t_1)^{-3/2}$ and replaced $\delta f(\alpha' t^{-1/2}, t_1)$ by $\delta f(\alpha=0, t_1)$. Corrections arising from these approximations are, respectively, of order $t^{-5/2}$ and

$$\int d\vec{\alpha}\, \alpha^2 \,|\, \delta f(\vec{\alpha}, t)|^2 \sim \frac{1}{t} \int d\vec{\alpha}\,|\, \delta f(\vec{\alpha}, t)|^2 .$$

Now we shall prove that the "non-Navier-Stokes" correction to $\psi_{\eta,\kappa,\zeta}(t)$ arising from the $\beta^{5/2}$ term in the expansions of $\omega_{V,\theta,S}(\beta)$ is of order $t^{-7/4}$ and dominates every correction considered above.

Consider, for example, the expansion at large t of $\int \delta S^2(\vec{r}, t)d\vec{r}$. As indicated in Eq. (2.19), the Navier-Stokes approximation yields

$$\int \delta S^2(\vec{r}, t)d\vec{r} = \int |\delta S(\vec{\alpha}, t)|^2 d\vec{\alpha} \underset{t\to\infty, d=3}{\simeq} \left(\frac{\rho}{8\pi\eta_\theta t}\right)^{3/2} \frac{(\delta E - h\delta M)^2}{\rho^2 T^2} . \quad (7.1)$$

The next-order term (or "non-Navier-Stokes" contribution) is obtained by subtracting from $|\delta S(\vec{\alpha}, t)|^2$ its Navier-Stokes value

$$\delta S^0(\vec{\alpha}, t) = e^{-(2\pi\alpha)^2 \eta_\theta t/\rho} \frac{(\delta E - h\delta M)}{\rho T}$$

and then carrying the limit $t \to \infty$ through the change of variable $\vec{\alpha}' = \vec{\alpha} t^{1/2}$. We obtain in this way

$$\int d\vec{\alpha}\,[\,|\delta S(\vec{\alpha}, t)|^2 - |\delta S^0(\vec{\alpha}, t)|^2\,] \underset{t\to\infty, d=3}{\simeq} \frac{2(\delta E - h\delta M)}{\rho T} t^{-3/2} \int d\vec{\alpha}'\, e^{-(2\pi\alpha')^2 \eta_\theta/\rho} \times 2\,\mathrm{Re} \lim_{t\to\infty} [\delta S(\vec{\alpha}' t^{-1/2}, t) - \delta S^0(\vec{\alpha}' t^{-1/2}, t)] , \quad (7.2)$$

where Re [ ] means the real part of [ ].

Accounting for (6.21) and

$$\delta S(\vec{\alpha}, t) \underset{\alpha\to 0}{=} e^{-i\omega_\theta(\alpha)t} \delta S(0, t_1) ,$$

we have

$$\delta S(\vec{\alpha}' t^{-1/2}, t) - \delta S^0(\vec{\alpha}' t^{-1/2}, t) \simeq -\delta S(0, t_1) e^{-(2\pi\alpha')^2 \eta_\theta/\rho} \times (2\pi\alpha')^{5/2} (\pi^2 C^2/t)^{1/4} (A^s_\kappa/3\rho C_p) , \quad (7.3)$$

which yields, once inserted into (7.2),

$$\int d\vec{\alpha}\,[\,|\delta S(\vec{\alpha}, t)|^2 - |\delta S^0(\vec{\alpha}, t)|^2\,] \underset{\substack{t\to\infty\\ d=3}}{\simeq} -\frac{(\delta E - h\delta M)^2}{\rho^2 T^2} t^{-7/4} \left(\frac{\rho}{2\eta_\theta}\right)^{11/4} \frac{2\pi^{3/2} C^{1/2} A^s_\kappa \Gamma(\frac{11}{4})}{3\rho\, C_p} . \quad (7.4)$$

Very similar calculations would give the non-Navier-Stokes correction for any quantity of the form $\int \delta f^2(\vec{r}, t)d\vec{r}$. By inserting these corrections into the hydrodynamic approximation for $\psi_{\eta,\kappa,\zeta}(t)$, terms of order $t^{-7/4}$ appear which follow the $t^{-3/2}$ asymptotic value of $\psi_{\eta,\kappa,\zeta}(t)$ found in Sec. III. Calling $\psi^0_{\eta,\kappa,\zeta}(t)$ the asymptotic terms of order $t^{-3/2}$ in the expansions of $\psi_{\eta,\kappa,\zeta}(t)$, we find

$$\psi_\xi(t) - \psi^0_\xi(t) \simeq kTB_\xi t^{-7/4} , \quad t\to\infty, \quad \xi = \eta, \kappa, \zeta \quad (7.5)$$

where

$$B_\eta = -\frac{2\pi}{15} \frac{kT(\pi C)^{1/2}}{\rho} \Gamma\left(\frac{11}{4}\right) \left[\frac{7}{3} A^s_\eta \left(\frac{\rho}{2\eta}\right)^{11/4} + \sqrt{2}\, A_{\eta_s} \left(\frac{\rho}{2\eta_s}\right)^{11/4}\right] , \quad (7.6a)$$

$$B_\kappa = -\frac{2\pi}{3} \frac{kT(\pi C)^{1/2}}{\rho} \Gamma\left(\frac{11}{4}\right) \left[\frac{A_\kappa + C_p A^s_\eta}{3} \left(\frac{\rho}{\eta+\eta_\theta}\right)^{11/4} + \sqrt{2}\, C_p \chi^2(\gamma-1) A_{\eta_s} \left(\frac{\rho}{2\eta_s}\right)^{11/4}\right] , \quad (7.6b)$$

and

$$B_\zeta = -\frac{16\pi^3}{\rho} C^{1/2} \Gamma\left(\frac{11}{4}\right) \left[\frac{A^s_\eta A^V_\zeta}{3} \left(\frac{\rho}{2\eta}\right)^{5/4} + \frac{A^s_\kappa A^\theta_\zeta}{3C_p} \times \left(\frac{\rho}{2\eta_\theta}\right)^{5/4} + \sqrt{2}\, A_{\eta_s} A^s_\zeta \left(\frac{\rho}{2\eta_s}\right)^{5/4}\right] . \quad (7.6c)$$

One may again deduce from the expansion of $\psi_\xi(t)$ given in (7.5) a property of $\xi(\omega)$ near $\omega = 0$. A reasoning very similar to that which led to (5.8) gives

$$\xi(\omega) - \xi + |2\pi\omega|^{1/2} A_\xi (1 + i\,\mathrm{sgn}\omega) \underset{\omega\to 0}{\simeq} -|\omega|^{3/4} B_\xi (\cos\tfrac{3}{8}\pi + i\,\mathrm{sgn}\omega \sin\tfrac{3}{8}\pi) . \quad (7.7)$$

As a conclusion we shall examine the following question: Is it possible to deduce again from (7.7) [and similar formulas for the expansion of $\xi(\beta, \omega)$ near $\omega = \beta = 0$] terms after the order $\beta^{5/2}$ in $\omega_{V,s,\theta}(\beta)$ and then corrections to the $t^{-7/4}$ term in the expansion of $\psi_\xi(t)$? Although this leads to cumbersome formulas, it seems that there is no essential difficulty in proceeding in this way, both after the order $t^{-7/4}$ and even at higher order. Rough estimations seem to indicate that we shall obtain an expansion of $\psi_\xi(t)$ where the successive terms are of order $t^{-(2-1/2^n)}$, where n is an integer ≥ 1. The corresponding expansion of $\xi(\omega)$ near $\omega = 0$ includes terms of order $\omega^{1-1/2^n}$. It is worth noticing that this expansion is carried out in the frame of the Landau-Placzeck approximation, provided one assumes that it gives the asymptotic value of $\psi_\xi(t)$ up to terms of order t^{-2}.

APPENDIX A

This appendix is devoted to the calculation of the grand-canonical fluctuations $\Phi_\kappa^{1,2}$ occurring in the value of $\psi_\kappa(t)$ for large times.

These fluctuations are defined as

$$\Phi_\kappa^1 = \frac{m}{\Delta V^0}\left\langle(\delta E - h\delta M)\sum_{i,\vec{r}_i\in\Delta V^0} v_{ix}^2 \times\left(E_i - mh - \frac{1}{2d}\sum_j \vec{r}_{ij}\cdot\frac{\partial V_{ij}}{\partial\vec{r}_i}\right)\right\rangle \quad \text{(A1a)}$$

and

$$\Phi_\kappa^2 = \frac{m}{\Delta V^0}\left\langle \delta M \sum_{i,\vec{r}_i\in\Delta V^0} v_{ix}^2 \times\left(E_i - mh - \frac{1}{2d}\sum_j \vec{r}_{ij}\cdot\frac{\partial V_{ij}}{\partial\vec{r}_i}\right)\right\rangle . \quad \text{(A1b)}$$

These definitions coincide with those given in (3.14), except that the tensor $\vec{r}_{ij}\,\partial V_{ij}/\partial\vec{r}_i$ has been replaced by

$$\frac{\overleftrightarrow{1}}{d}\,\vec{r}_{ij}\cdot\frac{\partial V_{ij}}{\partial\vec{r}_i} .$$

This is allowed from statistical independence between positions and velocities. The first step in the calculation of $\Phi_\kappa^{1,2}$ is carried out by replacing v_{ix}^2 in (A1) by $(v_{ix}^2 - kT/m) + kT/m$. The contributions arising from $(v_{ix}^2 - kT/m)$ may be computed straightforwardly, since they involve only fluctuations of the kinetic energy. One obtains

$$\Phi_\kappa^1 = \rho(kT/m)\langle(\delta E - h\delta M)\delta(H/M)\rangle \quad \text{(A2a)}$$

and

$$\Phi_\kappa^2 = \rho(kT/m)\langle\delta M\,\delta(H/M)\rangle , \quad \text{(A2b)}$$

where δH is the enthalpy fluctuation in the volume ΔV^0, the enthalpy of this volume being defined microscopically as

$$H = \sum_{i,\vec{r}_i\in\Delta V^0}\left(E_i - \frac{1}{2d}\sum_j \vec{r}_{ij}\cdot\frac{\partial\vec{V}_{ij}}{\partial\vec{r}_i} + \frac{mv_i^2}{d}\right).$$

The fluctuations on the right-hand side of (A2) are given, as usual, by the second derivatives of the logarithm of the grand partition function, and we have

$$\Phi_\kappa^1 = \rho\frac{kT}{m}\left(kT^2\frac{\partial}{\partial T}\bigg|_{z,V} - h\frac{\partial}{\partial \ln z}\bigg|_{T,V}\right)h , \quad \text{(A3)}$$

where V is the volume and z the fugacity defined from the chemical potential per unit mass as

$$m\mu = kT\ln z . \quad \text{(A4)}$$

The derivative $\partial/\partial T|_{z,V}$ may be replaced by

$$\frac{\partial}{\partial T}\bigg|_p + \frac{\partial p}{\partial T}\bigg|_{z,V}\frac{\partial}{\partial p}\bigg|_T \equiv \frac{\partial}{\partial T}\bigg|_p + \frac{h}{T}\frac{\partial}{\partial p}\bigg|_T ,$$

and the derivative

$$\frac{\partial}{\partial \ln z}\bigg|_{T,V} \text{ by } kT\frac{\partial}{\partial p}\bigg|_T$$

from the Gibbs-Duhem relation. Thus we have from (A3)

$$\Phi_\kappa^1 = \rho\frac{k^2T^3}{m}\frac{\partial h}{\partial T}\bigg|_p = \rho\frac{k^2T^3}{m}C_p . \quad \text{(A5a)}$$

Similarly,

$$\Phi_\kappa^2 = \rho\frac{k^2T^2}{m}\frac{1+\chi}{\chi} . \quad \text{(A5b)}$$

APPENDIX B

In this appendix, we shall compute fluctuations occurring in the asymptotic value of $\psi_\xi(t)$. Let $\Phi_\xi^{\theta,s}$ be those two fluctuations that occur, respectively, in ψ_ξ^θ and ψ_ξ^s. They are given by

$$\Phi_\xi^\theta = \left\langle\left(\delta E - \frac{h}{m}\delta M\right)^2\left(\Delta V^0\delta p - \frac{\partial p}{\partial\epsilon}\bigg|_\rho\delta E - \frac{\partial p}{\partial\rho}\bigg|_\epsilon\delta M\right)\right\rangle_{\Delta V^0} \quad \text{(B1a)}$$

and

$$\Phi_\xi^s = \left\langle\left(\delta E - \frac{\partial\epsilon}{\partial\rho}\bigg|_p\delta M\right)^2\left(\Delta V^0\delta p - \frac{\partial p}{\partial\epsilon}\bigg|_\rho\delta E - \frac{\partial p}{\partial\rho}\bigg|_\epsilon\delta M\right)\right\rangle_{\Delta V^0} . \quad \text{(B1b)}$$

The principles used in this calculation are those that were used in Appendix A: $\Phi_\xi^{\theta,s}$ are expressed as derivatives of the logarithm of the grand partition function. Let us examine at first Φ_ξ^θ. From (A4), and considerations which follow,

$$\Phi_\xi^\theta = \Delta V^0\left[kT^2\left(\frac{\partial}{\partial T}\bigg|_p + \frac{\rho}{T}(h-\bar{h})\frac{\partial}{\partial p}\bigg|_T\right)\right]^2 \times\left(p - \frac{\overline{\partial p}}{\partial\epsilon}\bigg|_\rho\epsilon - \frac{\overline{\partial p}}{\partial\rho}\bigg|_\epsilon\right). \quad \text{(B2)}$$

In (B2) the notation

$$\bar{h},\ \frac{\overline{\partial p}}{\partial\epsilon}\bigg|_\rho,\ \frac{\overline{\partial p}}{\partial\rho}\bigg|_\epsilon$$

means that these quantities cannot be derived with respect to the thermodynamic variables. Considering now p as a function of ϵ and ρ, we obtain from (B2)

$$\Phi_\xi^\theta = \Delta V^0k^2T^4\frac{\partial}{\partial T}\bigg|_p\left(\frac{\partial p}{\partial\epsilon}\bigg|_\rho\frac{\overline{\partial\epsilon}}{\partial T}\bigg|_p + \frac{\partial p}{\partial\rho}\bigg|_\epsilon\frac{\overline{\partial\rho}}{\partial T}\bigg|_p\right), \quad \text{(B3)}$$

which, from

$$\frac{\partial p}{\partial\rho}\bigg|_\epsilon = -\frac{\partial p}{\partial\epsilon}\bigg|_\rho\frac{\partial\epsilon}{\partial\rho}\bigg|_p , \quad \text{(B4)}$$

reads

$$\Phi_\xi^\theta = \Delta V^0 k^2 T^4 \frac{\partial\rho}{\partial T}\bigg|_p^2 \frac{\partial}{\partial\rho}\bigg|_p \left(\frac{\partial p}{\partial\epsilon}\bigg|_\rho \frac{\overline{\partial\epsilon}}{\partial\rho}\bigg|_p - \frac{\partial p}{\partial\epsilon}\bigg|_\rho \frac{\partial\epsilon}{\partial\rho}\bigg|_p\right)$$

$$= -\Delta V^0 k^2 T^4 \frac{\partial\rho}{\partial T}\bigg|_p^2 \frac{\partial p}{\partial\epsilon}\bigg|_\rho \frac{\partial^2\epsilon}{\partial\rho^2}\bigg|_p . \tag{B5}$$

The derivative $\partial^2\epsilon/\partial\rho^2|_p$ may be given in terms of usual thermodynamical quantities. From

$$\frac{\partial\epsilon}{\partial\rho}\bigg|_p = h + T\frac{\partial S}{\partial\rho}\bigg|_p = h + T\frac{\partial T}{\partial\rho}\bigg|_p C_p$$

and from

$$\frac{\partial C_p}{\partial p}\bigg|_T = -T\frac{\partial^2(1/\rho)}{\partial T^2}\bigg|_p ,$$

we obtain

$$\frac{\partial^2\epsilon}{\partial\rho^2}\bigg|_p = \chi^2 C_p T\left(\frac{T}{C_p}\frac{\partial C_p}{\partial T}\bigg|_p - \chi T\frac{\partial C_p}{\partial p}\bigg|_T\right).$$

The fluctuation Φ_ξ^s is calculated along similar lines. Writing Φ_ξ^s as a third derivative of the logarithm of the grand partition function, we have

$$\Phi_\xi^s = \Delta V^0\left\{kT^2\left[\frac{\partial}{\partial T}\bigg|_p + \frac{\rho}{T}\left(h - \frac{\partial\epsilon}{\partial\rho}\right)\frac{\partial}{\partial p}\bigg|_T\right]\right\}^2 \times\left(p - \frac{\overline{\partial p}}{\partial\epsilon}\bigg|_\rho - \frac{\overline{\partial p}}{\partial\rho}\bigg|_\epsilon\right).$$

Using now the relation

$$\frac{\partial}{\partial T}\bigg|_S = \frac{\partial}{\partial T}\bigg|_p + \frac{\partial p}{\partial T}\bigg|_S\frac{\partial}{\partial p}\bigg|_T = \frac{\partial}{\partial T}\bigg|_p + \frac{\rho}{T}\left(h - \frac{\partial\epsilon}{\partial\rho}\bigg|_p\right)\frac{\partial}{\partial p}\bigg|_T ,$$

and the fact that any first derivative of

$$p - \frac{\overline{\partial p}}{\partial\epsilon}\bigg|_\rho \epsilon - \frac{\overline{\partial p}}{\partial\rho}\bigg|_\epsilon \rho$$

vanishes, we have

$$\Phi_\xi^s = \Delta V^0 k^2 T^4 \frac{\partial^2}{\partial T^2}\bigg|_S\left(p - \frac{\overline{\partial p}}{\partial\epsilon}\bigg|_\rho \epsilon - \frac{\overline{\partial p}}{\partial\rho}\bigg|_\epsilon \rho\right)$$

$$= \Delta V^0 k^2 T^4 \frac{\partial\rho}{\partial T}\bigg|_S \frac{\partial}{\partial\rho}\bigg|_S\left(\frac{\partial p}{\partial\rho}\bigg|_\epsilon \frac{\overline{\partial\rho}}{\partial T}\bigg| + \frac{\partial p}{\partial\epsilon}\bigg|_\rho \frac{\overline{\partial\epsilon}}{\partial T}\bigg|_S\right).$$

Using now the identity

$$\frac{\partial p}{\partial\rho}\bigg|_\epsilon \frac{\overline{\partial\rho}}{\partial T}\bigg|_S + \frac{\partial p}{\partial\epsilon}\bigg|_\rho \frac{\overline{\partial\rho}}{\partial T}\bigg|_S = \frac{\partial p}{\partial\epsilon}\bigg|_\rho\left(\frac{\overline{\partial\epsilon}}{\partial\rho}\bigg|_S \frac{\overline{\partial\rho}}{\partial T}\bigg|_S - \frac{\partial\epsilon}{\partial\rho}\bigg|_S \frac{\overline{\partial\rho}}{\partial T}\bigg|_S\right) + \frac{\partial p}{\partial\rho}\bigg|_S \frac{\overline{\partial\rho}}{\partial T}\bigg|_S$$

we obtain

$$\Phi_\xi^s = \Delta V^0 k^2 T^4 \frac{\partial\rho}{\partial T}\bigg|_S^2\left(2C\frac{\partial C}{\partial\rho}\bigg|_S - \frac{\partial p}{\partial\epsilon}\bigg|_\rho \frac{C^2}{\rho}\right).$$

APPENDIX C

It has been shown that, in three-dimensional fluids,

$$\xi(\omega) - \xi(\omega=0) \underset{\omega\to 0}{\sim} |\omega|^{1/2} , \tag{C1}$$

which is a direct consequence of the $t^{-3/2}$ behavior of Green-Kubo integrands. This property can be extended to any dimensionality $d>2$. For this purpose, we shall consider in order two cases: d even and d odd.

1. *d Odd = 2l + 1, l Integer ≥ 1*

Frequency-dependent transport coefficients are defined again by (5.1) and the asymptotic value of $\psi_\xi(t)$ verifies

$$\psi_\xi(t) \underset{t\to\infty}{\simeq} kTA_\xi(d)\,t^{-d/2} , \tag{C2}$$

where the values of $A_\xi(d)$ are obvious from (3.12), (3.15), (3.34), and (3.35). The coefficients $A_{\eta,\kappa,\xi}$ defined in (5.3) are simply equal to $A_{\eta,\kappa,\xi}(3)$. Consider now the quantity

$$\Delta^l\xi(\omega) \equiv \xi(\omega) - \xi(0) - \omega\frac{\partial\xi}{\partial\omega}\bigg|_{\omega=0} \cdots - \frac{\omega^{l-1}}{(l-1)!}\frac{\partial^{l-1}\xi(\omega)}{(\partial\omega)^{l-1}}\bigg|_{\omega=0} . \tag{C3}$$

This function may be expressed straightforwardly as a Fourier transform:

$$\Delta^l\xi(\omega) = \frac{1}{kT}\int_0^\infty dt \times\left(e^{-i\omega t} - 1 + i\omega t \cdots - \frac{(-i\omega t)^{l-1}}{(l-1)!}\right)\psi_\xi(t). \tag{C4}$$

Taking now $|\omega|t$ as the integration variable and integrating by parts, we have

$$\Delta^l\xi(\omega) \underset{\omega\to 0}{\simeq} (i\omega)^{l-1}\,(\tfrac{1}{2}\omega)^{1/2}\,(1+i\,\mathrm{sgn}\omega)\,[\pi/\Gamma(l+\tfrac{1}{2})]\,A_\xi(d) , \tag{C5}$$

which is the generalization of (5.8) at any odd dimensionality.

2. *d Even ≡ 2l, l Integer ≥ 2*

Consider first the case $d=4$ and the quantity

$$\xi(\omega) - \xi(\omega=0) = (1/kT)\int_0^\infty dt\,(e^{-i\omega t} - 1)\,\psi_\xi(t) . \tag{C6}$$

For t larger than some time t_0, we may replace $\psi_\xi(t)$ in (C6) by its asymptotic value $(kT/t^2)A_\xi(4)$ and obtain

$$\xi(\omega) - \xi \simeq \omega^2 A_\xi(4)\int_{t_0}^\infty dt\,\ln t\, e^{-i\omega t} \simeq i\omega\ln|\omega|\,A_\xi(4), \quad \omega\to 0,\ d=4 . \tag{C7}$$

Proceeding as in the case of odd dimensionality, we may extend this result at any even d to find

$$\Delta_l'\xi(\omega) \simeq -\frac{A_l(2l)}{(l-1)!}\,(-i\omega)^l \ln|\omega|\;,\;\omega\to 0,\; d=2l \qquad \text{(C8)}$$

where

$$\Delta_l'\xi(\omega) = \xi(\omega) - \xi - \omega\left.\frac{\partial\xi}{\partial\omega}\right|_{\omega=0} - \cdots - \frac{\omega^{l-2}}{(l-2)!}\left.\frac{\partial^{l-2}\xi(\omega)}{(\partial\omega)^{l-2}}\right|_{\omega=0}.$$

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Onset of Turbulence for Counterflow in He II

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Two mutual friction numbers are derived for superfluid helium which can describe the onset of turbulence in counterflowing helium. The numbers are $M_n = A\rho_s\rho_n\langle\vec{V}_r\rangle^3 d^2/\eta_n\langle\vec{V}_n\rangle$ and $M_s = A\rho_s\rho_n\langle\vec{V}_r\rangle^3 d^2/\eta_n\langle\vec{V}_s\rangle$, where M_n predicts the onset of turbulence in the normal fluid and M_s predicts the onset of turbulence in the superfluid. Staas, Taconis, and van Alphen's Reynolds number is found to apply only to flow conditions for which $\vec{V}_n \simeq \vec{V}_s$.

INTRODUCTION

For many years, now, considerable attention has been given to the heat transport properties of superfluid helium. For this liquid, total isothermal fluid flow in the presence of small heat currents can be described in terms of a two-fluid model in which a counterflow of two-fluid components, normal fluid, and superfluid can be envisioned. As a consequence, the heat transport properties of He II are intimately related to its hydrodynamic flow properties. The same might also be true for larger heat currents where the two-fluid model breaks down and nonlinear relationships develop between the heat current and temperature gradient[1] as well as the heat current and pressure gradient.[2,3] The nonlinearities have been described in terms of an empirical mutual friction force F_{sn} originally proposed by Gorter and Mellink[4] and are known to accompany a developed tangled mass of vorticity and/or turbulence within the fluid.[5] Although several experimental investigations have been made into the nature of the tangled mass of vorticity,[6–9] very little is known about the onset of turbulence in superfluid helium. By deriving a set of dimensionless numbers similar to the Reynolds number[10] of classical hydrodynamics, a possible explanation for this phenomenon will follow.

CRITICAL-HEAT PROBLEM

The generally accepted equations of motion for the steady-state flow of liquid helium are