ON SOME ASPECTS OF FLUCTUATING HYDRODYNAMICS

G. VAN DER ZWAN

ON SOME ASPECTS OF FLUCTUATING HYDRODYNAMICS

Proefschrift

ter verkrijging van de graad van doctor in
de wiskunde en natuurwetenschappen aan de
Rijksuniversiteit te Leiden, op gezag van
de Rector Magnificus Dr. A.A.H. Kassenaar,
hoogleraar in de faculteit der geneeskunde,
volgens besluit van het college van dekanen
te verdedigen op woensdag 23 januari 1980
te klokke 14.15 uur

door

Gerrit van der Zwan

geboren te Leiderdorp in 1951

Krips Repro - Meppel

Promotor: Prof.dr. P. Mazur

Het in dit proefschrift beschreven werk is een onderdeel van het onderzoekprogramma van de "Stichting voor Fundamenteel Onderzoek der Materie" (F.O.M.) financiëel gesteund door de "Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek" (Z.W.O.).

CONTENTS

Chapter I and chapter II have appeared before in Physica as
Mazur, P. and van der Zwan G, Physica 92A (1978) 483.
Van der Zwan, G. and Mazur, P., Physica 98A (1979) 169.
(Physica is published by The North-Holland Publishing Co., Amsterdam).

INTRODUCTION

On a length scale much larger than molecular dimensions a classical one component fluid can be described by its velocity field and two independent thermodynamic variables, e.g. the density field and the temperature field. The behaviour of these fields is governed by a set of non-linear (hydrodynamic) equations. These equations can be derived from the conservation equations of mass, momentum and total energy, the thermodynamic Gibbs relation and phenomenological laws which relate the heat current to the gradient of the temperature field (Fourier's law) and the viscous pressure tensor to the gradient of the velocity field (Newton's law) [1,2]. In general it is not possible to solve this set of non-linear equations. These equations may, however, be linearized around the equilibrium or some other stationary reference state, assuming the deviations of the various fluid fields from this state to be sufficiently small. This procedure yields a set of linear equations in the fluid fields which is in principle solvable upon specification of boundary conditions and initial values.

In fluctuating hydrodynamics the basic assumption is that the above discussed linear equations for the regression of macroscopic deviations hold for the mean regression of small fluctuations around the reference state. These small fluctuations are generated by generalized "random force" fields which must be included in the linear equations. The "random forces" have zero expectation values and their correlation functions are connected through fluctuation-dissipation theorems with the dissipative phenomena occurring in the fluid [1]. It is then possible to derive properties of the fluctuating fluid fields as e.g. their correlation functions from the stochastic properties of the "random forces".

The method of fluctuating hydrodynamics has proved to be very useful in the study of fluid fluctuations if the processes considered involve length scales between 10^{-5} cm and 10^{-2} cm, which are very small on a macroscopic scale but still large compared to molecular lengths of the order of 10^{-8} cm. For Brownian motion the characteristic length is the radius of the Brownian particle which is of the order of 10^{-3} - 10^{-5} cm. Similarly in light scattering the typical length is the wavelength of light which is of the order of 10^{-5} cm. Both Brownian particles and light can therefore be used as probes for fluctuations in the fluid whose behaviour may be analyzed by means of the equations of fluctuating hydrodynamics.

In the first part of this thesis Brownian motion in a fluid near its equilibrium critical point is studied. It is well known that close to a liquid-gas critical point the isothermal compressibility approaches infinity while the density fluctuations become correlated over large distances [3,4]. It is to be expected that these long-range correlations will affect the motion of a Brownian particle, especially when the correlation length of the density fluctuations exceeds the radius of the particle.

In chapter I an expression is derived, using fluctuating hydrodynamics, for the friction coefficient of a spherical Brownian particle. To this end one starts from the set of linear equations, obtained by linearizing the hydrodynamic equations around the equilibrium state of the fluid. Close to the critical point the specific heat of the fluid diverges [4]. The motion of the fluid is therefore almost isothermal so that the temperature fluctuations may be neglected. As a consequence it is sufficient to consider a reduced set of linear hydrodynamic equations. In addition to these equations a relation between the pressure and density fluctuations is needed, for which one may take the non-local Ornstein-Zernike expression. This expression accounts for the long-range correlations of density fluctuations in the fluid in the critical region [3].

To find,from the above set of equations of motion of the fluid supplemented with the equation of motion of the sphere, the frequency dependent friction coefficient it is convenient to use the method of induced forces developed by Mazur and Bedeaux [5,6,7]. In this way one obtains (chapter I, § 3) an expression for the force excerted by the fluid on the sphere which is an extension of the well-known Faxén theorem to the case of a spherical particle held fixed in a fluid close to its critical point in non-stationary and non-uniform flow. From this generalized theorem the friction coefficient and the random force acting on the particle can be obtained.

The low frequency behaviour of the friction coefficient is indeed modified close to the critical point as compared to its low frequency behaviour far from the critical region. On the basis of the expression found for the random force acting on the Brownian particle one may derive a fluctuation-dissipation theorem for this quantity, a theorem which is derived in a more formal way in chapter II. Using this fluctuation-dissipation theorem it is then possible to evaluate the velocity auto-correlation function of the Brownian particle. It turns out that there is a small negative contribution to the usual $t^{-3/2}$ long-time tail of this velocity autocorrelation function if the correlation length of the density fluctuations becomes larger than the radius of the Brownian particle, i.e. sufficiently close to the critical point.

In chapter II a formal derivation is given of the fluctuation-dissipation theorem for the random force on a Brownian particle of arbitrary shape taking also into account the temperature fluctuations in the fluid. The method which is used was first developed by Fox and Uhlenbeck [8] for a particle immersed in an incompressible fluid and extended in various ways by other authors [6,9-12]. This method is based on the systematic use of Green identities for the fluctuating and average fluid fields together with boundary conditions for these fields at the surface of the Brownian particle. The theorem used in chapter I is a special case of the theorem derived in this chapter.

In the second part of this thesis light scattering from a fluid in a non-equilibrium stationary state is studied.

The light scattering spectrum is determined by the density-density correlation function of the fluid which can be obtained from fluctuating hydrodynamics. In equilibrium this spectrum, as a function of the frequency, is symmetric around the frequency ω_0 of the incident monochromatic lightwave and consists of three lines of Lorentzian shape: the central, or Rayleigh, line centered at frequency $\omega = \omega_0$, due to scattering from the entropy fluctuations, and two symmetrically shifted lines, the Brillouin doublet, due to scattering from sound waves. The width of the central line is determined by the thermal diffusivity and the width of the Brillouin lines by the sound attenuation coefficient [13].

Possible modifications of the equilibrium spectrum in the presence of stationary gradients in the fluid system will be studied in chapters III and IV. In order to evaluate the light scattering spectrum it is necessary to derive first an expression for the density-density correlation function under these circumstances.

In chapter III a fluid layer under the influence of a gravitational field in which a stationary temperature gradient is maintained, is considered. In order to study this system the hydrodynamic equations are linearized around the stationary state. As is well known a convective instability, the Rayleigh-Bénard instability, can occur for certain values of the temperature difference between the two boundaries of the fluid layer. Assuming the stochastic properties of the "random forces" in the linear equations to be essentially the same as in equilibrium [1,14], it is possible to calculate fluctuation spectra in the system considered in the pretransitional regime. Close to the Rayleigh-Bénard instability the temperature fluctuations become anomolously large [14]. This leads to a modification of the density-density correlation function. It is shown, however, that this modification does not lead to an experimentally measurable change in the light scattering spectrum due to the small wave number at which the corresponding change in the density-density correlation function takes place. This is in agreement with previously found results [15].

In chapter IV a fluid layer is studied in which only a stationary temperature gradient is present. Starting again from a linearized set of stochastic hydrodynamic equations one may derive an expression for the density-density correlation function which is correct up to linear order in the (applied) temperature gradient and in which the temperature dependence of the stationary values of the thermodynamic quantities is now taken into account. These last dependences were neglected in the analysis presented in chapter III. In order to simplify the treatment the temperature dependence of the shear and volume viscosity is neglected. Furthermore it is assumed that the heat conductivity is sufficiently small and may be taken equal to zero. One then finds in the light scattering spectrum a modification of the Brillouin lines. These two lines become unequal in amplitude and are not of Lorentzian shape anymore. Modifications of the spectrum of this type have recently also been obtained on the one hand by Kirkpatrick, Cohen and Dorfman [16] by means of kinetic theory and on the other hand by Procaccia, Ronis and Oppenheim who use non-linear response theory [17-20]. The explicit expressions for the light scattering spectrum found by the above mentioned authors are, however, in disagreement with each other and also with the results obtained in this thesis by the more direct method of fluctuating hydrodynamics.

References

1. L. Landau and E.M. Lifshitz, Fluid mechanics (Pergamon Press, New York, 1959).
2. S.R. de Groot and P. Mazur, Non-equilibrium thermodynamics (North-Holland, Amsterdam 1962).

3. L. Landau and E.M. Lifshitz, Statistical physics (Pergamon Press, New York, 1959).
4. P. Heller, Rep.Prog.Phys. 30 (1967) 731.
5. P. Mazur and D. Bedeaux, Physica 76 (1974) 235.
6. D. Bedeaux and P. Mazur, Physica 76 (1974) 247.
7. D. Bedeaux and P. Mazur, Physica 78 (1974) 505.
8. R.F. Fox and G.E. Uhlenbeck, Phys.Fluids 13 (1970) 1893.
9. T.S. Chow and J.J. Hermans, J.C.P. 56 (1972) 3150.
10. E.H. Hauge and A. Martin-Löf, J.Stat.Phys. 7 (1973) 259.
11. D. Bedeaux, A.M. Albano and P. Mazur, Physica 88A (1977) 574.
12. D.H. Berman, J.Stat.Phys. 20 (1979) 57.
13. R.D. Mountain, Rev.Mod.Phys. 38 (1966) 205.
14. V.M. Zaǐtsev and M.I. Shliomis, Sov.Phys. JETP 32 (1971) 866.
15. H.N.W. Lekkerkerker and J.P. Boon, Phys.Rev. A10 (1974) 1355.
16. T. Kirkpatrick, E.G.D. Cohen and J.R. Dorfman, Phys.Rev.Lett. 42 (1979) 862.
17. I. Procaccia, D. Ronis and I. Oppenheim, Phys.Rev.Lett. 42 (1979) 287, 614 E.
18. I. Procaccia, D. Ronis, M.A. Collins, J. Ross and I. Oppenheim, Phys.Rev. A19 (1979) 1290.
19. D. Ronis, I. Procaccia and I. Oppenheim, Phys.Rev. A19 (1979) 1307.
20. D. Ronis, I. Procaccia and I. Oppenheim, Phys.Rev. A19 (1979) 1324.

PART A

BROWNIAN MOTION IN A FLUID CLOSE TO ITS CRITICAL POINT

I. THE FRICTION COEFFICIENT

The frequency dependent friction coefficient of a spherical Brownian particle of radius a in a compressible fluid close to its critical point is evaluated taking into account the large correlation length ξ of the density fluctuations in the fluid. The expression found depends for finite frequencies on the ratio a/ξ. It is furthermore shown that a negative contribution to the amplitude of the usual $t^{-3/2}$ long time tail of the velocity autocorrelation function of the particle appears very close to the critical point when $\xi \gg a$.

1. Introduction

It has been suggested in recent years that Brownian motion experiments could yield information about the properties of a fluid either close to a hydrodynamic instability or close to its equilibrium critical point. Thus Lekkerkerker[1]) has analysed the effect of the enhanced hydrodynamic fluctuations in a fluid near the convective instability (Bénard instability) on the motion of a suspended spherical Brownian particle.

On the other hand Lyons, Mockler and O'Sullivan[2]) investigated the diffusion of Brownian particles in a critical binary mixture and interpreted their experimental results theoretically assuming essentially Stokes' law for the friction coefficient of a spherical Brown particle to hold while at the same time attempting to incorporate the effect of a logarithmic anomaly in the shear viscosity[3]) as well as certain effects of the large concentration fluctuations. The Brownian particle would therefore act as a probe for the weak anomaly in the shear viscosity. It is not clear however whether the various effects have been properly taken into account.

Earlier Giterman and Gertsenshtein[4]) had considered the simpler case of Brownian motion in a one-component fluid close to its critical point. For this purpose they derived an expression for the friction coefficient of a spherical particle in a compressible fluid assuming the induced flow to be isothermal and treating the shear and bulk viscosity coefficients as constants. They neglected moreover the large correlation length of density fluctuations in the critical region. They show within the limitations of their model that, as the compressibility tends to infinity, the friction coefficient tends to a Stokes' value with an effective viscosity smaller than the constant shear viscosity of the fluid. They also study the implications of this result for the diffusion coefficient.

We shall study here the effects which the large correlation length of density fluctuations could have on the Brownian motion behaviour in a simple fluid. One would expect that these effects become important if one is very close to the critical point where the correlation length exceeds the radius of the Brownian particle. Indeed if one considers the Brownian particle as a probe for the fluid with characteristic length a, the radius of the sphere, there should exist an analogy to light scattering experiments where the characteristic length is the wavelength λ of the incident light and where the scattered intensity behaves differently in the two extreme cases $\lambda \gg \xi$ and $\lambda \ll \xi$. Similarly here one would expect a different behaviour in the two cases $a \gg \xi$ and $a \ll \xi$. As we shall see this is indeed the case. We shall find in particular that in the latter case the velocity autocorrelation function of the Brownian particle has an additional negative contribution to its $t^{-3/2}$ long time tail.

As a first step to study Brownian motion in a critical fluid we shall derive (in sections 2 and 3) an expression for the friction coefficient of a sphere in a compressible fluid taking into account, on the basis of the Ornstein–Zernike theory, the nonlocal relationship between the perturbed pressure and the density field which exists for large values of ξ. We shall use for this derivation the method of induced forces, which was developed previously[5–7]) to obtain generalisations of Faxén's theorem for compressible and incompressible fluids and to establish the connection between fluctuating hydrodynamics and Brownian motion. We shall then also study (section 4) the low frequency behaviour of the friction coefficient and the low frequency and long time behaviour of the velocity autocorrelation function.

2. Stochastic equations of motion

We consider a macroscopic sphere of radius a immersed in a viscous compressible fluid close to its critical point. The motion of the fluid is described by the linearised stochastic Landau–Lifshitz equations of motion

$$\frac{\partial}{\partial t}\rho(\boldsymbol{r}, t) = -\rho_c \operatorname{div} \boldsymbol{v}(\boldsymbol{r}, t), \qquad r > a, \tag{2.1}$$

$$\rho_e \frac{\partial}{\partial t} \boldsymbol{v}(\boldsymbol{r}, t) = -\operatorname{div} \mathbf{P}(\boldsymbol{r}, t), \qquad r > a, \tag{2.2}$$

where ρ is the deviation of the fluid density from its uniform equilibrium value ρ_e, $\boldsymbol{v}$ is the fluid velocity field and $\mathbf{P}$ is the deviation of the pressure tensor from its equilibrium value $p_e\mathbf{I}$ (p_e is the equilibrium value of the hydrostatic pressure, $\mathbf{I}$ the 3-dimensional unit tensor). The tensor $\mathbf{P}$ has elements

$$P_{ij} = p\delta_{ij} - \eta\left(\frac{\partial v_i}{\partial r_j} + \frac{\partial v_j}{\partial r_i}\right) + (\tfrac{2}{3}\eta - \eta_v) \operatorname{div} \boldsymbol{v}\delta_{ij} + \sigma_{ij}. \tag{2.3}$$

Here $\boldsymbol{\sigma}$ is the symmetric random stress tensor which has the usual stochastic properties, p is the deviation of the hydrostatic pressure from its equilibrium value; η and η_v are the shear and bulk viscosity, respectively. We shall assume here that even in the critical region both η and η_v may be considered to be constants*.

We shall furthermore assume that in the critical region the fluctuating motion of the fluid may be considered to be isothermal to a sufficiently good approximation due to the smallness of temperature fluctuations and perturbations† caused by the motion of the sphere. This implies that p will only be a linear function(al) of ρ and not of the temperature T. However in the critical region the connection between p and ρ will be a nonlocal one. On the basis of the Ornstein–Zernike theory for critical density fluctuations this connection is of the form[8,9])

$$p(\boldsymbol{r}, t) = c_0^2(1 - \xi^2\nabla^2)\rho(\boldsymbol{r}, t). \tag{2.4}$$

In eq. (2.4) ξ is the correlation length and c_0 the isothermal sound velocity of the fluid which tends to zero as $1/\xi$ at the critical point within the context of the Ornstein–Zernike theory. The small deviations from this theory very close to the critical point cannot be taken into account in our treatment which is based on the analysis of a partial differential equation of integer order.

The translational motion of the sphere is described by

$$m \frac{\mathrm{d}}{\mathrm{d}t} \boldsymbol{u}(t) = \boldsymbol{K}(t) + \boldsymbol{K}_{\text{ext}}(t) = -\int_S \mathbf{P}(\boldsymbol{r}, t) \cdot \boldsymbol{n} \, \mathrm{d}S + \boldsymbol{K}_{\text{ext}}(t), \tag{2.5}$$

where m is the mass of the sphere, $\boldsymbol{u}$ its velocity and $\boldsymbol{K}$ the force exerted by

* This is not strictly the case, since in particular η_v diverges at the critical point. See also section 5.

† As the critical point is approached both the specific heat at constant pressure and at constant volume diverge so that hydrodynamic processes are then almost isothermal.

the fluid on the sphere; S is the surface of the sphere and $\boldsymbol{n}$ a unit vector normal to the surface pointing out of the sphere. In addition $\boldsymbol{K}_{ext}$ is the external force acting on the sphere. The set of equations (2.1)–(2.5) must be supplemented with boundary conditions on the surface of the sphere. For the velocity field we shall use stick boundary conditions

$$\boldsymbol{v}(\boldsymbol{r}, t) = \boldsymbol{u}(t) + \boldsymbol{\Omega}(t) \times \boldsymbol{r} \quad \text{for } r = a, \tag{2.6}$$

where $\boldsymbol{\Omega}(t)$ is the angular velocity of the sphere. Strictly speaking the boundary conditions apply on the surface of the moving sphere; due to complete linearization, however, eq. (2.6) may be used. Similar simplifications have been made in eqs. (2.1), (2.2) and (2.5). See, for a more detailed discussion of this point, ref. 5. If the correlation length ξ vanishes, i.e. far from the critical point, condition (2.6) is sufficient to solve the above set of equations (upon specification of the boundary condition at infinity). However in view of eq. (2.4) one obtains upon substitution of eqs. (2.1), (2.3) and (2.4) into eq. (2.2) a fourth order differential equation for the irrotational part of the velocity field. Therefore an additional boundary condition at the surface of the sphere is necessary to determine the solution. Simple choices are

$$\text{either} \quad \rho(\boldsymbol{r}, t) = 0 \qquad \text{for } r = a, \tag{2.7a}$$

$$\text{or} \quad \operatorname{grad} \rho(\boldsymbol{r}, t) \cdot \boldsymbol{n} = 0 \quad \text{for } r = a. \tag{2.7b}$$

It is rather difficult to justify either choice on physical grounds although (2.7a) seems a more natural one. It turns out however that for low frequencies our results are in fact independent of the precise form of the boundary condition for ρ. For the time being we shall pursue our analysis assuming (2.7a).

Similarly to the discussion in ref. (5, 7) one may extend the fluid fields $\boldsymbol{v}$ and ρ inside the sphere if one introduces an induced-force density $\boldsymbol{F}_{ind}(\boldsymbol{r}, t)$ inside and on the surface of the sphere. Eq. (2.2) then becomes

$$\rho_e \frac{\partial}{\partial t} \boldsymbol{v}(\boldsymbol{r}, t) = -\operatorname{div} \mathbf{P}(\boldsymbol{r}, t) + \boldsymbol{F}_{ind}(\boldsymbol{r}, t). \tag{2.8}$$

Eqs. (2.1), (2.3) and (2.4) remain the same but are now valid for all r. The induced-force density must be chosen in such a way that

$$\boldsymbol{F}_{ind}(\boldsymbol{r}, t) = 0 \quad \text{for } r > a, \tag{2.9}$$

$$\boldsymbol{v}(\boldsymbol{r}, t) = \boldsymbol{u}(t) + \boldsymbol{\Omega}(t) \times \boldsymbol{r} \quad \text{for } r \leqslant a, \tag{2.10}$$

$$\rho(\boldsymbol{r}, t) = 0 \qquad \text{for } r \leqslant a. \tag{2.11}$$

This alternative set of equations together with the conditions (2.9) and (2.10) is equivalent to the original set (2.1)–(2.4) with the boundary conditions (2.6) and (2.7a).

We may also express the force $K(t)$ exerted by the fluid on the sphere in terms of the induced-force density. According to eq. (2.5) we have

$$K(t) = -\int_S \mathsf{P}(r,t)\cdot n\,\mathrm{d}S = -\int_{r\le a} \mathrm{div}\,\mathsf{P}(r,t)\,\mathrm{d}r, \tag{2.12}$$

which yields upon substitution of eq. (2.8) with eq. (2.10)

$$K(t) = \frac{4\pi}{3}a^3\rho_e\frac{\mathrm{d}}{\mathrm{d}t}u(t) - \int F_{\mathrm{ind}}(r,t)\,\mathrm{d}r. \tag{2.13}$$

We now define the space-time Fourier transform of e.g. the velocity field by

$$v(k,\omega) = \int \mathrm{d}r \int_{-\infty}^{\infty} \mathrm{d}t\; \mathrm{e}^{\mathrm{i}(\omega t - k\cdot r)}v(r,t) \tag{2.14}$$

and similarly for the other fields.

The equations of motion for the fluid then become in wavevector-frequency representation:

$$\frac{\mathrm{i}\omega}{\rho_e}\rho(k,\omega) = \mathrm{i}k\cdot v(k,\omega), \tag{2.15}$$

$$\begin{aligned} -\mathrm{i}\omega\rho_e v(k,\omega) &= -\mathrm{i}c_0^2(1+\xi^2k^2)k\rho(k,\omega) - \eta k^2 v(k,\omega) \\ &\quad -(\tfrac{1}{3}\eta+\eta_v)kk\cdot v(k,\omega) - \mathrm{i}k\cdot\sigma + F_{\mathrm{ind}}(k,\omega), \end{aligned} \tag{2.16}$$

where the pressure tensor and the hydrostatic pressure field have been eliminated using eqs. (2.3) and (2.4).

We shall now write the velocity field as a sum of its transverse and its longitudinal parts

$$v(k,\omega) = \left(1 - \frac{kk}{k^2}\right)\cdot v(k,\omega) + \frac{kk}{k^2}\cdot v(k,\omega) \equiv v_{\mathrm{T}}(k,\omega) + v_{\mathrm{L}}(k,\omega). \tag{2.17}$$

Applying the operators $1 - kk/k^2$ and kk/k^2 to both sides of eq. (2.16) and using (2.15) one obtains for v_{T} and v_{L} the two equations

$$(-i\omega\rho_e + \eta k^2)v_{\mathrm{T}}(k,\omega) = -\left(1-\frac{kk}{k^2}\right)\cdot[\mathrm{i}\sigma\cdot k - F_{\mathrm{ind}}(k,\omega)], \tag{2.18}$$

$$\frac{\rho_e}{\mathrm{i}\omega}\left[\omega^2 - \frac{\eta'}{\rho_e}k^2 + c_0^2k^2(1+\xi^2k^2)\right]v_{\mathrm{L}}(k,\omega) = -\frac{kk}{k^2}\cdot[\mathrm{i}\sigma\cdot k - F_{\mathrm{ind}}(k,\omega)], \tag{2.19}$$

where $\eta' = \frac{4}{3}\eta + \eta_v$.

The formal solutions for $\boldsymbol{v}(\boldsymbol{k},\omega)=\boldsymbol{v}_{\mathrm{T}}(\boldsymbol{k},\omega)+\boldsymbol{v}_{\mathrm{L}}(\boldsymbol{k},\omega)$ and $\rho(\boldsymbol{k},\omega)$ may then be written as

$$\boldsymbol{v}(\boldsymbol{k},\omega)=\boldsymbol{v}_0(\boldsymbol{k},\omega)+\frac{1}{\eta(k^2+\alpha^2)}\left(1-\frac{\boldsymbol{k}\boldsymbol{k}}{k^2}\right)\cdot\boldsymbol{F}_{\mathrm{ind}}(\boldsymbol{k},\omega)$$

$$-\frac{\mathrm{i}\omega}{\rho_{\mathrm{e}}c_0^2\xi^2}\frac{1}{(k^2-k_1^2)(k^2-k_2^2)}\frac{\boldsymbol{k}\boldsymbol{k}}{k^2}\cdot\boldsymbol{F}_{\mathrm{ind}}(\boldsymbol{k},\omega), \tag{2.20}$$

$$\rho(\boldsymbol{k},\omega)=\rho_0(\boldsymbol{k},\omega)-\frac{1}{c_0^2\xi^2}\frac{1}{(k^2-k_1^2)(k^2-k_2^2)}\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{F}_{\mathrm{ind}}(\boldsymbol{k},\omega). \tag{2.21}$$

Here $\boldsymbol{v}_0(\boldsymbol{k},\omega)$ and $\rho_0(\boldsymbol{k},\omega)$ are the solutions of eqs. (2.18) and (2.19) in absence of induced forces and therefore the fluctuating velocity and density fields unperturbed by the presence of the sphere. We have furthermore introduced the following constants

$$\alpha=\left(-\frac{\mathrm{i}\omega\rho_{\mathrm{e}}}{\eta}\right)^{1/2},\quad \mathrm{Re}\,\alpha>0, \tag{2.22}$$

$$k_{1,2}=-\tfrac{1}{2}\sqrt{2}\left\{\frac{-c^2}{c_0^2\xi^2}\pm\left[\left(\frac{c^2}{c_0^2\xi^2}\right)^2+\frac{4\omega^2}{c_0^2\xi^2}\right]^{1/2}\right\}^{1/2}\quad \mathrm{Im}\,k_{1,2}>0, \tag{2.23}$$

as well as the complex frequency dependent sound velocity c

$$c^2=c_0^2-\frac{\mathrm{i}\omega}{\rho_{\mathrm{e}}}\eta',\quad \mathrm{Im}\,c>0. \tag{2.24}$$

Finally we obtain from eq. (2.13) upon Fourier transformation in time

$$\boldsymbol{K}(\omega)=-\frac{4\pi}{3}\rho_{\mathrm{e}}a^3\mathrm{i}\omega\boldsymbol{u}(\omega)-\int\boldsymbol{F}_{\mathrm{ind}}(\boldsymbol{r},\omega)\,\mathrm{d}\boldsymbol{r}$$

$$=-\frac{4\pi}{3}\rho_{\mathrm{e}}a^3\mathrm{i}\omega\boldsymbol{u}(\omega)-\boldsymbol{F}_{\mathrm{ind}}(\boldsymbol{k}=0,\omega). \tag{2.25}$$

In order to determine the force exerted by the fluid on the sphere one must therefore calculate the zero wavenumber component of the induced force.

3. Frequency dependent friction coefficient near the critical point

In order to evaluate $\boldsymbol{F}_{\mathrm{ind}}(\boldsymbol{k}=0,\omega)$ in terms of the velocity $\boldsymbol{u}$ of the sphere and the unperturbed fluid velocity and density fields we average $\boldsymbol{v}(\boldsymbol{r},\omega)$ and $\boldsymbol{r}\rho(\boldsymbol{r},\omega)$ both over the surface and the volume of the sphere:

$$\bar{\boldsymbol{v}}^{\mathrm{s}}(\omega)\equiv(4\pi a^2)^{-1}\int_S \mathrm{d}S\,\boldsymbol{v}(\boldsymbol{r},\omega)=\frac{1}{(2\pi)^3}\int\mathrm{d}\boldsymbol{k}\,\boldsymbol{v}(\boldsymbol{k},\omega)\frac{\sin ka}{ka}, \tag{3.1}$$

$$\overline{v}^{v}(\omega) \equiv (\tfrac{4}{3}\pi a^3)^{-1} \int_{r\leq a} \mathrm{d}\boldsymbol{r}\, \boldsymbol{v}(\boldsymbol{r}, \omega)$$

$$= \frac{3}{(2\pi)^3} \int \mathrm{d}\boldsymbol{k}\, \boldsymbol{v}(\boldsymbol{k}, \omega) \frac{ka \cos ka - \sin ka}{(ka)^3}, \tag{3.2}$$

$$\overline{r\rho}^{s}(\omega) \equiv (4\pi a^2)^{-1} \int_S \mathrm{d}S\, \boldsymbol{r}\rho(\boldsymbol{r}, \omega)$$

$$= (2\pi)^{-3} \int \mathrm{d}\boldsymbol{k}\, \mathrm{i}\frac{\partial}{\partial \boldsymbol{k}} \rho(\boldsymbol{k}, \omega) \frac{\sin ka}{ka}, \tag{3.3}$$

$$\overline{r\rho}^{v}(\omega) \equiv (\tfrac{4}{3}\pi a^3)^{-1} \int_{r\leq a} \mathrm{d}\boldsymbol{r} \rho(\boldsymbol{r}, \omega)$$

$$= 3(2\pi)^{-3} \int \mathrm{d}\boldsymbol{k}\, \mathrm{i}\frac{\partial}{\partial \boldsymbol{k}} \rho(\boldsymbol{k}, \omega) \frac{ka \cos ka - \sin ka}{(ka)^3}. \tag{3.4}$$

We first consider the average quantity defined through (3.1). Using the fact that $\boldsymbol{v}(\boldsymbol{r}, \omega) = \boldsymbol{u}(\omega) + \boldsymbol{\Omega} \times \boldsymbol{r}$ for $r \leq a$ and substituting the formal solution (2.20) into the last member of eq. (3.1) we find

$$\boldsymbol{u}(\omega) = \overline{\boldsymbol{v}_0}^{s}(\omega) + (2\pi)^{-3} \int \mathrm{d}\boldsymbol{\Omega} \int_0^{\infty} \mathrm{d}k\, k^2 \Big(\frac{1}{\eta(k^2 + \alpha^2)} (1 - \boldsymbol{\Omega\Omega}) \cdot \boldsymbol{F}_{\mathrm{ind}}(k\omega, \omega)$$

$$- \frac{\mathrm{i}\omega}{\rho_e c_0^2 \xi^2} \frac{1}{(k^2 - k_1^2)(k^2 - k_2^2)} \boldsymbol{\Omega\Omega} \cdot \boldsymbol{F}_{\mathrm{ind}}(k\boldsymbol{\Omega}, \omega) \Big) \frac{\sin ka}{ka}. \tag{3.5}$$

Here $\overline{\boldsymbol{v}_0}^{s}(\omega)$ is the surface average of the unperturbed fluctuating velocity field, and $\boldsymbol{\Omega}$ the unit vector in the direction of $\boldsymbol{k}$ and $k = |\boldsymbol{k}|$. The integrand in eq. (3.5) is invariant under the transformation $k \to -k$, $\boldsymbol{\Omega} \to -\boldsymbol{\Omega}$. Eq. (3.5) may therefore be written in the form

$$\boldsymbol{u}(\omega) = \overline{\boldsymbol{v}_0}^{s}(\omega) + \frac{1}{(2\pi)^3} \int \mathrm{d}\boldsymbol{\Omega} (1 - \boldsymbol{\Omega\Omega}) \cdot \int_{-\infty}^{\infty} \mathrm{d}k \frac{k^2}{k^2 + \alpha^2} \boldsymbol{F}_{\mathrm{ind}}(k\boldsymbol{\Omega}, \omega) \frac{\sin ka}{ka}$$

$$- \frac{1}{(2\pi)^3} \frac{\mathrm{i}\omega}{2\rho_e c_0^2 \xi^2} \times \int \mathrm{d}\boldsymbol{\Omega\Omega\Omega} \cdot \int_{-\infty}^{\infty} \mathrm{d}k \frac{k^2}{(k^2 - k_1^2)(k^2 - k_2^2)} \boldsymbol{F}_{\mathrm{ind}}(k\boldsymbol{\Omega}, \omega) \frac{\sin ka}{ka}. \tag{3.6}$$

In appendix A we show that $\boldsymbol{F}_{\mathrm{ind}}(k\boldsymbol{\Omega}, \omega)$ has, in view of (2.9) and for complex values of k, the property

$$|\boldsymbol{F}_{\mathrm{ind}}(k\boldsymbol{\Omega}, \omega)| \leq M\, \mathrm{e}^{|k''|a}, \quad M < \infty, \tag{3.7}$$

where k'' is the imaginary part of k. The integrals over k in eq. (3.6) may then be evaluated by complex integration (see appendix B). One finds

$$u(\omega) = \overline{v_0}^{\mathrm{s}}(\omega) + \frac{1}{8\pi\eta a}F^{\mathrm{T}} - \frac{\mathrm{i}\omega}{8\rho_e c_0^2 \xi^2 (k_1^2 - k_2^2) a}(F_1^{\mathrm{L}} - F_2^{\mathrm{L}}), \tag{3.8}$$

where

$$F^{\mathrm{T}}(\omega) = \frac{1}{2\pi}\mathrm{e}^{-\alpha a}\int \mathrm{d}\Omega(1 - \Omega\Omega)\cdot F_{\mathrm{ind}}(\mathrm{i}\alpha\Omega, \omega), \tag{3.9}$$

$$F_{1,2}^{\mathrm{L}}(\omega) = \frac{1}{2\pi}\mathrm{e}^{\mathrm{i}k_{1,2}a}\int \mathrm{d}\Omega\Omega\Omega\cdot F_{\mathrm{ind}}(k_{1,2}\Omega, \omega). \tag{3.10}$$

In the same way one obtains from eqs. (3.2)–(3.4) applying conditions (2.10) and (2.11)

$$u(\omega) = \overline{v_0}^{\mathrm{v}}(\omega) + \frac{3}{4\pi\eta\alpha^2 a^3}F_0 - \frac{3(1+\alpha a)}{8\eta\alpha^2 a^3}F^{\mathrm{T}}$$

$$- \frac{3\mathrm{i}\omega}{8\rho_e c_0^2 \xi^2 (k_1^2 - k_2^2) a^3}\left(\frac{1 - \mathrm{i}k_1 a}{k_1^2}F_1^{\mathrm{L}} - \frac{1 - \mathrm{i}k_2 a}{k_2^2}F_2^{\mathrm{L}}\right), \tag{3.11}$$

$$0 = \overline{r\rho_0}^{\mathrm{s}}(\omega) - \frac{1}{8a^3 c_0^2 \xi^2 (k_1^2 - k_2^2)}((1 - \mathrm{i}k_1 a)F_1^{\mathrm{L}} - (1 - \mathrm{i}k_2 a)F_2^{\mathrm{L}}), \tag{3.12}$$

$$0 = \overline{r\rho_0}^{\mathrm{v}}(\omega) - \frac{3}{4\pi\omega^2 a^3}F_0 + \frac{3}{8a^3 c_0^2 \xi^2 (k_1^2 - k_2^2)}$$

$$\times\left(\frac{3(1 - \mathrm{i}k_1 a) - k_1^2 a^2}{k_1^2}F_1^{\mathrm{L}} - \frac{3(1 - \mathrm{i}k_2 a) - k_2^2 a^2}{k_2^2}F_2^{\mathrm{L}}\right). \tag{3.13}$$

Here $\overline{v_0}^{\mathrm{v}}(\omega)$, $\overline{r\rho_0}^{\mathrm{s}}(\omega)$ and $\overline{r\rho_0}^{\mathrm{v}}(\omega)$ denote surface and volume averages of the unperturbed fluctuating fields; F_0 is defined as

$$F_0 \equiv F_{\mathrm{ind}} \quad (k = 0, \omega). \tag{3.14}$$

Together with (2.25) the eqs. (3.8) and (3.11)–(3.13) form a set of 5 linear equations for the 5 unknown quantities $K(\omega)$, F_0, F^{T}, F_1^{L} and F_2^{L} which can be solved.

One finds in particular for the quantity of interest $K(\omega)$:

$$K(\omega) = -12\pi\eta a(\alpha a)^2[(1 + \alpha a + \alpha^2 a^2)C + 2\alpha^2 a^2 D]^{-1}$$

$$\times\Big\{[\tfrac{2}{9}(1 + \alpha a)C + (1 + \alpha a + \tfrac{1}{9}\alpha^2 a^2)D]u(\omega)$$

$$-(1 + \alpha a)(\tfrac{1}{3}C + D)\overline{v_0}^{\mathrm{s}}(\omega) - \tfrac{1}{3}\alpha^2 a^2(\tfrac{1}{3}C + D)\overline{v_0}^{\mathrm{v}}(\omega)$$

$$-\frac{1}{9}\frac{\mathrm{i}\omega}{\rho_e}[(1 + \alpha a)C - \alpha^2 a^2 D]\overline{r\rho_0}^{\mathrm{v}}(\omega)$$

$$
-\frac{1}{3}\frac{\mathrm{i}\omega a^2}{\rho_e}(1 + \alpha a + \tfrac{1}{3}\alpha^2 a^2)\frac{k_1^2(1 - \mathrm{i}k_1 a) - k_2^2(1 - \mathrm{i}k_2 a)}{(\mathrm{i}ak_1 - \mathrm{i}ak_2)(k_1^2 - k_2^2)}\overline{r\rho_0^{\rightarrow s}}(\omega)\}. \tag{3.15}
$$

with

$$
C = \frac{a^2 k_1^2 k_2^2}{k_1^2 - k_2^2}, \tag{3.16}
$$

$$
D = \frac{(1 - \mathrm{i}ak_1)(1 - \mathrm{i}ak_2)}{(\mathrm{i}ak_1 - \mathrm{i}ak_2)}. \tag{3.17}
$$

Eq. (3.15) can be written in the form

$$
\boldsymbol{K}(\omega) = -\zeta(\omega)\boldsymbol{u}(\omega) + \boldsymbol{K}_{\mathrm{R}}(\omega), \tag{3.18}
$$

where $\zeta(\omega)$ is the frequency-dependent friction coefficient for the motion of a sphere in a compressible fluid close to its critical point, defined through eq. (3.15) as the coefficient of $\boldsymbol{u}(\omega)$ and where $\boldsymbol{K}_{\mathrm{R}}(\omega)$ is the random force on a spherical Brownian particle of which the stochastic properties are completely determined by the stochastic properties of the unperturbed fluid.

The expression for $\boldsymbol{K}_{\mathrm{R}}(\omega)$ which follows from eq. (3.15) represents to say a generalisation of Faxén's theorem to the case of a sphere held fixed in a compressible fluid close to its critical point in nonstationary nonhomogeneous flow.

It can be verified* using the stochastic properties of the random stress tensor $\boldsymbol{\sigma}$ which determines the unperturbed fluid velocity and density fluctuation spectra that the correlation function of the random force $\boldsymbol{K}_{\mathrm{R}}(\omega)$ obeys the fluctuation-dissipation theorem

$$
\langle K_{\mathrm{R},i}(\omega)K_{\mathrm{R},j}(\omega')\rangle = 2k_{\mathrm{B}}T\ \mathrm{Re}\ \zeta(\omega)\delta_{ij}2\pi\delta(\omega - \omega'), \tag{3.19}
$$

where the angular brackets denote averages over an equilibrium ensemble. Thus as expected the usual fluctuation-dissipation theorem also holds for Brownian motion in a critical fluid.

Note that substitution of eq. (3.18) in time representation into eq. (2.5) yields the generalised Langevin equation valid for the case studied above.

In the next section we shall study in somewhat more detail the frequency behaviour of the friction coefficient.

* The fluctuation-dissipation theorem (3.19) can best be derived by appropriately generalising the method developed by Fox and Uhlenbeck[10]) for the derivation from fluctuating hydrodynamics of the analogous theorem for Brownian motion in an incompressible fluid. Direct derivation from eq. (3.15) is exceedingly cumbersome.

4. Low frequency behaviour

The small frequency behaviour of the friction coefficient is of particular interest since it determines the long time behaviour of the corresponding friction memory kernel and therefore also of the velocity autocorrelation function of the spherical Brownian particle. From eq. (3.15) together with eqs. (3.16) and (3.17) it follows that $\zeta(\omega)$ may explicitly be written as

$$\begin{aligned}\zeta(\omega) = {} & 12\pi\eta a(\alpha a)^2\{\tfrac{2}{9}(1+\alpha a)a^4k_1^2k_2^2 - (1+\alpha a+\tfrac{1}{9}\alpha^2a^2)\\ & \times[(iak_1+iak_2)-(iak_1+iak_2)^2 - a^2k_1k_2(iak_1+iak_2)]\}\\ & \times((1+\alpha a+\alpha^2a^2)a^4k_1^2k_2^2 - 2\alpha^2a^2[(iak_1+iak_2)\\ & -(iak_1+iak_2)^2 - a^2k_1k_2(iak_1+iak_2)])^{-1}.\end{aligned} \tag{4.1}$$

Let us introduce 3 characteristic times

$$\tau_1 = a^2\nu^{-1}, \quad \tau_2 = a^2\nu'^{-1}, \quad \tau_3 = a^2\nu'/c_0^2\xi^2, \tag{4.2}$$

where ν and ν' are the kinematic viscosities η/ρ_e and η'/ρ_e, respectively. Since $c_0^2\xi^2$ behaves as a constant in the critical region, the ratios of the characteristic times are all constant and independent of the size of the particle. As we shall see below τ_1, τ_2 and τ_3 are for a typical fluid all of approximately equal magnitude.

Note that according to def. (2.22) and def. (4.2)

$$\alpha^2a^2 = -i\omega\tau_1. \tag{4.3}$$

Moreover according to eqs. (2.23) and (2.24) and the definitions (4.2)

$$a^2k_{1,2}^2 = \tfrac{1}{2}[-(a^2/\xi^2 - i\omega\tau_3) \pm ((a^2/\xi^2 - i\omega\tau_3)^2 + 4\omega^2\tau_2\tau_3)^{1/2}]. \tag{4.4}$$

We shall now study the low frequency behaviour of $\zeta(\omega)$ in two limiting cases.

(i) Sufficiently far from the critical point so that $\xi \ll a$ and for frequencies such that $\omega\tau_1$, $\omega\tau_2$ and $\omega\tau_3$ are all smaller than 1 we have from eq. (4.4)

$$a^2k_1^2 \simeq \omega^2\tau_2\tau_3(\xi^2/a^2) = a^2\omega^2c_0^{-2}, \tag{4.5}$$

$$a^2k_2^2 \simeq -(a^2/\xi^2), \tag{4.6}$$

where in the last member of eq. (4.5) the definitions (4.2) have again been used.

Therefore in this case

$$|ak_1| \ll 1, \quad |ak_2| \gg 1. \tag{4.7}$$

Dividing both numerator and denominator of eq. (4.1) by $a^2k_2^2$, $\zeta(\omega)$ reduces then in view of (4.7) in good approximation to

$$\begin{aligned}\zeta(\omega) &= 12\pi\eta a(\alpha a)^2\{\tfrac{2}{9}(1+\alpha a)a^2k_1^2-(1+\alpha a+\tfrac{1}{9}\alpha^2a^2)(1-\mathrm{i}ak_1)\}\\ &\quad\times[(1+\alpha a+\alpha^2a^2)a^2k_1^2-2\alpha^2a^2(1-\mathrm{i}ak_1)]^{-1}\\ &= 6\pi\eta a(1-(-\mathrm{i}\omega\tau_1)^{1/2}+\tfrac{1}{9}\mathrm{i}\omega\tau_1)(1+\mathcal{O}(\xi^2/a^2)),\\ &\quad \xi\ll a,\ \omega\tau_1\leqslant 1.\end{aligned} \tag{4.8}$$

Thus in this frequency domain the friction coefficient has to a very good approximation the form of the friction coefficient for a sphere of radius a moving in an incompressible fluid. Note that this result will hold even rather close to the critical point if the sphere is sufficiently large.

(ii) Very close to the critical point so that $\xi\gg a$ one has according to eq. (4.4) and for frequencies such that $\omega\gg(a^2/\xi^2)\tau_3^{-1}$

$$a^2k_{1,2}^2=\tfrac{1}{2}\mathrm{i}\omega\tau_3[1\pm\sqrt{1-4\tau_2/\tau_3}]. \tag{4.9}$$

At the critical point, $\xi\to\infty$, eq. (4.9) will hold for all frequencies.

From eq. (4.9) one finds

$$a^2k_1k_2=-\omega^2\tau_2\tau_3, \tag{4.10}$$

$$(\mathrm{i}ak_1+\mathrm{i}ak_2)=-\sqrt{-\mathrm{i}\omega\tau_3}[1+\sqrt{4\tau_2/\tau_3}]^{1/2},\quad \mathrm{Re}\sqrt{-\mathrm{i}}>0. \tag{4.11}$$

Substituting eqs. (4.10) and (4.11) into eq. (4.1) and expanding subsequently in powers of $\omega^{1/2}$ we obtain

$$\begin{aligned}\zeta(\omega) &= 6\pi\eta a\left[1-\sqrt{-\mathrm{i}\omega}\left(\sqrt{\tau_1}-\frac{\tau_2}{2\tau_1}\sqrt{\tau_3}\Big/(1+\sqrt{4\tau_2/\tau_3})^{1/2}\right)+\mathcal{O}(\omega)\right],\\ &\quad \xi\gg a,\ \omega\gg(a^2/\xi^2)\tau_3^{-1}.\end{aligned} \tag{4.12}$$

Extremely close to the critical point therefore the coefficient of $-(-\mathrm{i}\omega)^{1/2}$ is modified. While this coefficient far from the critical point is equal to $\sqrt{\tau_1}$ (cf. eq. (4.8)) it becomes smaller and may in principle even become negative at the critical point or extremely close to it.

One may verify in a similar way that for frequencies $\omega\ll(a^2/\xi^2)\tau_3^{-1}$ and $\xi\gg a$ one has up to order $\omega^{1/2}$

$$\begin{aligned}\zeta(\omega) &= 6\pi\eta a[1-(-\mathrm{i}\omega\tau_1)^{1/2}+\mathcal{O}(\omega)],\\ &\quad \xi\gg a,\ \omega\ll(a^2/\xi^2)\tau_3^{-1}.\end{aligned} \tag{4.13}$$

It is clear from eqs. (4.8), (4.12) and (4.13) that the zero frequency value of ζ is always the Stokes' value $6\pi\eta a$, whether one first takes the limit $\xi\to\infty$ or not.

From eqs. (4.6) and (4.12) one may determine the long time behaviour of the friction memory kernel $\zeta(t)$ which is the Fourier transform of $\zeta(\omega)$. One finds from eq. (4.8) for the asymptotic form of $\zeta(t)$ for positive values of t

$$\zeta(t) = -3\eta\alpha\sqrt{\pi\tau_1}\,t^{-3/2}, \quad \xi \ll a, \tag{4.14}$$

and from eq. (4.13)

$$\zeta(t) = -3\eta a\sqrt{\pi}\left(\sqrt{\tau_1} - \frac{\tau_2}{2\tau_1}\sqrt{\tau_3}\Big/(1+\sqrt{4\tau_2/\tau_3})^{1/2}\right)t^{-3/2},$$

$$\xi \gg a,\ t \ll \tau_3\xi^2/a^2. \tag{4.15}$$

Using the results obtained above we shall now study the long time behaviour of the velocity autocorrelation function of the spherical Brownian particle.

For a particle not subjected to an external force it follows directly from eqs. (3.18) and (3.19) together with eq. (2.5) that

$$\langle u(\omega)u(\omega')\rangle = 2\pi\delta(\omega-\omega')S(\omega), \tag{4.16}$$

with

$$S(\omega) = 2k_{\mathrm{B}}T\,\mathrm{Re}[-im\omega + \zeta(\omega)]^{-1}. \tag{4.17}$$

Fourier transformation of eq. (4.16) with respect to ω and ω' leads to

$$S(\tau) \equiv \langle u(t)u(t+\tau)\rangle = \frac{1}{2\pi}\int_{-\infty}^{\infty} S(\omega)\,\mathrm{e}^{i\omega\tau}\,\mathrm{d}\omega. \tag{4.18}$$

The function $S(\omega)$ is the spectral density of the velocity autocorrelation function of the Brownian particle.

It is now possible by standard methods[11]) to determine the long time behaviour of $S(t)$ from the low frequency behaviour of $\zeta(\omega)$.

(i) $\xi \ll a$. From eq. (4.8) and using eqs. (4.17) and (4.18) one finds for the asymptotic behaviour of $S(t)$

$$S(t) \simeq (k_{\mathrm{B}}T/12\pi^2\eta a)\sqrt{\pi\tau_1}|t|^{-3/2}. \tag{4.19}$$

This is the usual positive long time tail caused by the interaction of the particle with the vortices in the fluid which it creates in its random motion. This long time behaviour will be found even close to the critical point as long as the particle is sufficiently large, $\xi \ll a$.

(ii) $\xi \gg a$. From eq. (4.12) together with eqs. (4.17) and (4.18) one now obtains for the long time behaviour of $S(t)$

$$S(t) \simeq (k_B T/12\pi^2\eta a)\sqrt{\pi}[\sqrt{\tau_1} - (\tau_2/2\tau_1)\sqrt{\tau_3}/[1 + \sqrt{4\tau_2/\tau_3}]^{1/2}]|t|^{-3/2},$$
$$t \ll \tau_3\xi^2/a^2. \tag{4.20}$$

At the critical point eq. (4.20) holds asymptotically. A negative contribution to the long time tail thus appears extremely close to the critical point, $\xi \gg a$. This contribution is related to the fact that the particle creates in the direction of its motion a positive density fluctuation and a negative density fluctuation behind it. These fluctuations are long ranged and propagate slowly at low wavenumber. As a result the particle is to say partially trapped in a cage formed by the density fluctuations it creates.

5. Discussion

It has been shown that the relative size of the correlation length and the radius of the particle has a marked influence on the frequency dependence of the friction coefficient and the time behaviour of the velocity autocorrelation function of a Brownian particle. Contrary to a result previously obtained by Giterman and Gertsenshtein the zero frequency limit of $\zeta(\omega)$ is always equal to $6\pi\eta a$ whether one takes the critical limit ($\xi \to \infty$) first, or not. Therefore a critical anomaly in a quantity like the diffusion constant which is related to the zero frequency friction coefficient must be interpreted in terms of the weak critical anomaly in the shear viscosity of the fluid[12]) which has been considered constant in this paper. This justifies at least for a simple fluid the point of view taken by Lyons, Mockler and O'Sullivan.

The low frequency behaviour of $\zeta(\omega)$ found by Giterman and Gertsenshtein close to the critical point assuming that the influence of the correlation length may be neglected cannot be justified. Their result can be obtained from our general expression if one were first to take the limit $\xi \to 0$, thus obtaining the general expression for the friction coefficient in a compressible fluid far from the critical point, and then the limit $c_0 \to 0$, which is clearly an inconsistent procedure.

As we have seen the velocity autocorrelation function of the Brownian particle has in the critical region but not too close to the critical point ($\xi < a$) the usual $t^{-3/2}$ long time tail while sufficiently close to the critical point ($\xi > a$) a negative critical contribution to this tail appears.

From an analysis of critical data[13–15]) one may obtain an estimate of the relative magnitude of the positive and negative contribution to the critical long time behaviour of the velocity autocorrelation function. The ratio γ of the negative and positive contribution is equal to

$$\gamma = \tfrac{1}{2}(\tau_2/\tau_3)/(\tau_1/\tau_3)^{3/2}[1 + (4\tau_2/\tau_3)^{1/2}]^{1/2}. \tag{5.1}$$

We shall consider two typical fluids and neglect entirely the contribution of the volume viscosity η_v so that $\nu' = \frac{4}{3}\nu$. For Xe one has the following data: $\nu \simeq 5 \times 10^{-4}\,\mathrm{cm}^2\,\mathrm{sec}^{-1}$ [14]), $c_0^2\xi^2 \simeq 4 \times 10^{-7}\,\mathrm{cm}^4\,\mathrm{sec}^{-2}$ [12,13]). Consequently $\tau_1/\tau_3 \simeq 1.2$, $\tau_2/\tau_3 \simeq 0.9$ and $\gamma \simeq 0.2$.

For CO_2 one has $\nu \simeq 7 \times 10^{-4}\,\mathrm{cm}^2\,\mathrm{sec}^{-1}$ [14]), $c_0^2\xi^2 \simeq 2.3 \times 10^{-6}\,\mathrm{cm}^4\,\mathrm{sec}^{-2}$ [12,13]) so that $\tau_1/\tau_3 \simeq 3.5$, $\tau_2/\tau_3 \simeq 2.6$ and $\gamma \simeq 0.1$. We must conclude that the negative contribution to the critical $t^{-3/2}$ tail is in general small compared to the usual $t^{-3/2}$ tail*.

Since at present it is still rather doubtful that the $t^{-3/2}$ behaviour can be experimentally observed a small critical modification in this result cannot adequately be probed.

In the calculation of the friction coefficient we have assumed not only the shear viscosity but also the volume viscosity to be constant. The volume viscosity however is believed to diverge as ξ at zero wavevector and to become independent of ξ for sufficiently high values of k [17]). In order to include effects due to this k dependent behaviour of η_v the preceding treatment would have to be modified and might then lead for the negative part of the critical long time tail of the velocity autocorrelation function to a slightly smaller amplitude and a slightly smaller time exponent. Such modifications in the long time behaviour are at present not experimentally measurable.

Let us finally make a remark concerning the boundary condition for the fluid density perturbation at the surface of the sphere. In our analysis we have chosen condition (2.7a). If we had made the alternative choice, eq. (2.7b), the expression (3.15) for the force on the Brownian particle exerted by the fluid would have been modified. It may be shown however that all low frequency results of section 4 remain unaltered. In fact the low frequency results may also be obtained from eq. (2.8) by expanding $\boldsymbol{F}^{\mathrm{T}}$, $\boldsymbol{F}_1^{\mathrm{L}}$ and $\boldsymbol{F}_2^{\mathrm{L}}$ around $\boldsymbol{F}_0$. In this equation the boundary condition for ρ has not yet been used.

* In a recent letter[16]) we strongly overestimated γ on the basis of a value for ν given by Giterman and Gertsenshtein. These authors quote as a typical value for υ' in the critical region 0.1 $\mathrm{cm}^2\,\mathrm{sec}^{-1}$. This value is too large by a factor 10^2 and lead us to an incorrect value for γ which was also too large by a factor of the order 10^2.

Appendix A

From eq. (2.8) together with eqs. (2.1), (2.3) and (2.4) as well as the conditions (2.10) and (2.11) it follows that $F_{ind}(r, \omega)$ has the following form:

$$F_{ind}(r, \omega) = f_1(r, \theta, \phi; \omega) + f_2(\theta, \phi; \omega)\delta(r-a) + f_3(\theta, \phi; \omega)\delta'(r-a), \quad \text{(A.1)}$$

where f_1 must be zero for $r > a$ and where θ and ϕ are polar angles in a coordinate frame of which the z-axis may be chosen in an arbitrary direction. The functions f_1, f_2 and f_3 and in addition the derivative of f_3 with respect to θ are all bounded.

$$|f_1| < A_1, \quad |f_2| < A_2, \quad |f_3| < A_3, \quad \left|\frac{\partial f_3}{\partial \theta}\right| < A_4. \quad \text{(A.2)}$$

The Fourier transform of $F_{ind}(r, \omega)$ may then be written as

$$F(k\boldsymbol{\Omega}, \omega) = \int \mathrm{d}\boldsymbol{r}\, \mathrm{e}^{-\mathrm{i}k\boldsymbol{\Omega}\cdot\boldsymbol{r}}\, F_{ind}(\boldsymbol{r}, \omega)$$
$$= I_1(k, \omega) + I_2(k, \omega) + \mathrm{i}akI_3(k, \omega), \quad \text{(A.3)}$$

where

$$I_1 = \int_{r<a} r^2 f_1(r, \theta', \phi'; \omega)\, \mathrm{e}^{-\mathrm{i}kr\boldsymbol{\Omega}\cdot\boldsymbol{\Omega}'}\, \mathrm{d}r\, \mathrm{d}\boldsymbol{\Omega}', \quad \text{(A.4)}$$

with $\boldsymbol{\Omega}'$ the unit vector in the direction of $\boldsymbol{r}$,

$$I_2 = a^2 \int f_2(\theta', \phi'; \omega)\, \mathrm{e}^{-\mathrm{i}ka\boldsymbol{\Omega}\cdot\boldsymbol{\Omega}'}\, \mathrm{d}\boldsymbol{\Omega}', \quad \text{(A.5)}$$

and

$$I_3 = a^2 \int f_3(\theta', \phi'; \omega)\boldsymbol{\Omega}\cdot\boldsymbol{\Omega}'\, \mathrm{e}^{-\mathrm{i}ka\boldsymbol{\Omega}\cdot\boldsymbol{\Omega}'}\, \mathrm{d}\boldsymbol{\Omega}. \quad \text{(A.6)}$$

Using the first inequality in (A.2) we find for I_1

$$|I_1| < 4\pi a^3 A_1\, \mathrm{e}^{|k''|a}, \quad \text{(A.7)}$$

where k'' is the imaginary part of k.

Similarly we have from (A.5) and the second inequality in (A.2)

$$|I_2| \leq 4\pi a^2 A_2 \, e^{|k''|a}. \tag{A.8}$$

The integral I_3 may be written in the form

$$I_3 = a^2 \int_0^{2\pi} d\phi \int_{-1}^{+1} d\xi \, \xi f_3(\theta, \phi; \omega) \, e^{-ika\xi}, \tag{A.9}$$

where $\xi = \cos\theta$ and θ is the angle between $\boldsymbol{\Omega}$ and $\boldsymbol{\Omega}'$. In this way the z-axis of our polar coordinate frame (cf. (A.1)) has been chosen along the direction of $\boldsymbol{\Omega}$.

Partially integrating (A.9) with respect to ξ one obtains

$$I_3 = \frac{a^2\xi}{-ika} e^{-ika\xi} \int_0^{2\pi} d\phi \, f_3(\theta, \phi; \omega)\Big|_{\xi=-1}^{\xi=+1}$$

$$+ \frac{a^2}{ika} \int_0^{2\pi} d\phi \int_{-1}^{+1} d\xi \, e^{-ika\xi} \left(f_3(\theta, \phi; \omega) + \frac{\xi}{(1-\xi^2)^{1/2}} \frac{\partial f_3}{\partial\theta}(\theta, \phi; \omega) \right). \tag{A.10}$$

It then follows from the last two inequalities in (A.2) that

$$|I_3| \leq 4\pi a (A_3 + A_4) \frac{e^{|k''|a}}{|k|}. \tag{A.11}$$

Collecting (A.7), (A.8) and (A.11) it then follows from (A.3) that

$$|\boldsymbol{F}_{\text{ind}}(k\boldsymbol{\Omega}, \omega)| \leq M \, e^{|k''|a}, \tag{A.12}$$

which is inequality (3.7).

Appendix B

Consider first the integral

$$\boldsymbol{I}_1 = \int d\boldsymbol{\Omega} (1 - \boldsymbol{\Omega}\boldsymbol{\Omega}) \cdot \boldsymbol{I}_1', \tag{B.1}$$

where

$$\boldsymbol{I}_1' = \lim_{\epsilon \to 0} \int_{-\infty}^{\infty} dk \frac{k}{k^2 + \alpha^2} \boldsymbol{F}_{\text{ind}}(k\boldsymbol{\Omega}, \omega) \frac{\sin k(a+\epsilon)}{a+\epsilon}$$

$$= \lim_{\epsilon \to 0} \left(\frac{1}{2i(a+\epsilon)} \int_{-\infty}^{\infty} dk \frac{k \, e^{ik(a+\epsilon)}}{k^2 + \alpha^2} \boldsymbol{F}_{\text{ind}}(k\boldsymbol{\Omega}, \omega) \right.$$

$$- \frac{1}{2i(a+\epsilon)} \int_{-\infty}^{\infty} dk \frac{k\, e^{-ik(a+\epsilon)}}{(k^2+\alpha^2)} \boldsymbol{F}_{ind}(k\boldsymbol{\Omega}, \omega)\Bigg), \tag{B.2}$$

where $\epsilon > 0$.

As a consequence of inequality (3.7) the first integral of the left hand side of (A.2) can be closed in the upper halfplane and the second one in the lower halfplane. The only poles in the integrand are the simple poles $k = \pm i\alpha$ of which $k = +i\alpha$ lies in the upper halfplane and $k = -i\alpha$ in the lower halfplane due to def. (2.22).

Applying Cauchy's theorem and taking subsequently the limit $\epsilon \to 0$ one therefore has

$$\begin{aligned} \boldsymbol{I}_1' &= \frac{1}{2i} 2\pi i (\tfrac{1}{2} e^{-\alpha a} \boldsymbol{F}_{ind}(i\alpha\boldsymbol{\Omega}, \omega) + \tfrac{1}{2} e^{-\alpha a} \boldsymbol{F}_{ind}(-i\alpha\boldsymbol{\Omega}, \omega)) \\ &= \frac{\pi}{2} e^{-\alpha a} (\boldsymbol{F}_{ind}(i\alpha\boldsymbol{\Omega}, \omega) + \boldsymbol{F}_{ind}(-i\alpha\boldsymbol{\Omega}, \omega)). \end{aligned} \tag{B.3}$$

Inserting this result into (B.1) one obtains

$$\begin{aligned} \boldsymbol{I}_1 &= \frac{\pi}{2} e^{-\alpha a} \left(\int d\boldsymbol{\Omega} (1 - \boldsymbol{\Omega}\boldsymbol{\Omega}) \cdot \boldsymbol{F}_{ind}(i\alpha\boldsymbol{\Omega}, \omega) + \int d\boldsymbol{\Omega} (1 - \boldsymbol{\Omega}\boldsymbol{\Omega}) \cdot \boldsymbol{F}_{ind}(-i\alpha\boldsymbol{\Omega}, \omega) \right) \\ &= \pi\, e^{-\alpha a} \int d\boldsymbol{\Omega} (1 - \boldsymbol{\Omega}\boldsymbol{\Omega}) \cdot \boldsymbol{F}_{ind}(i\alpha\boldsymbol{\Omega}, \omega), \end{aligned} \tag{B.4}$$

where the last member of (B.4) is obtained by performing the transformation $\boldsymbol{\Omega} \to -\boldsymbol{\Omega}$ in the second integral of the first member. The integral

$$\boldsymbol{I}_2 = \int d\boldsymbol{\Omega}\boldsymbol{\Omega}\boldsymbol{\Omega} \cdot \boldsymbol{I}_2', \tag{B.5}$$

where

$$\begin{aligned} \boldsymbol{I}_2' &= \lim_{\epsilon \to 0} \int_{-\infty}^{\infty} dk \frac{k}{(k^2 - k_1^2)(k^2 - k_2^2)} \boldsymbol{F}_{ind}(k\boldsymbol{\Omega}, \omega) \frac{\sin k(a+\epsilon)}{a+\epsilon} \\ &= \lim_{\epsilon \to 0} \frac{1}{2i(a+\epsilon)} \Bigg(\int_{-\infty}^{\infty} dk \frac{k\, e^{ik(a+\epsilon)}}{(k^2 - k_1^2)(k^2 - k_2^2)} \boldsymbol{F}_{ind}(k\boldsymbol{\Omega}, \omega) \\ &\quad - \frac{1}{2i(a+\epsilon)} \int_{-\infty}^{\infty} dk \frac{k\, e^{-ik(a+\epsilon)}}{(k^2 - k_1^2)(k^2 - k_2^2)} \boldsymbol{F}_{ind}(k\boldsymbol{\Omega}, \omega) \Bigg) \end{aligned} \tag{B.6}$$

is evaluated in a similar way. There are now 4 simple poles $k = \pm k_1$, $k = \pm k_2$ of which $k = k_1$ and $k = k_2$ are in the upper halfplane due to def. (2.23).

Using Cauchy's theorem one obtains in this case

$$I_2' = \frac{\pi}{2}\frac{e^{ik_1a}}{(k_1^2 - k_2^2)}(F_{ind}(k_1\Omega, \omega) + F_{ind}(-k_1\Omega, \omega))$$
$$-\frac{\pi}{2}\frac{e^{ik_2a}}{(k_1^2 - k_2^2)}(F_{ind}(k_2\Omega, \omega) + F_{ind}(-k_2\Omega, \omega)). \quad (B.7)$$

Inserting (B.7) into (B.6) one obtains

$$I_2 = \frac{\pi}{k_1^2 - k_2^2}\Big(e^{ik_1a}\int d\Omega\Omega\Omega \cdot F_{ind}(k_1\Omega, \omega)$$
$$- e^{ik_2a}\int d\Omega\Omega\Omega \cdot F_{ind}(k_2\Omega, \omega)\Big). \quad (B.8)$$

Substitution of eqs. (B.4) and (B.8) into eq. (3.6) then yields the expression for $u(\omega)$ given in eq. (3.8).

Eqs. (3.11)–(3.13) are obtained in a similar way.

References

1) H.N.W. Lekkerkerker, Physica **80A** (1975) 415.
2) K.B. Lyons, R.C. Mockler and W.J. O'Sullivan, Phys. Rev. A **10** (1974) 393.
3) R. Perl and R.A. Ferrell, Phys. Rev. A **6** (1972) 2358.
4) M.Sh. Giterman and M.E. Gertsenshtein, Sov. Phys. JETP **23** (1966) 722.
5) P. Mazur and D. Bedeaux, Physica **76** (1974) 235.
6) D. Bedeaux and P. Mazur, Physica **76** (1974) 247.
7) D. Bedeaux and P. Mazur, Physica **78** (1974) 505.
8) L.D. Landau and E.M. Lifshitz, Statistical Physica (Pergamon Press, Oxford, 1970).
9) M.Sh. Giterman and V.M. Kontorovich, Sov. Phys. JETP **20** (1965) 1433.
10) R.F. Fox and G.E. Uhlenbeck, Phys. Fluids **13** (1970) 1893.
11) See e.g. E.G. Hauge and A. Martin-Löf, J. Stat. Phys. **7** (1973) 259.
12) E.D. Siggia, B.I. Halperin and P.C. Hohenberg, Phys. Rev. **13** (1976) 2110.
13) M.E. Stanley, Introduction to Phase Transitions and Critical Phenomena (Clarendon Press Oxford, 1971).
14) P. Heller, Rep. Prog. Phys. **30** (1967) 731.
15) H.J. Strumpf, A.F. Collings and C.J. Pings, J. Chem. Phys. **60** (1974) 3109.
16) P. Mazur and G. Van der Zwan, Phys. Lett. **62A** (1977) 201.
17) L.P. Kadanoff and J. Swift, Phys. Rev. **166** (1968) 89.

II. THE FLUCTUATION-DISSIPATION THEOREM

Fluctuation–dissipation theorems for the random force and the random torque on a Brownian particle of arbitrary shape immersed in a fluid close to its critical point are derived from fluctuating hydrodynamics, taking also into account the temperature fluctuations in the fluid. It is assumed that the particle is either a perfect insulator for heat or an ideal conductor. In the latter case the fluctuation–dissipation theorems involve also the random heat source generated by the fluid fluctuations.

1. Introduction

In recent years a considerable number of papers have been devoted to the derivation of the Langevin equation for a Brownian particle, and of the stochastic properties of the random force, from fluctuating hydrodynamics i.e. from the so called Landau–Lifshitz equations for a fluctuating fluid. Two types of derivations have been proposed.

The first type of derivation is based on generalisations of Faxén's theorem for the force exerted on a sphere by a viscous fluid and makes use of the method of induced forces[1-3]). One obtains within this framework an explicit expression for the frequency dependent friction coefficient and an expression for the random force in terms of the unperturbed fluctuating fluid fields. This has been done for a particle immersed in an incompressible fluid[1]) and also in a compressible fluid with isentropic flow[3]). The fluctuation–dissipation theorem for the autocorrelation function of the random force on the Brownian particle should then follow from the stochastic properties of the unperturbed fluctuating fluid fields. This has been established explicitly for the case of a Brownian particle immersed in an incompressible fluid and could in principle also be verified in the other case.

An alternative type of derivation for a particle immersed in an incompressible fluid was first given by Fox and Uhlenbeck[4]) and extended by various authors[2,5-7]). The main emphasis here is centered on the establishment of the fluctuation–dissipation theorem for the random force. Explicit knowledge of the friction coefficient is not needed nor an expression for the random force in terms of the fluctuating fluid fields. This second method has the advantage that it also applies to particles of arbitrary shape. In both types of derivations independent temperature fluctuations in the fluid have until now not been taken into account.

In a previous paper[8]) we studied Brownian motion in a fluid near its critical point along the lines of the first method using the procedure of induced forces and assuming the flow to be isothermal. We were able to obtain an explicit expression for the frequency dependent friction coefficient which depends in an essential way on the correlation length of density fluctuations in the fluid. We also obtained an expression for the random force in terms of the unperturbed velocity and density fields in the critical fluid. We then studied the behaviour of the velocity autocorrelation function of the Brownian particle assuming the fluctuation–dissipation theorem for the random force to hold. Alt ugh this theorem could have been directly verified in principle on the basis f the expression for the random force, this was not done since it would h: : been exceedingly cumbersome.

In this paper we wish to extend the second method to the case of a particle immersed in a fluid close to its critical point taking also temperature fluctuations into account. By this method the fluctuation–dissipation theorem can be established in a straightforward way .

In section 2 we formulate the stochastic linearized equations of motion for the fluid density-, velocity- and temperature-fields. The hydrostatic pressure in the fluid is assumed to be related to the density according to the Ornstein–Zernike approximation. In section 3 we derive to fundamental Green identities for the average and fluctuating fluid fields. In section 4 we formulate the equations of motion for the particle velocity, angular velocity and internal energy and specify the boundary conditions valid on the surface of the particle. For the temperature field we consider the case that a particle is a thermal insulator and also the case that a particle is an ideal conductor for heat. In section 5 we then derive the fluctuation–dissipation theorems for the random force and the random torque acting on a heat insulating spherical particle using the two fundamental Green identities derived in section 3. In section 6 we derive the fluctuation–dissipation theorems for the random force, random torque and random heat source for an ideal heat conducting spherical particle. Finally in section 7 we discuss particles of arbitrary shape, for which cross effects between translation, rotation and cooling can occur, and derive the relevant fluctuation–dissipation theorems. Here the symmetry properties of the coefficient scheme in the equations of motion of the particle plays an essential role. These properties are derived in appendix B using hydrodynamics and boundary conditions only.

2. Stochastic equations of motion of the fluid

We consider a rigid particle of mass density ρ_s and of arbitrary shape immersed in a fluid. The centre of mass of the particle is located at position $\boldsymbol{R}$†; the particle has a volume V while the fluid outside the particle occupies a volume V_c. The linearized stochastic equations of motion of the fluid are in frequency representation[9])

$$\mathrm{i}\omega\rho(\boldsymbol{r},\omega)=\rho_c\boldsymbol{\nabla}\cdot\boldsymbol{v}(\boldsymbol{r},\omega),\quad \boldsymbol{r}\in V_c, \tag{2.1}$$

$$\mathrm{i}\omega\rho_c\boldsymbol{v}(\boldsymbol{r},\omega)=\boldsymbol{\nabla}\cdot\boldsymbol{P}(\boldsymbol{r},\omega),\quad \boldsymbol{r}\in V_c, \tag{2.2}$$

$$\mathrm{i}\omega\rho_c c_v T(\boldsymbol{r},\omega)=\alpha T_c\boldsymbol{\nabla}\cdot\boldsymbol{v}(\boldsymbol{r},\omega)+\boldsymbol{\nabla}\cdot\boldsymbol{J}(\boldsymbol{r},\omega),\quad \boldsymbol{r}\in V_c. \tag{2.3}$$

In these equations $\rho(\boldsymbol{r},\omega)$, $T(\boldsymbol{r},\omega)$ and $\boldsymbol{v}(\boldsymbol{r},\omega)$ denote the deviations of the density, temperature and velocity fields from their uniform equilibrium values ρ_c, T_c and $\boldsymbol{v}_c=0$. Furthermore c_v is the heat capacity at constant volume and α is the derivative of the hydrostatic pressure with respect to the temperature at constant density in equilibrium. The pressure tensor $\boldsymbol{P}$ and the heat current $\boldsymbol{J}$ are given by

$$\boldsymbol{P}(\boldsymbol{r},\omega)=p(\boldsymbol{r},\omega)\boldsymbol{U}-2\eta\overline{\boldsymbol{\nabla}\boldsymbol{v}(\boldsymbol{r},\omega)}-\eta_v\boldsymbol{\nabla}\cdot\boldsymbol{v}(\boldsymbol{r},\omega)\boldsymbol{U}+\boldsymbol{\sigma}(\boldsymbol{r},\omega),\quad \boldsymbol{r}\in V_c \tag{2.4}$$

$$\boldsymbol{J}(\boldsymbol{r},\omega)=-\lambda\boldsymbol{\nabla}T(\boldsymbol{r},\omega)+\boldsymbol{J}_R(\boldsymbol{r},\omega),\quad \boldsymbol{r}\in V_c, \tag{2.5}$$

where $p(\boldsymbol{r},\omega)$ is the deviation from the uniform equilibrium hydrostatic pressure p_c, η the shear viscosity and η_v the bulk viscosity of the fluid and λ the heat conduction coefficient. The symmetric traceless part of a tensor has been denoted by $\overline{\ldots}$ while the symbol $\boldsymbol{U}$ stands for the unit tensor.

The fluctuations in the fluid fields are generated by the random stress tensor $\boldsymbol{\sigma}(\boldsymbol{r},\omega)$ and the random heat current $\boldsymbol{J}_R(\boldsymbol{r},\omega)$ which have the following stochastic properties, for $\boldsymbol{r},\boldsymbol{r}'\in V_c$ [10]):

$$\langle\boldsymbol{J}_R(\boldsymbol{r},\omega)\rangle=0,\quad \langle\boldsymbol{\sigma}(\boldsymbol{r},\omega)\rangle=0, \tag{2.6}$$

$$\langle\sigma_{ij}(\boldsymbol{r},\omega)\sigma^*_{kl}(\boldsymbol{r}',\omega')\rangle=2k_BT_c\delta(\boldsymbol{r}-\boldsymbol{r}')2\pi\delta(\omega-\omega')[\eta\Delta_{ijkl}+\eta_v\delta_{ij}\delta_{kl}], \tag{2.7}$$

$$\langle J_{Ri}(\boldsymbol{r},\omega)\sigma^*_{kl}(\boldsymbol{r}',\omega')\rangle=\langle\sigma_{ij}(\boldsymbol{r},\omega)J^*_{Rk}(\boldsymbol{r}',\omega')\rangle=0, \tag{2.8}$$

$$\langle J_{Ri}(\boldsymbol{r},\omega)J^*_{Rj}(\boldsymbol{r}',\omega')\rangle=2k_BT_c^2\delta(\boldsymbol{r}-\boldsymbol{r}')2\pi\delta(\omega-\omega')\lambda\delta_{ij}. \tag{2.9}$$

† Although the centre of mass coordinate is a function of time this dependence may be neglected in the fully linearized scheme within which Brownian motion is discussed here. Cf. ref. 1.

In eq. (2.7) Δ_{ijkl} is a symmetric traceless tensor of rank four

$$\Delta_{ijkl} = \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} - (2/3)\delta_{ij}\delta_{kl} \tag{2.10}$$

and the square brackets denote averaging over an equilibrium ensemble.

We will assume the density dependence of a pressure in the equation of state to be of the Ornstein–Zernike form, i.e. $p(\boldsymbol{r}, \omega)$ is dependent on $\rho(\boldsymbol{r}, \omega)$ and $\nabla^2\rho(\boldsymbol{r}, \omega)$. Moreover $p(\boldsymbol{r}, \omega)$ is a local function of $T(\boldsymbol{r}, \omega)$. Therefore for $\boldsymbol{r} \in V_c$ [11])

$$p(\boldsymbol{r}, \omega) = c_0^2\rho(\boldsymbol{r}, \omega) - c_0^2\xi^2\nabla^2\rho(\boldsymbol{r}, \omega) + \alpha T(\boldsymbol{r}, \omega). \tag{2.11}$$

In this equation c_0 is the isothermal sound velocity and ξ the correlation length of density fluctuations. Far from the liquid–gas critical point ξ will be zero whereas close to the critical point $\xi \to \infty$ and $c_0^2\xi^2$ remains finite within the context of the Ornstein–Zernike approximation.

3. Green identities

In this section we shall derive two Green identities which will be of use in our further analysis of the fluctuation–dissipation theorem for the Brownian particle. We define for an arbitrary field quantity $f(\boldsymbol{r}, \omega)$ its fluctuation $\Delta f(\boldsymbol{r}, \omega)$

$$\Delta f(\boldsymbol{r}, \omega) = f(\boldsymbol{r}, \omega) - \langle f(\boldsymbol{r}, \omega)\rangle, \tag{3.1}$$

where $\langle f(\boldsymbol{r}, \omega)\rangle$ represents the mean value of $f(\boldsymbol{r}, \omega)$. We consider first the surface integral

$$\int\limits_{S+S_c} [\Delta\boldsymbol{v}\cdot\langle\boldsymbol{P}\rangle - \langle\boldsymbol{v}\rangle\cdot\Delta\boldsymbol{P}]\cdot\boldsymbol{n}\,\mathrm{d}S$$

$$= \int\limits_{S} [\Delta\boldsymbol{v}\cdot\langle\boldsymbol{P}\rangle - \langle\boldsymbol{v}\rangle\cdot\Delta\boldsymbol{P}]\cdot\boldsymbol{n}\,\mathrm{d}S + \int\limits_{S_c} [\Delta\boldsymbol{v}\cdot\langle\boldsymbol{P}\rangle - \langle\boldsymbol{v}\rangle\cdot\Delta\boldsymbol{P}]\cdot\boldsymbol{n}\,\mathrm{d}S,$$

where S is the surface of the particle and S_c the outer surface of the fluid (the walls of the container of fluid and particle) and $\boldsymbol{n}$ a unit vector normal to the surface pointing into the fluid. Using Gauss' theorem one has for this integral

$$\int\limits_{S+S_c} [\Delta\boldsymbol{v}\cdot\langle\boldsymbol{P}\rangle - \langle\boldsymbol{v}\rangle\cdot\Delta\boldsymbol{P}]\cdot\boldsymbol{n}\,\mathrm{d}S$$

$$= -\int\limits_{V_c} \nabla\cdot[\Delta\boldsymbol{v}\cdot\langle\boldsymbol{P}\rangle - \langle\boldsymbol{v}\rangle\cdot\Delta\boldsymbol{P}]\,\mathrm{d}\boldsymbol{r}$$

$$= - \int_{V_c} [(\nabla \Delta \boldsymbol{v}) : \langle \boldsymbol{P} \rangle - (\nabla \langle \boldsymbol{v} \rangle) : \Delta \boldsymbol{P}] \, \mathrm{d}\boldsymbol{r}, \tag{3.2}$$

where we have used eq. (2.2). Substituting eq. (2.4) for both $\langle \boldsymbol{P} \rangle$ and $\Delta \boldsymbol{P}$ on the right hand side of eq. (3.2) and using eqs. (2.11) and (2.1) the surface integral may also be written as

$$\int_{S+S_c} [\Delta \boldsymbol{v} \cdot \langle \boldsymbol{P} \rangle - \langle \boldsymbol{v} \rangle \cdot \Delta \boldsymbol{P}] \cdot \boldsymbol{n} \, \mathrm{d}S$$

$$= \int_{V_c} (\nabla \langle \boldsymbol{v} \rangle) : \boldsymbol{\sigma} \, \mathrm{d}\boldsymbol{r} + \frac{\mathrm{i}\omega}{\rho_e} c_0^2 \xi^2 \int_{V_c} [\Delta \rho \nabla^2 \langle \rho \rangle - \langle \rho \rangle \nabla^2 \Delta \rho] \, \mathrm{d}\boldsymbol{r}$$

$$- \alpha \int_{V_c} [\langle T \rangle \nabla \cdot \Delta \boldsymbol{v} - \Delta T \nabla \cdot \langle \boldsymbol{v} \rangle] \, \mathrm{d}\boldsymbol{r}. \tag{3.3}$$

Applying once more Gauss' theorem to the second integral on the right hand side of eq. (3.3) we finally obtain

$$\int_{S+S_c} [(\Delta \boldsymbol{v} \cdot \langle \boldsymbol{P} \rangle - \langle \boldsymbol{v} \rangle \cdot \Delta \boldsymbol{P}) + \frac{\mathrm{i}\omega}{\rho_e} c_0^2 \xi^2 (\Delta \rho \nabla \langle \rho \rangle - \langle \rho \rangle \nabla \Delta \rho)] \cdot \boldsymbol{n} \, \mathrm{d}S$$

$$= \int_{V_c} (\nabla \langle \boldsymbol{v} \rangle) : \boldsymbol{\sigma} \, \mathrm{d}\boldsymbol{r} - \alpha \int_{V_c} [\langle T \rangle \nabla \cdot \Delta \boldsymbol{v} - \Delta T \nabla \cdot \langle \boldsymbol{v} \rangle] \, \mathrm{d}\boldsymbol{r}. \tag{3.4}$$

In a similar way we find using eqs. (2.3) and (2.5)

$$\int_{S+S_c} [\Delta T \langle \boldsymbol{J} \rangle - \langle T \rangle \Delta \boldsymbol{J}] \cdot \boldsymbol{n} \, \mathrm{d}S$$

$$= \int_{V_c} (\nabla \langle T \rangle) \cdot \boldsymbol{J}_\mathrm{R} \, \mathrm{d}\boldsymbol{r} - \alpha T_e \int_{V_c} [\langle T \rangle \nabla \cdot \Delta \boldsymbol{v} - \Delta T \nabla \cdot \langle \boldsymbol{v} \rangle] \, \mathrm{d}\boldsymbol{r}. \tag{3.5}$$

Combining eqs. (3.4) and (3.5) we find the first identity

$$\int_{S+S_c} [\Delta \boldsymbol{v} \cdot \langle \boldsymbol{P} \rangle - \langle \boldsymbol{v} \rangle \cdot \Delta \boldsymbol{P} - \frac{1}{T_e} (\Delta T \langle \boldsymbol{J} \rangle - \langle T \rangle \Delta \boldsymbol{J})$$

$$+ \frac{\mathrm{i}\omega}{\rho_e} c_0^2 \xi^2 (\Delta \rho \nabla \langle \rho \rangle - \langle \rho \rangle \nabla \Delta \rho)] \cdot \boldsymbol{n} \, \mathrm{d}S$$

$$= \int_{V_c} (\nabla \langle \boldsymbol{v} \rangle) : \boldsymbol{\sigma} \, \mathrm{d}\boldsymbol{r} - \frac{1}{T_e} \int_{V_c} \boldsymbol{J}_\mathrm{R} \cdot \nabla \langle T \rangle \, \mathrm{d}\boldsymbol{r}. \tag{3.6}$$

Consider next the surface integral

$$\tfrac{1}{2}\int\limits_{S+S_c} [\langle \boldsymbol{v}\rangle \cdot \langle \boldsymbol{P}\rangle^* + \langle \boldsymbol{v}\rangle^* \cdot \langle \boldsymbol{P}\rangle] \cdot \boldsymbol{n}\, \mathrm{d}S.$$

Using Gauss' theorem, eqs. (2.1), (2.2) and (2.11), one can show, proceeding as in the derivation of eq. (3.4)

$$\begin{aligned}
&\tfrac{1}{2}\int\limits_{S+S_c} [\langle \boldsymbol{v}\rangle \cdot \langle \boldsymbol{P}\rangle^* + \langle \boldsymbol{v}\rangle^* \cdot \langle \boldsymbol{P}\rangle] \cdot \boldsymbol{n}\, \mathrm{d}S \\
&\qquad + \tfrac{1}{2}\frac{\mathrm{i}\omega}{\rho_c} c_0^2 \xi^2 \int\limits_{S+S_c} [\langle \rho\rangle \nabla\langle \rho\rangle^* - \langle \rho\rangle^* \nabla\langle \rho\rangle] \cdot \boldsymbol{n}\, \mathrm{d}S \\
&= 2\eta \int\limits_{V_c} \overline{\nabla\langle \boldsymbol{v}\rangle} : \overline{\nabla\langle \boldsymbol{v}\rangle}^*\, \mathrm{d}\boldsymbol{r} + \eta_v \int\limits_{V_c} \nabla\cdot\langle \boldsymbol{v}\rangle \nabla\cdot\langle \boldsymbol{v}\rangle^*\, \mathrm{d}\boldsymbol{r} \\
&\qquad - \alpha \int\limits_{V_c} [\langle T\rangle^* \nabla\cdot\langle \boldsymbol{v}\rangle + \langle T\rangle \nabla\cdot\langle \boldsymbol{v}\rangle^*]\, \mathrm{d}\boldsymbol{r}.
\end{aligned} \tag{3.7}$$

In a similar way we find, using eqs. (2.3) and (2.5)

$$\begin{aligned}
&\tfrac{1}{2}\int\limits_{S+S_c} [\langle T\rangle\langle \boldsymbol{J}\rangle^* + \langle T\rangle^*\langle \boldsymbol{J}\rangle] \cdot \boldsymbol{n}\, \mathrm{d}S \\
&= \lambda \int\limits_{V_c} \nabla\langle T\rangle \cdot \nabla\langle T\rangle^*\, \mathrm{d}\boldsymbol{r} + \alpha T_e \int\limits_{V_c} [\langle T\rangle \nabla\cdot\langle \boldsymbol{v}\rangle^* + \langle T\rangle^* \nabla\cdot\langle \boldsymbol{v}\rangle]\, \mathrm{d}\boldsymbol{r}.
\end{aligned} \tag{3.8}$$

Combining eqs. (3.7) and (3.8) we find

$$\begin{aligned}
&\tfrac{1}{2}\int\limits_{S+S_c} \Big[\langle \boldsymbol{v}\rangle \cdot \langle \boldsymbol{P}\rangle^* + \langle \boldsymbol{v}\rangle^* \cdot \langle \boldsymbol{P}\rangle + \frac{1}{T_e}(\langle T\rangle\langle \boldsymbol{J}\rangle^* + \langle T\rangle^*\langle \boldsymbol{J}\rangle) \\
&\qquad + \frac{\mathrm{i}\omega}{\rho_c} c_0^2 \xi^2 (\langle \rho\rangle \nabla\langle \rho\rangle^* - \langle \rho\rangle^* \nabla\langle \rho\rangle)\Big] \cdot \boldsymbol{n}\, \mathrm{d}S \\
&= 2\eta \int\limits_{V_c} \overline{\nabla\langle \boldsymbol{v}\rangle} : \overline{\nabla\langle \boldsymbol{v}\rangle}^*\, \mathrm{d}\boldsymbol{r} + \eta_v \int\limits_{V_c} \nabla\cdot\langle \boldsymbol{v}\rangle \nabla\langle \boldsymbol{v}\rangle^*\, \mathrm{d}\boldsymbol{r} + \frac{\lambda}{T_e}\int\limits_{V_c} \nabla\langle T\rangle \cdot \nabla\langle T\rangle^*\, \mathrm{d}\boldsymbol{r},
\end{aligned} \tag{3.9}$$

which is the second identity of interest.

4. Equations of motion of the particle; boundary conditions

The linear equations of motion of the particle follow from linearizing the exact equations of motion which are derived in appendix A. These equations are for the translational velocity $\boldsymbol{u}(\omega)$, the rotational velocity $\boldsymbol{\Omega}(\omega)$ and the internal energy $U(\omega)$ of the particle

$$-\mathrm{i}m\omega\boldsymbol{u}(\omega) = -\int_S \boldsymbol{P}\cdot\boldsymbol{n}\,\mathrm{d}S + \boldsymbol{K}_{\mathrm{ext}}(\omega) \equiv \boldsymbol{K}(\omega) + \boldsymbol{K}_{\mathrm{ext}}(\omega), \tag{4.1}$$

$$-\mathrm{i}\omega\boldsymbol{I}\cdot\boldsymbol{\Omega}(\omega) = -\int_S (\boldsymbol{r}-\boldsymbol{R})\times(\boldsymbol{P}\cdot\boldsymbol{n})\,\mathrm{d}S + \boldsymbol{M}_{\mathrm{ext}}(\omega) \equiv \boldsymbol{M}(\omega) + \boldsymbol{M}_{\mathrm{ext}}(\omega), \tag{4.2}$$

$$-\mathrm{i}\omega U(\omega) = -\int_S \boldsymbol{J}\cdot\boldsymbol{n}\,\mathrm{d}S + Q_{\mathrm{ext}}(\omega) \equiv Q(\omega) + Q_{\mathrm{ext}}(\omega), \tag{4.3}$$

where $\boldsymbol{I}$ is the inertia tensor defined by

$$\boldsymbol{I} = \int_V \rho_{\mathrm{s}}[|\boldsymbol{r}-\boldsymbol{R}|^2\boldsymbol{U} - (\boldsymbol{r}-\boldsymbol{R})(\boldsymbol{r}-\boldsymbol{R})]\,\mathrm{d}\boldsymbol{r}. \tag{4.4}$$

Furthermore $\boldsymbol{K}(\omega)$ is the force and $\boldsymbol{M}(\omega)$ the torque exerted on the particle by the fluid and $Q(\omega)$ the heat flowing from the fluid into the particle. Finally $\boldsymbol{K}_{\mathrm{ext}}$ and $\boldsymbol{M}_{\mathrm{ext}}$ represent the external force and torque acting on the particle and Q_{ext} is an externally controlled heat source in the particle. The set of equations (2.1)–(2.3) and (4.1)–(4.3) must be supplemented by boundary conditions at the surface of the particle and the walls of the container.

1) For the fluid velocity field we choose stick conditions so that

$$\boldsymbol{v}(\boldsymbol{r},\omega) = \boldsymbol{u}(\omega) + \boldsymbol{\Omega}(\omega)\times(\boldsymbol{r}-\boldsymbol{R}), \quad \boldsymbol{r}\in S \tag{4.5a}$$

at the surface of the particle and

$$\boldsymbol{v}(\boldsymbol{r},\omega) = 0, \quad \boldsymbol{r}\in S_{\mathrm{c}} \tag{4.5b}$$

at the outer surface of the fluid.

2) In the critical region ($\xi \neq 0$) where the differential equation for the fluid velocity field becomes of fourth order for the irrotational part an additional boundary condition is needed for div $\boldsymbol{v}$ or, equivalently, for the fluid density field $\rho(\boldsymbol{r},\omega)$. We shall assume the following boundary condition to hold both at the surface of the particle and at the walls of the container

$$\boldsymbol{n}\cdot\nabla\rho(\boldsymbol{r},\omega) = \mu\rho(\boldsymbol{r},\omega), \quad \boldsymbol{r}\in S \ \text{ or } \ \boldsymbol{r}\in S_{\mathrm{c}}, \tag{4.6}$$

where μ is a parameter which characterizes the interface and may have different values on both surfaces†.

3) In connection with the fluid temperature field $T(r, \omega)$ we shall consider two cases

a) The particle is a perfect insulator; in that case the normal component of J must be zero at the surface of the particle, i.e.

$$J \cdot n = 0, \quad r \in S \tag{4.7}$$

and consequently

$$Q(\omega) = 0. \tag{4.8}$$

b) The particle is an ideal conductor for heat (i.e. its intrinsic heat conductivity is infinite) and there is no temperature jump at its surface. In that case

$$T(r, \omega) = T_s(\omega), \quad r \in S, \tag{4.9}$$

where $T_s(\omega)$ is the deviation of the (uniform) temperature of the particle from the equilibrium temperature of the system and is related to the internal energy of the particle by

$$\mathrm{i}\omega C T_s(\omega) = \mathrm{i}\omega U(\omega). \tag{4.10}$$

Here C is the heat capacity of the particle. Furthermore the walls of the container are thermally insulating so that the normal component of the heat current vanishes on S_c. As a consequence of the boundary conditions on the outer surface the surface integral over S_c vanishes in the two Green identities eqs. (3.6) and (3.9). Alternatively these integrals over S_c would have vanished if the outer surface were at infinity and the mean fields would tend to zero sufficiently rapidly.

The average hydrodynamic force $\langle K(\omega)\rangle$, torque $\langle M(\omega)\rangle$ and the average heat flowing into the particle $\langle Q(\omega)\rangle$ can be calculated in principle from macroscopic linearized hydrodynamics. For simplicity's sake we shall consider, in the subsequent analysis the particle to be spherical. Then, for reasons of symmetry, and assuming the particle to be located sufficiently far from the walls of the container, $\langle K(\omega)\rangle$, $\langle M(\omega)\rangle$ and $\langle Q(\omega)\rangle$ satisfy relations of the form

$$\begin{aligned} \langle K(\omega)\rangle &= -\zeta_1(\omega)\langle u(\omega)\rangle, \\ \langle M(\omega)\rangle &= -\zeta_2(\omega)\langle \Omega(\omega)\rangle, \\ \langle Q(\omega)\rangle &= 0 \end{aligned} \tag{4.11}$$

† In a previous paper[8]) we have assumed the particle surface to be characterized by $\mu = \infty$, i.e. by the additional boundary conditions $\rho(r, \omega) = 0$, $r \in S$.

for the perfect heat insulator, for which boundary condition (4.8) holds and

$$\begin{aligned}\langle \boldsymbol{K}(\omega)\rangle &= -\zeta_1(\omega)\langle \boldsymbol{u}(\omega)\rangle,\\ \langle \boldsymbol{M}(\omega)\rangle &= -\zeta_2(\omega)\langle \boldsymbol{\Omega}(\omega)\rangle,\\ \langle Q(\omega)\rangle &= -\zeta_3(\omega)\langle T_s(\omega)\rangle\end{aligned} \tag{4.12}$$

for the ideal heat conductor, for which boundary condition (4.9) holds. In these equations ζ_1 is the frequency dependent friction coefficient, ζ_2 the rotational friction coefficient and ζ_3 the cooling coefficient. The coefficients ζ_1 and ζ_2 are not the same in the two cases considered.

We now write

a) For the perfect heat insulator

$$\begin{aligned}\boldsymbol{K}(\omega) &= -\zeta_1(\omega)\boldsymbol{u}(\omega) + \boldsymbol{K}_{\mathrm{R}}(\omega),\\ \boldsymbol{M}(\omega) &= -\zeta_2(\omega)\boldsymbol{\Omega}(\omega) + \boldsymbol{M}_{\mathrm{R}}(\omega),\\ Q(\omega) &= 0\end{aligned} \tag{4.13}$$

and

b) for the ideal heat conductor

$$\begin{aligned}\boldsymbol{K}(\omega) &= -\zeta_1(\omega)\boldsymbol{u}(\omega) + \boldsymbol{K}_{\mathrm{R}}(\omega),\\ \boldsymbol{M}(\omega) &= -\zeta_2(\omega)\boldsymbol{\Omega}(\omega) + \boldsymbol{M}_{\mathrm{R}}(\omega),\\ Q(\omega) &= -\zeta_3(\omega)T_s(\omega) + Q_{\mathrm{R}}(\omega).\end{aligned} \tag{4.14}$$

These equations define the random force, the random torque and in case b also the random heat source whose mean values automatically vanish. Substitution of the set (4.13) or (4.14) with (4.10) into eqs. (4.1)–(4.3) leads to stochastic equations of motion for $\boldsymbol{u}(\omega)$, $\boldsymbol{\Omega}(\omega)$ and in case b also for $T_s(\omega)$. These stochastic equations are generalized Langevin equations if one can also show that the following fluctuation–dissipation theorems hold

$$\langle \boldsymbol{K}_{\mathrm{R}}(\omega)\boldsymbol{K}_{\mathrm{R}}^*(\omega')\rangle = 2k_{\mathrm{B}}T_{\mathrm{e}}\,\mathrm{Re}\,\zeta_1(\omega)\boldsymbol{U}2\pi\delta(\omega-\omega'), \tag{4.15}$$

$$\langle \boldsymbol{M}_{\mathrm{R}}(\omega)\boldsymbol{M}_{\mathrm{R}}^*(\omega')\rangle = 2k_{\mathrm{B}}T_{\mathrm{e}}\,\mathrm{Re}\,\zeta_2(\omega)\boldsymbol{U}2\pi\delta(\omega-\omega') \tag{4.16}$$

and also, in case b

$$\langle Q_{\mathrm{R}}(\omega)Q_{\mathrm{R}}^*(\omega')\rangle = 2k_{\mathrm{B}}T_{\mathrm{e}}^2\,\mathrm{Re}\,\zeta_3(\omega)2\pi\delta(\omega-\omega'). \tag{4.17}$$

Cross correlations between $\boldsymbol{K}_{\mathrm{R}}$, $\boldsymbol{M}_{\mathrm{R}}$ and Q_{R} should vanish for reasons of symmetry.

In the next two sections we shall derive eqs. (4.15), (4.16) and (4.17).

5. The fluctuation–dissipation theorem for the heat insulating Brownian particle

If the Brownian particle is a heat insulator the hydrodynamic force and torque are given by the first two equations of the set (4.13) while in addition the boundary condition (4.7) holds. In order to derive eqs. (4.15) and (4.16) we consider the bilinear form

$$\begin{aligned}\langle \boldsymbol{u}\rangle\cdot \boldsymbol{K}_{\mathrm{R}}+\langle \boldsymbol{\Omega}\rangle\cdot \boldsymbol{M}_{\mathrm{R}} &= \langle \boldsymbol{u}\rangle\cdot(\Delta \boldsymbol{K}+\zeta_1\Delta \boldsymbol{u})+\langle \boldsymbol{\Omega}\rangle\cdot(\Delta \boldsymbol{M}+\zeta_2\Delta \boldsymbol{\Omega})\\ &= \langle \boldsymbol{u}\rangle\cdot\Delta \boldsymbol{K}-\boldsymbol{K}\cdot\Delta \boldsymbol{u}+\langle \boldsymbol{\Omega}\rangle\cdot\Delta \boldsymbol{M}-\langle \boldsymbol{M}\rangle\cdot\Delta \boldsymbol{\Omega},\end{aligned} \tag{5.1}$$

where we have used eqs. (4.11) and (4.13).

In terms of the pressure tensor, cf. eqs. (4.1) and (4.2), one then obtains

$$\begin{aligned}\langle \boldsymbol{u}\rangle\cdot \boldsymbol{K}_{\mathrm{R}}+\langle \boldsymbol{\Omega}\rangle\cdot \boldsymbol{M}_{\mathrm{R}} &= -\langle \boldsymbol{u}\rangle\cdot\int_S \Delta \boldsymbol{P}\cdot \boldsymbol{n}\,\mathrm{d}S+\Delta \boldsymbol{u}\cdot\int_S\langle \boldsymbol{P}\rangle\cdot \boldsymbol{n}\,\mathrm{d}S\\ &\quad -\langle \boldsymbol{\Omega}\rangle\cdot\int_S(\boldsymbol{r}-\boldsymbol{R})\times(\Delta \boldsymbol{P}\cdot \boldsymbol{n})\,\mathrm{d}S+\Delta \boldsymbol{\Omega}\cdot\int_S(\boldsymbol{r}-\boldsymbol{R})\\ &\quad\times(\langle \boldsymbol{P}\rangle\cdot \boldsymbol{n})\,\mathrm{d}S.\end{aligned} \tag{5.2}$$

Using the stick boundary condition (4.5a) and the fact that for any three vectors $\boldsymbol{a}\cdot(\boldsymbol{b}\times\boldsymbol{c})=(\boldsymbol{a}\times\boldsymbol{b})\cdot\boldsymbol{c}$, eq. (5.2) may be rewritten as

$$\langle \boldsymbol{u}\rangle\cdot \boldsymbol{K}_{\mathrm{R}}+\langle \boldsymbol{\Omega}\rangle\cdot \boldsymbol{M}_{\mathrm{R}} = -\int_S[\langle \boldsymbol{v}\rangle\cdot\Delta \boldsymbol{P}-\Delta \boldsymbol{v}\cdot\langle \boldsymbol{P}\rangle]\cdot \boldsymbol{n}\,\mathrm{d}S. \tag{5.3}$$

We now use for the right hand side of this equation the first Green identity eq. (3.6), derived previously, together with eqs. (4.6) and (4.7) and the fact that the integral over S_c vanishes, to obtain

$$\langle \boldsymbol{u}\rangle\cdot \boldsymbol{K}_{\mathrm{R}}+\langle \boldsymbol{\Omega}\rangle\cdot \boldsymbol{M}_{\mathrm{R}} = \int_{V_c}\nabla\langle \boldsymbol{v}\rangle:\boldsymbol{\sigma}\,\mathrm{d}\boldsymbol{r}-\frac{1}{T_e}\int_{V_c}\boldsymbol{J}_{\mathrm{R}}\cdot\nabla\langle T\rangle\,\mathrm{d}\boldsymbol{r}. \tag{5.4}$$

We also consider the quadratic form

$$\begin{aligned}&\tfrac{1}{2}\langle \boldsymbol{u}\rangle\cdot(\zeta_1+\zeta_1^*)\langle \boldsymbol{u}\rangle^*+\tfrac{1}{2}\langle \boldsymbol{\Omega}\rangle\cdot(\zeta_2+\zeta_2^*)\langle \boldsymbol{\Omega}\rangle^*\\ &\quad= -\tfrac{1}{2}\langle \boldsymbol{u}\rangle\cdot\langle \boldsymbol{K}\rangle^*-\tfrac{1}{2}\langle \boldsymbol{u}\rangle^*\cdot\langle \boldsymbol{K}\rangle-\tfrac{1}{2}\langle \boldsymbol{\Omega}\rangle\cdot\langle \boldsymbol{M}\rangle^*-\tfrac{1}{2}\langle \boldsymbol{\Omega}\rangle^*\cdot\langle \boldsymbol{M}\rangle\\ &\quad= \tfrac{1}{2}\int_S[\langle \boldsymbol{v}\rangle\cdot\langle \boldsymbol{P}\rangle^*+\langle \boldsymbol{v}\rangle^*\cdot\langle \boldsymbol{P}\rangle]\cdot \boldsymbol{n}\,\mathrm{d}S,\end{aligned} \tag{5.5}$$

where we have again used boundary condition (4.5).

With the second Green identity eq. (3.9) and boundary conditions (4.6) and (4.7) one then obtains

$$\langle u\rangle\cdot(\mathrm{Re}\,\zeta_1)\langle u\rangle^* + \langle \Omega\rangle\cdot(\mathrm{Re}\,\zeta_2)\langle \Omega\rangle^*$$
$$= 2\eta \int_{V_c} \overline{\nabla\langle v\rangle} : \overline{\nabla\langle v\rangle}^* \,\mathrm{d}r + \eta_v \int_{V_c} \nabla\cdot\langle v\rangle \nabla\cdot\langle v\rangle^* \,\mathrm{d}r$$
$$+ \frac{\lambda}{T_e}\int_{V_c} \nabla\langle T\rangle\cdot\nabla\langle T\rangle^*\,\mathrm{d}r. \tag{5.6}$$

The right hand side of eq. (5.6), if integrated over all frequencies, represents the total entropy production (multiplied by T_e) in the fluid due to viscous phenomena and heat conductivity as a result of the motion of the sphere.

Let us now evaluate the correlation functions of the random force and the random torque using eq. (5.4)

$$\langle u(\omega)\rangle\cdot\langle K_R(\omega)K_R^*(\omega')\rangle\cdot\langle u(\omega')\rangle + \langle u(\omega)\rangle\cdot\langle K_R(\omega)M_R^*(\omega')\rangle\cdot\langle \Omega(\omega')\rangle^*$$
$$+ \langle \Omega(\omega)\rangle\cdot\langle M_R(\omega)K_R^*(\omega')\rangle\cdot\langle u(\omega')\rangle$$
$$+ \langle \Omega(\omega)\rangle\cdot\langle M_R(\omega)M_R^*(\omega')\rangle\cdot\langle \Omega(\omega')\rangle^*$$
$$= \int_{V_c}\mathrm{d}r\int_{V_c}\mathrm{d}r'\Big[\nabla\langle v(r,\omega)\rangle : \langle \sigma(r,\omega)\sigma^*(r',\omega')\rangle : \nabla'\langle v(r',\omega')\rangle^*$$
$$-\frac{1}{T_e}\nabla\langle v(r,\omega)\rangle : \langle \sigma(r,\omega)J_R^*(r',\omega')\rangle\cdot\nabla'\langle T(r',\omega')\rangle^*$$
$$-\frac{1}{T_e}\nabla\langle T(r,\omega)\rangle\cdot\langle J_R(r,\omega)\sigma^*(r',\omega')\rangle : \nabla'\langle v(r',\omega')\rangle^*$$
$$+\frac{1}{T_e^2}\nabla\langle T(r,\omega)\rangle\cdot\langle J_R(r,\omega)J_R^*(r',\omega)\rangle\cdot\nabla'\langle T(r',\omega')\rangle^*\Big]$$
$$= 2k_B T_e 2\pi\delta(\omega-\omega')\int_{V_c}\mathrm{d}r\Big[2\eta\overline{\nabla\langle v(r,\omega)\rangle} : \overline{\nabla\langle v(r,\omega)\rangle}^*$$
$$+\eta_v\nabla\cdot\langle v(r,\omega)\rangle\nabla\cdot\langle v(r,\omega)\rangle^* + \frac{\lambda}{T_e}\nabla\langle T(r,\omega)\rangle\cdot\nabla\langle T(r,\omega)\rangle^*\Big], \tag{5.7}$$

where we have used eqs. (2.7)–(2.9).

Comparing eq. (5.6) and eq. (5.7) one finds, using the validity for all u and Ω

$$\langle K_R(\omega)K_R^*(\omega')\rangle = 2k_B T_e\,\mathrm{Re}\,\zeta_1 U 2\pi\delta(\omega-\omega'), \tag{5.8}$$

$$\langle K_R(\omega)M_R^*(\omega')\rangle = \langle M_R(\omega)K_R^*(\omega')\rangle = 0, \tag{5.9}$$

$$\langle M_R(\omega) M_R^*(\omega')\rangle = 2k_B T_e \operatorname{Re} \zeta_2 U 2\pi\delta(\omega - \omega'); \tag{5.10}$$

these are the fluctuations–dissipation theorems (4.15) and (4.16) which we set out to derive.

6. The fluctuation–dissipation theorem for the ideal heat conducting Brownian particle

If the Brownian particle is an ideal heat conductor the set of equations (4.14) holds. We now consider the bilinear form

$$\begin{aligned}&\langle \boldsymbol{u}\rangle \cdot \boldsymbol{K}_R + \langle \boldsymbol{\Omega}\rangle \cdot \boldsymbol{M}_R - \frac{1}{T_e}\langle T_s\rangle Q_R \\ &\quad = \langle \boldsymbol{u}\rangle \cdot \Delta\boldsymbol{K} - \langle \boldsymbol{K}\rangle \cdot \Delta\boldsymbol{u} + \langle \boldsymbol{\Omega}\rangle \cdot \Delta\boldsymbol{M} - \langle \boldsymbol{M}\rangle \cdot \Delta\boldsymbol{\Omega} - \frac{1}{T_e}(\langle T_s\rangle \Delta Q - \langle Q\rangle \Delta T_s),\end{aligned} \tag{6.1}$$

where we have used eqs. (4.12) and (4.14). Replacing $\boldsymbol{K}$, M and Q by the corresponding surface integrals over $\boldsymbol{P}$ and $\boldsymbol{J}$ (cf. eqs. (4.1)–(4.3)) and applying boundary conditions (4.5) and (4.9) we obtain, similar to the transformation of eq. (5.2) to eq. (5.3)

$$\begin{aligned}&\langle \boldsymbol{u}\rangle \cdot \boldsymbol{K}_R + \langle \boldsymbol{\Omega}\rangle \cdot \boldsymbol{M}_R - \frac{1}{T_e}\langle T_s\rangle Q_R \\ &\quad = -\int_S [\langle \boldsymbol{v}\rangle \cdot \Delta\boldsymbol{P} - \Delta\boldsymbol{v} \cdot \langle \boldsymbol{P}\rangle] \cdot \boldsymbol{n}\, dS + \frac{1}{T_e}\int_S [\langle T\rangle \Delta\boldsymbol{J} - \Delta T\langle \boldsymbol{J}\rangle] \cdot \boldsymbol{n}\, dS.\end{aligned} \tag{6.2}$$

Together with the first Green identity eq. (3.6) and the boundary condition (4.6) we then obtain

$$\begin{aligned}&\langle \boldsymbol{u}\rangle \cdot \boldsymbol{K}_R + \langle \boldsymbol{\Omega}\rangle \cdot \boldsymbol{M}_R - \frac{1}{T_e}\langle T_s\rangle Q_R \\ &\quad = \int_{V_c} \nabla\langle \boldsymbol{v}\rangle : \boldsymbol{\sigma}\, d\boldsymbol{r} - \frac{1}{T_e}\int_{V_c} \boldsymbol{J}_R \cdot \nabla\langle T\rangle\, d\boldsymbol{r}.\end{aligned} \tag{6.3}$$

This equation replaces eq. (5.4) for the present case.

On the other hand we now have, analogous to eq. (5.5),

$$\begin{aligned}&\langle \boldsymbol{u}\rangle \cdot (\operatorname{Re} \zeta_1)\langle \boldsymbol{u}\rangle^* + \langle \boldsymbol{\Omega}\rangle \cdot (\operatorname{Re} \zeta_2)\langle \boldsymbol{\Omega}\rangle^* + \frac{1}{T_e}\langle T_s\rangle(\operatorname{Re} \zeta_3)\langle T_s\rangle^* \\ &\quad = -\tfrac{1}{2}\langle \boldsymbol{u}\rangle \cdot \langle \boldsymbol{K}\rangle^* - \tfrac{1}{2}\langle \boldsymbol{u}\rangle^* \cdot \langle \boldsymbol{K}\rangle - \tfrac{1}{2}\langle \boldsymbol{\Omega}\rangle \cdot \langle \boldsymbol{M}\rangle^* - \tfrac{1}{2}\langle \boldsymbol{\Omega}\rangle^* \cdot \langle \boldsymbol{M}\rangle\end{aligned}$$

$$-\frac{1}{2T_e}\langle T_s\rangle\langle Q\rangle^* - \frac{1}{2T_e}\langle T_s\rangle^*\langle Q\rangle$$

$$= \tfrac{1}{2}\int_S \langle \boldsymbol{v}\rangle\cdot\langle \boldsymbol{P}\rangle^* + \langle \boldsymbol{v}\rangle^*\cdot\langle \boldsymbol{P}\rangle]\cdot \boldsymbol{n}\,\mathrm{d}S + \frac{1}{2T_e}\int_S [\langle T\rangle\langle \boldsymbol{J}\rangle^* + \langle T\rangle\langle \boldsymbol{J}\rangle]\cdot\boldsymbol{n}\,\mathrm{d}S, \tag{6.4}$$

where we have used boundary conditions (4.5) and (4.9).

Together with the second Green identity eq. (3.9) and the boundary condition (4.6) one then obtains

$$\langle \boldsymbol{u}\rangle\cdot(\mathrm{Re}\,\zeta_1)\langle \boldsymbol{u}\rangle^* + \langle \boldsymbol{\Omega}\rangle\cdot(\mathrm{Re}\,\zeta_2)\langle \boldsymbol{\Omega}\rangle^* + \frac{1}{T_e}\langle T_s\rangle(\mathrm{Re}\,\zeta_3)\langle T_s\rangle^*$$

$$= 2\eta\int_{V_c} \overline{\nabla\langle \boldsymbol{v}\rangle}:\overline{\nabla\langle \boldsymbol{v}\rangle}^*\,\mathrm{d}\boldsymbol{r} + \eta_v\int_{V_c}\nabla\cdot\langle \boldsymbol{v}\rangle\nabla\langle \boldsymbol{v}\rangle^*\,\mathrm{d}\boldsymbol{r} + \frac{\lambda}{T_e}\int_{V_c}\nabla\langle T\rangle\cdot\nabla\langle T\rangle^*\,\mathrm{d}\boldsymbol{r}. \tag{6.5}$$

As in the previous case we evaluate the correlation functions of the random force, the random torque and the random heat source from eq. (6.3) using eqs. (2.7)–(2.9). Since the right hand side of eq. (6.3) is identical with the right hand side of eq. (5.4) this evaluation of correlation functions leads immediately to (cf. eq. (5.7))

$$\begin{aligned}
&\langle \boldsymbol{u}(\omega)\rangle\cdot\langle \boldsymbol{K}_R(\omega)\boldsymbol{K}_R^*(\omega')\rangle\cdot\langle \boldsymbol{u}(\omega')\rangle^* + \langle \boldsymbol{u}(\omega)\rangle\cdot\langle \boldsymbol{K}_R(\omega)\boldsymbol{M}_R^*(\omega')\rangle\cdot\langle \boldsymbol{\Omega}(\omega')\rangle^*\\
&\quad -\frac{1}{T_e}\langle \boldsymbol{u}(\omega)\rangle\cdot\langle \boldsymbol{K}_R(\omega)Q_R^*(\omega')\rangle\langle T_s(\omega')\rangle^*\\
&\qquad + \langle \boldsymbol{\Omega}(\omega)\rangle\cdot\langle \boldsymbol{M}_R(\omega)\boldsymbol{K}_R^*(\omega')\rangle\cdot\langle \boldsymbol{u}(\omega')\rangle^*\\
&\quad + \langle \boldsymbol{\Omega}(\omega)\rangle\cdot\langle \boldsymbol{M}_R(\omega)\boldsymbol{M}_R^*(\omega')\rangle\cdot\langle \boldsymbol{\Omega}(\omega')\rangle^*\\
&\qquad -\frac{1}{T_e}\langle \boldsymbol{\Omega}(\omega)\rangle\cdot\langle \boldsymbol{M}_R(\omega)Q_R^*(\omega')\rangle\langle T_s(\omega')\rangle^*\\
&\quad -\frac{1}{T_e}\langle T_s(\omega)\rangle\langle Q_R(\omega)\boldsymbol{K}_R^*(\omega')\rangle\cdot\langle \boldsymbol{u}(\omega')\rangle^*\\
&\qquad -\frac{1}{T_e}\langle T_s(\omega)\rangle\langle Q_R(\omega)\boldsymbol{M}_R^*(\omega')\rangle\cdot\langle \boldsymbol{\Omega}(\omega')\rangle^*\\
&\quad +\frac{1}{T_e^2}\langle T_s(\omega)\rangle\langle Q_R(\omega)Q_R^*(\omega')\rangle\langle T_s(\omega')\rangle^*\\
&= 2k_B T_e 2\pi\delta(\omega-\omega')\int_{V_c}\mathrm{d}\boldsymbol{r}\Big[2\eta\,\overline{\nabla\langle \boldsymbol{v}(\boldsymbol{r},\omega)\rangle}:\overline{\nabla\langle \boldsymbol{v}(\boldsymbol{r},\omega)\rangle}^*\\
&\quad + \eta_v\nabla\cdot\langle \boldsymbol{v}(\boldsymbol{r},\omega)\rangle\nabla\cdot\langle \boldsymbol{v}(\boldsymbol{r},\omega)\rangle^* + \frac{\lambda}{T_e}\nabla\langle T\rangle\cdot\nabla\langle T\rangle^*\Big].
\end{aligned} \tag{6.6}$$

Comparing eqs. (6.5) and (6.6) one finds directly, using the validity for all $\boldsymbol{u}$, $\boldsymbol{\Omega}$ and T_s, the fluctuation–dissipation theorems (4.15)–(4.17) as well as the fact that all cross correlations between $\boldsymbol{K}_R$, $\boldsymbol{M}_R$ and Q_R vanish.

7. Conclusion

In the preceeding two sections we have derived fluctuation–dissipation theorems for the random force, the random torque and also the random heat source for the case of a spherical Brownian particle. These theorems may also be obtained for Brownian particles of arbitrary shape. The general identities derived in section 3 are still valid in that case, however, the sets of equations (4.13) and (4.14) must be replaced by more general linear relations. Thus we have then for the case of the perfect heat insulator

$$\begin{aligned} \boldsymbol{K}(\omega) &= -\zeta_{11}(\omega)\cdot\boldsymbol{u}(\omega) - \zeta_{12}(\omega)\cdot\boldsymbol{\Omega}(\omega) + \boldsymbol{K}_R(\omega), \\ \boldsymbol{M}(\omega) &= -\zeta_{21}(\omega)\cdot\boldsymbol{u}(\omega) - \zeta_{22}(\omega)\cdot\boldsymbol{\Omega}(\omega) + \boldsymbol{M}_R(\omega), \\ Q(\omega) &= 0 \end{aligned} \tag{7.1}$$

and for the case of the ideal heat conductor

$$\begin{aligned} \boldsymbol{K}(\omega) &= -\zeta_{11}(\omega)\cdot\boldsymbol{u}(\omega) - \zeta_{12}(\omega)\cdot\boldsymbol{\Omega}(\omega) - \boldsymbol{\zeta}_{13}(\omega)T_s(\omega) + \boldsymbol{K}_R, \\ \boldsymbol{M}(\omega) &= -\zeta_{21}(\omega)\cdot\boldsymbol{u}(\omega) - \zeta_{22}(\omega)\cdot\boldsymbol{\Omega}(\omega) - \boldsymbol{\zeta}_{23}(\omega)T_s(\omega) + \boldsymbol{M}_R, \\ Q(\omega) &= -\boldsymbol{\zeta}_{31}(\omega)\cdot\boldsymbol{u}(\omega) - \boldsymbol{\zeta}_{23}(\omega)\cdot\boldsymbol{\Omega}(\omega) - \zeta_{33}(\omega)T_s(\omega) + Q_R. \end{aligned} \tag{7.2}$$

The matrices ζ_{12} and ζ_{21} characterize cross effects between rotation and translation of the Brownian particle, while the vector coefficients $\boldsymbol{\zeta}_{13}$, $\boldsymbol{\zeta}_{31}$, $\boldsymbol{\zeta}_{32}$ and $\boldsymbol{\zeta}_{23}$ characterize cross effects between the scalar phenomenon of cooling and translation and rotation, respectively. (For the spherical particle the cross effects were zero for reasons of symmetry, while the matrices ζ_{11} and ζ_{22} reduced to scalar multiples of the unit tensor.)

In appendix B we show, using only hydrodynamics and boundary conditions that the following symmetry relations exist between the coefficients occurring in the sets (7.1) and (7.2)

$$\zeta_{11} = \tilde{\zeta}_{12}, \quad \zeta_{22} = \tilde{\zeta}_{22}, \quad \zeta_{12} = \tilde{\zeta}_{21}, \tag{7.3}$$

$$T_e\boldsymbol{\zeta}_{13} = -\boldsymbol{\zeta}_{31}, \quad T_e\boldsymbol{\zeta}_{23} = -\boldsymbol{\zeta}_{32}. \tag{7.4}$$

Here $\tilde{\boldsymbol{A}}$ denotes the transposed matrix of $\boldsymbol{A}$.

The symmetry relations (7.3) and (7.4) are the Onsager–Casimir relations for the phenomenological sets of equations (7.1) or (7.2)†.

The fluctuation–dissipation theorems can now be derived along the same lines as in the sections 5 and 6, using in addition to the identities of section 3, the boundary condition of section 4 and the symmetry relations (7.3) and (7.4). One then finds instead of eqs. (4.15) and (4.16) for the perfect heat insulator

$$
\begin{aligned}
\langle \boldsymbol{K}_{\mathrm{R}}(\omega)\boldsymbol{K}^*_{\mathrm{R}}(\omega')\rangle &= k_{\mathrm{B}}T_{\mathrm{e}}(\zeta_{11}+\zeta^*_{11})2\pi\delta(\omega-\omega'),\\
\langle \boldsymbol{K}_{\mathrm{R}}(\omega)\boldsymbol{M}^*_{\mathrm{R}}(\omega')\rangle &= k_{\mathrm{B}}T_{\mathrm{e}}(\zeta_{12}+\zeta^*_{12})2\pi\delta(\omega-\omega'),\\
\langle \boldsymbol{M}_{\mathrm{R}}(\omega)\boldsymbol{K}^*_{\mathrm{R}}(\omega')\rangle &= k_{\mathrm{B}}T_{\mathrm{e}}(\zeta_{21}+\zeta^*_{21})2\pi\delta(\omega-\omega'),\\
\langle \boldsymbol{M}_{\mathrm{R}}(\omega)\boldsymbol{M}^*_{\mathrm{R}}(\omega')\rangle &= k_{\mathrm{B}}T_{\mathrm{e}}(\zeta_{22}+\zeta^*_{22})2\pi\delta(\omega-\omega')
\end{aligned}
\tag{7.5}
$$

and in addition for the ideal heat conductor

$$
\begin{aligned}
\langle Q_{\mathrm{R}}(\omega)Q^*_{\mathrm{R}}(\omega')\rangle &= k_{\mathrm{B}}T^2_{\mathrm{e}}(\zeta_{33}+\zeta^*_{33})2\pi\delta(\omega-\omega'),\\
\langle \boldsymbol{K}_{\mathrm{R}}(\omega)Q^*_{\mathrm{R}}(\omega')\rangle &= -\langle Q_{\mathrm{R}}(\omega)\boldsymbol{K}^*_{\mathrm{R}}(\omega')\rangle\\
&= k_{\mathrm{B}}T_{\mathrm{e}}(\zeta_{31}-\zeta^*_{31})2\pi\delta(\omega-\omega'),\\
\langle \boldsymbol{M}_{\mathrm{R}}(\omega)Q^*_{\mathrm{R}}(\omega')\rangle &= -\langle Q_{\mathrm{R}}(\omega)\boldsymbol{M}^*_{\mathrm{R}}(\omega')\rangle\\
&= k_{\mathrm{B}}T_{\mathrm{e}}(\zeta_{32}-\zeta^*_{32})2\pi\delta(\omega-\omega').
\end{aligned}
\tag{7.6}
$$

The last two correlation functions are purely imaginary as they should since they connect even and odd functions in the "particle velocities". The above fluctuation–dissipation theorem can also be derived for more general boundary conditions at the surface of the particle. For the case of arbitrary slip boundary conditions at the surface of a Brownian particle this necessitates the inclusion of a random frictional surface force as was shown in ref. 7. Similarly arbitrary temperature jump conditions at the surface of the particle would require inclusion of a random surface heat source of which the correlation function is related to the temperature jump coefficient. In essence however, the derivation proceeds along the lines developed in the previous sections.

† That Onsager reciprocal relations follow directly from hydrodynamics is a consequence of the fact that the property of microscopic reversibility is already embodied in the hydrodynamic equations themselves.

Appendix A

In this appendix we derive the exact equations of motion of a particle in a fluid from the momentum, angular momentum and energy conservation laws of the fluid particle system in the absence of external force, torque and an externally controlled heat source. The generalisation to the case that external "forces" are acting on the particle is straightforward.

According to the momentum conservation law the following relation holds

$$\int_{V(t)} \rho_s \boldsymbol{v}_s \, \mathrm{d}\boldsymbol{r} + \int_{V_c(t)} \rho_f \boldsymbol{v}_f \, \mathrm{d}\boldsymbol{r} = \text{constant}, \tag{A.1}$$

where ρ_s, ρ_f, $\boldsymbol{v}_s$ and $\boldsymbol{v}_f$ are the density and velocity fields in the solid and fluid respectively. The velocity of a point inside the particle is given by

$$\boldsymbol{v}_s(\boldsymbol{r}, t) = \boldsymbol{u}(t) + \boldsymbol{\Omega}(t) \times (\boldsymbol{r} - \boldsymbol{R}(t)), \quad \boldsymbol{r} \in V(t), \tag{A.2}$$

where $\boldsymbol{R}(t)$ is the centre of mass coordinate defined by

$$\boldsymbol{R}(t) = m^{-1} \int_{V(t)} \rho_s \boldsymbol{r} \, \mathrm{d}\boldsymbol{r}, \qquad m = \int_{V(t)} \rho_s \, \mathrm{d}\boldsymbol{r}. \tag{A.3}$$

Furthermore $\boldsymbol{u}(t) = d\boldsymbol{R}(t)/dt$ is the centre of mass velocity and $\boldsymbol{\Omega}(t)$ the rotational velocity.

Substitution of eq. (A.2) into eq. (A.1) and taking the time derivative yields with (A.3)

$$m \frac{\mathrm{d}\boldsymbol{u}(t)}{\mathrm{d}t} + \int_{V_c(t)} \frac{\partial}{\partial t} \rho_f \boldsymbol{v}_f \, \mathrm{d}\boldsymbol{r} - \int_{S(t)} \rho_f \boldsymbol{v}_f \boldsymbol{v}_s \cdot \boldsymbol{n} \, \mathrm{d}S$$

$$= m \frac{\mathrm{d}\boldsymbol{u}(t)}{\mathrm{d}t} - \int_{V_c(t)} \boldsymbol{\nabla} \cdot (\rho_f \boldsymbol{v}_f \boldsymbol{v}_f + \boldsymbol{P}_f) \, \mathrm{d}\boldsymbol{r} - \int_{S(t)} \rho_f \boldsymbol{v}_f \boldsymbol{v}_s \cdot \boldsymbol{n} \, \mathrm{d}S = 0, \tag{A.4}$$

where the exact equation of momentum conservation for the fluid[12]) has been used and where $\boldsymbol{P}_f$ is the pressure tensor field in the fluid. Using now Gauss' theorem and the boundary condition

$$v_f \cdot n = v_s \cdot n, \quad r \in S(t) \tag{A.5}$$

one obtains

$$m \frac{du(t)}{dt} + \int_{S(t)} [\rho_f v_f v_f + P_f] \cdot n \, dS - \int_{S(t)} \rho_f v_f v_s \cdot n \, dS$$

$$= m \frac{d}{dt} u(t) + \int_{S(t)} P_f \cdot n \, dS = 0. \tag{A.6}$$

This is the equation of motion for the centre of mass velocity $u(t)$ of the particle.

Next we consider angular momentum conservation

$$\int_{V(t)} r \times \rho_s v_s \, dr + \int_{V_c(t)} r \times \rho_f v_f \, dr = \text{constant}. \tag{A.7}$$

Using eqs. (A.2), (A.3) and the vector relation $a \times (b \times c) = (a \cdot c)b - (a \cdot b)c$ one obtains for the first term in eq. (A.6)

$$\int_{V(t)} r \times \rho_s v s \, dr = mR(t) \times u(t) + \int_{V(t)} \rho_s (r - R(t)) \times [\Omega(t) \times (r - R(t))] \, dr$$

$$= mR(t) \times u(t) + I(t) \cdot \Omega(t), \tag{A.8}$$

where $I(t)$ is the inertia tensor, defined by

$$I(t) = \int_{V(t)} \rho_s [|r - R(t)|^2 U - (r - R(t))(r - R(t))] \, dr. \tag{A.9}$$

Substituting eq. (A.8) into eq. (A.7) and subsequently taking the time derivative one has, using eq. (A.6) and the momentum conservation equation for the fluid

$$R(t) \times m \frac{d}{dt} u(t) + \frac{d}{dt} I(t) \cdot \Omega(t)$$

$$+ \int_{V_c(t)} r \times \frac{\partial}{\partial t} \rho_f v_f \, dr - \int_{S(t)} (r \times \rho_f v_f) v_s \cdot n \, dr$$

$$= \frac{\mathrm{d}}{\mathrm{d}t} \boldsymbol{I}(t) \cdot \boldsymbol{\Omega}(t) - \boldsymbol{R}(t) \times \int_{S(t)} \boldsymbol{P}_{\mathrm{f}} \cdot \boldsymbol{n} \, \mathrm{d}S$$

$$+ \int_{V_c(t)} \boldsymbol{r} \times \boldsymbol{\nabla} \cdot (\rho_{\mathrm{f}} \boldsymbol{v}_{\mathrm{f}} \boldsymbol{v}_{\mathrm{f}} + \boldsymbol{P}_{\mathrm{f}}) \, \mathrm{d}\boldsymbol{r} - \int_{S(t)} (\boldsymbol{r} \times \rho_{\mathrm{f}} \boldsymbol{v}_{\mathrm{f}}) \boldsymbol{v}_{\mathrm{s}} \cdot \boldsymbol{n} \, \mathrm{d}\boldsymbol{r}$$

$$= \frac{\mathrm{d}}{\mathrm{d}t} \boldsymbol{I}(t) \cdot \boldsymbol{\Omega}(t) - \int_{S(t)} \boldsymbol{R}(t) \times (\boldsymbol{P}_{\mathrm{f}} \cdot \boldsymbol{n}) \, \mathrm{d}S$$

$$+ \int_{S(t)} \boldsymbol{r} \times [(\rho_{\mathrm{f}} \boldsymbol{v}_{\mathrm{f}} \boldsymbol{v}_{\mathrm{f}} + \boldsymbol{P}_{\mathrm{f}}) \cdot \boldsymbol{n}] \, \mathrm{d}S - \int_{S(t)} (\boldsymbol{r} \times \rho_{\mathrm{f}} \boldsymbol{v}_{\mathrm{f}}) \boldsymbol{v}_{\mathrm{s}} \cdot \boldsymbol{n} \, \mathrm{d}\boldsymbol{r} = 0. \tag{A.10}$$

In the final step the symmetry of the pressure tensor and Gauss' theorem have been employed. With the boundary condition (A.5) one then obtains the equation of motion for the rotational velocity $\boldsymbol{\Omega}(t)$ of the particle

$$\frac{\mathrm{d}}{\mathrm{d}t} (\boldsymbol{I}(t) \cdot \boldsymbol{\Omega}(t)) + \int_{S(t)} (\boldsymbol{r} - \boldsymbol{R}(t)) \times (\boldsymbol{P}_{\mathrm{f}} \cdot \boldsymbol{n}) \, \mathrm{d}S = 0. \tag{A.11}$$

Finally we consider the energy conservation law for the fluid–particle system

$$U(t) + \int_{V(t)} \tfrac{1}{2} \rho_{\mathrm{s}} v_{\mathrm{s}}^2 \, \mathrm{d}\boldsymbol{r} + \int_{V_c(t)} (\tfrac{1}{2} \rho_{\mathrm{f}} v_{\mathrm{f}}^2 + \rho_{\mathrm{f}} u_{\mathrm{f}}) \, \mathrm{d}\boldsymbol{r} = \text{constant}, \tag{A.12}$$

where $U(t)$ is the total internal energy of the particle and u_{f} the internal energy density of the fluid.

Using eqs. (A.2) and (A.3) one obtains for the second term of eq. (A.12)

$$\int_{V(t)} \tfrac{1}{2} \rho_{\mathrm{s}} v_{\mathrm{s}}^2 \, \mathrm{d}\boldsymbol{r} = \tfrac{1}{2} m u^2 + \tfrac{1}{2} \boldsymbol{\Omega} \cdot \boldsymbol{I} \cdot \boldsymbol{\Omega}. \tag{A.13}$$

Inserting eq. (A.13) into eq. (A.12) and taking the time derivative one has, using also eqs. (A.6), (A.11) and (A.2)

$$\frac{\mathrm{d}}{\mathrm{d}t} U(t) + m\boldsymbol{u} \cdot \frac{\mathrm{d}\boldsymbol{u}}{\mathrm{d}t} + \boldsymbol{\Omega} \cdot \frac{\mathrm{d}}{\mathrm{d}t} (\boldsymbol{I} \cdot \boldsymbol{\Omega}) + \frac{\mathrm{d}}{\mathrm{d}t} \int_{V_c(t)} (\tfrac{1}{2} \rho_{\mathrm{f}} v_{\mathrm{f}}^2 + \rho_{\mathrm{f}} u_{\mathrm{f}}) \, \mathrm{d}\boldsymbol{r}$$

$$= \frac{\mathrm{d}}{\mathrm{d}t} U(t) - \int_{S(t)} \boldsymbol{v}_{\mathrm{s}} \cdot \boldsymbol{P}_{\mathrm{f}} \cdot \boldsymbol{n} \, \mathrm{d}S + \int_{V_c(t)} \frac{\partial}{\partial t} (\tfrac{1}{2} \rho_{\mathrm{f}} v_{\mathrm{f}}^2 + \rho_{\mathrm{f}} u_{\mathrm{f}}) \, \mathrm{d}\boldsymbol{r}$$

$$- \int_{S(t)} (\tfrac{1}{2} \rho_{\mathrm{f}} v_{\mathrm{f}}^2 + \rho_{\mathrm{f}} u_{\mathrm{f}}) \boldsymbol{v}_{\mathrm{f}} \cdot \boldsymbol{n} \, \mathrm{d}S = 0. \tag{A.14}$$

In deriving eq. (A.14) use has also been made of the fact that $\boldsymbol{\Omega} \cdot (\mathrm{d}\boldsymbol{I}/\mathrm{d}t) \cdot \boldsymbol{\Omega} = 0$, which follows from (A.9). Inserting into eq. (A.14) the conservation equation for the total energy in the fluid[12]) and applying once more Gauss' theorem one finally obtains the equation of motion for the total internal energy of the particle

$$\frac{\mathrm{d}}{\mathrm{d}t} U(t) + \int_{S(t)} \boldsymbol{J}_\mathrm{f} \cdot \boldsymbol{n} \, \mathrm{d}S + \int_{S(t)} (\boldsymbol{v}_\mathrm{f} - \boldsymbol{v}_\mathrm{s}) \cdot \boldsymbol{P}_\mathrm{f} \cdot \boldsymbol{n} \, \mathrm{d}S = 0. \tag{A.15}$$

In this equation $\boldsymbol{J}_\mathrm{f}$ is the heat current in the fluid.

The equations of motion (4.1)–(4.3) follow if one strictly linearizes eqs. (A.6), (A.11) and (A.15): the fluid fields $\boldsymbol{v}_\mathrm{f}$, $\boldsymbol{J}_\mathrm{f}$ and $\boldsymbol{P}_\mathrm{f}$ are replaced by deviations from their equilibrium values, keeping linear terms only, and the time dependence of $\boldsymbol{R}(t)$ is neglected so that $S(t)$, $V(t)$ and $\boldsymbol{I}(t)$ also become time independent.

Appendix B

In this appendix we will derive the symmetry properties of the tensors ζ_{11}, ζ_{12}, ζ_{21} and ζ_{22}, and of the vectors ζ_{13}, ζ_{31}, ζ_{23} and ζ_{32} using hydrodynamics and boundary conditions only.

Suppose ρ_1, $\boldsymbol{v}_1$, T_1, $\boldsymbol{P}_1$, $\boldsymbol{J}_1$ and ρ_2, $\boldsymbol{v}_2$, T_2, $\boldsymbol{P}_2$, $\boldsymbol{J}_2$ are two deterministic solutions of the eqs. (2.1)–(2.5) (i.e. solutions of the averaged equations using eq. (2.6)). Using Gauss' theorem, eqs. (2.1)–(2.3) and the boundary conditions on the surface of the container one may show that

$$\int_S [\boldsymbol{v}_1 \cdot \boldsymbol{P}_2 - \boldsymbol{v}_2 \cdot \boldsymbol{P}_1 - \frac{1}{T_\mathrm{e}} (T_1 \boldsymbol{J}_2 - T_2 \boldsymbol{J}_1) + \frac{\mathrm{i}\omega c_0^2 \xi^2}{\rho_\mathrm{e}} (\rho_1 \nabla\rho_2 - \rho_2 \nabla\rho_1)] \cdot \boldsymbol{n} \, \mathrm{d}S = 0. \tag{B.1}$$

This identity is analogous to the Green identities derived in section 3. For the case of a particle which is an ideal heat conductor it then follows, using the boundary conditions (4.5a), (4.6) and (4.7) and the definitions of $\boldsymbol{K}$, $\boldsymbol{M}$ and Q (cf. eqs. (4.1)–(4.3), and also the derivation of eq. (5.3))

$$\boldsymbol{u}_1 \cdot \boldsymbol{K}_2 - \boldsymbol{u}_2 \cdot \boldsymbol{K}_1 + \boldsymbol{\Omega}_1 \cdot \boldsymbol{M}_2 - \boldsymbol{\Omega}_2 \cdot \boldsymbol{M}_1 - \frac{1}{T_\mathrm{e}} (T_{\mathrm{s}_1} Q_2 - T_{\mathrm{s}_2} Q_1) = 0. \tag{B.2}$$

Inserting the deterministic equations for $\boldsymbol{K}$, $\boldsymbol{M}$ and Q, which follow from the set (7.2), one then finds immediately the symmetry relations (7.3) and (7.4) since the relation (B.2) holds for all possible deterministic solutions. For the perfect heat insulator the symmetry relations (7.3) may be obtained in the same way.

References

1) P. Mazur and D. Bedeaux, Physica **76** (1974) 235.
2) D. Bedeaux and P. Mazur, Physica **76** (1974) 247.
3) D. Bedeaux and P. Mazur, Physica **78** (1974) 505.
4) R.F. Fox and G.E. Uhlenbeck, Phys. Fluids 13 (1970) 1893.
5) T.S. Chow and J.J. Hermans, J.C.P. **56** (1972) 3150.
6) E.H. Hauge and A. Martin-Löf, J. stat. Phys. **7** (1973) 259.
7) D. Bedeaux, A.M. Albano and P. Mazur, Physica **88A** (1977) 574.
8) P. Mazur and G. van der Zwan, Physica **92A** (1978) 483.
9) See e.g. R.D. Mountain, Rev. Mod. Phys. **38** (1966) 205.
10) L. Landau and E.M. Lifshitz, Fluid Mechanics (Pergamon, New York, 1959).
11) See e.g. M.Sh. Giterman and V.M. Kontorovich, Sov. Phys. JETP **20** (1965) 1433.
12) S.R. de Groot and P. Mazur, Non Equilibrium Thermodynamics (North-Holland Publ. Co., Amsterdam, 1962).

PART B

LIGHT SCATTERING FROM SYSTEMS IN STATIONARY NON-EQUILIBRIUM STATES

III. COMBINED EFFECTS OF GRAVITY AND A TEMPERATURE GRADIENT

1. Introduction

The derivation of the density autocorrelation function and the light scattering spectrum in non-equilibrium systems has recently been the subject of a number of papers. The systems considered are fluids in which stationary gradients of the fluid fields are present. Several approaches to the study of such systems have been proposed.

T. Kirkpatrick, E.G.D. Cohen and J.R. Dorfman [1] have developed a kinetic theory of fluctuations in a dilute gas not in equilibrium and have calculated on this basis the density autocorrelation function and the corresponding light scattering spectrum. A modification of the sound modes in the density autocorrelation function and the Brillouin lines of the light scattering spectrum was found in the presence of a stationary temperature gradient. In their method the temperature dependence of the transport coefficients and thermodynamic derivatives, as e.g. the compressibility, was taken into account.

I. Procaccia, D. Ronis and I. Oppenheim [2-5] have extended the framework of nonlinear response theory to include the description of non-equilibrium stationary states. They also found modifications of the sound modes in the density autocorrelation function in the presence of a temperature gradient. Their results differ from those found by kinetic theory.

Autocorrelation functions in stationary non-equilibrium states have also been studied within the framework of fluctuating hydrodynamics. V.M. Zaĭtsev and M.I. Shliomis [6] considered the anomalous hydrodynamic fluctuations near the convective threshold of a fluid heated from below. Their theory is based on the linearized hydrodynamic equations in the Boussinesq approximation. H.N.W. Lekkerkerker and J.P. Boon [7] analyzed in greater detail the hydrodynamic modes near the convective instability and showed that the light scattering intensity was, under experimentally accessible conditions, essentially unaffected.

We intend in the following two chapters to apply linearized fluctuating hydrodynamics in a systematic way to the description of fluctuating fluids in a stationary state.

In this chapter we will consider stationary states in which both a temperature gradient and a gravitational field are present and we will show that, if a set of consistent approximations is made no modifications of the light scattering spectrum is found, in agreement with the results of

H.N.W. Lekkerkerker and J.P. Boon [7].

In chapter IV we study a fluid under the influence of a temperature gradient only. For simplicity's sake we will neglect the influence of the phenomenon of heat conductivity and consider viscosity to be a constant. We shall then show, that if one retains consistently all other terms linear in the applied temperature gradient, (which were all neglected in chapter III), the light scattering spectrum contains small terms of the general nature predicted also within the framework of kinetic theory.

2. Linearized equations of motion

We consider a fluid layer confined between two parallel planes at $z=+L/2$ and $z=-L/2$ and of infinite extension in the xy-plane. In the fluid layer a steady temperature gradient can be maintained by fixing the temperatures of the upper and lower plane at different values. In the bulk of the fluid the usual conservation laws and balance equations hold [8]

$$\frac{\partial}{\partial t}\rho(\vec{r},t) = -\vec{\nabla}\cdot\rho(\vec{r},t)\vec{v}(\vec{r},t) \tag{2.1}$$

$$\frac{\partial}{\partial t}\rho(\vec{r},t)\vec{v}(\vec{r},t) = -\vec{\nabla}\cdot[\rho(\vec{r},t)\vec{v}(\vec{r},t)\vec{v}(\vec{r},t) + \overleftrightarrow{P}(\vec{r},t)] - g\rho(\vec{r},t)\hat{z} \tag{2.2}$$

$$\rho(\vec{r},t)T(\vec{r},t)\frac{d}{dt}s(\vec{r},t) \equiv \rho(\vec{r},t)T(\vec{r},t)\left[\frac{\partial}{\partial t}s(\vec{r},t) + \vec{v}(\vec{r},t)\cdot\vec{\nabla}s(\vec{r},t)\right] =$$
$$= -\vec{\nabla}\cdot\vec{J}(\vec{r},t) - [\overleftrightarrow{P}(\vec{r},t) - p(\vec{r},t)\overleftrightarrow{U}] : \vec{\nabla}\vec{v}(\vec{r},t) \tag{2.3}$$

where ρ is the density field, $\vec{v}$ the velocity field, T the temperature field; s is the entropy per unit mass and p the hydrostatic pressure in the fluid. Furthermore g is the acceleration due to gravity, $\overleftrightarrow{U}$ the unit tensor and $\hat{z}$ a unit vector in the z-direction.

The pressure tensor $\overleftrightarrow{P}(\vec{r},t)$ and the heat current $\vec{J}(\vec{r},t)$ are given by

$$\overleftrightarrow{P} = p\overleftrightarrow{U} - 2\eta\,\overline{\vec{\nabla}\vec{v}} - \eta_v\,\vec{\nabla}\cdot\vec{v}\overleftrightarrow{U} \tag{2.4}$$

$$\vec{J} = -\lambda\vec{\nabla}T\ . \tag{2.5}$$

In eq. (2.4) η is the shear and η_v the bulk viscosity in the fluid and in eq. (2.5) λ is the heat conduction coefficient. The symmetric traceless part of a tensor has been indicated by $\overbrace{....}$. The transport coefficients η, η_v and λ may in principle depend on space and time coordinates through their dependence on the density ρ and the temperature T.

We will consider only stationary states of the system for which the velocity is zero. In that case the stationary state is characterized by the equations

$$\vec{v}_s = 0 \tag{2.6}$$

$$\vec{\nabla} p_s = -g\rho_s \hat{z} \tag{2.7}$$

$$\vec{\nabla}\cdot\vec{J}_s = 0. \tag{2.8}$$

In eqs. (2.6) - (2.8) and throughout this chapter the index s will refer to stationary state values of the variables.

We now linearize eqs. (2.1) - (2.3) by considering small deviations of the fluid fields from their stationary state values. Using eqs. (2.6) - (2.8) we obtain

$$\frac{\partial \rho}{\partial t} = -\vec{\nabla}\cdot\rho_s\vec{v} \tag{2.9}$$

$$\rho_s \frac{\partial \vec{v}}{\partial t} = -\vec{\nabla}\cdot\overleftrightarrow{P} - g\rho\hat{z} \tag{2.10}$$

$$\rho_s T_s \left(\frac{\partial s}{\partial t} + \vec{v}\cdot\vec{\nabla}s_s\right) = -\vec{\nabla}\cdot\vec{J} . \tag{2.11}$$

In eqs. (2.9) (2.11) the fluid fields ρ, $\vec{v}$, $\overleftrightarrow{P}$, s and $\vec{J}$ now denote the deviations from their stationary state values ρ_s, $\vec{v}_s = 0$, p_s, s_s and $\vec{J}_s$ respectively.

The deviations of the pressure and entropy fields are related to the density and temperature fields in linear approximation by the following equations

$$p = \left(\frac{\partial p}{\partial \rho}\right)_T^s \rho + \left(\frac{\partial p}{\partial T}\right)_\rho^s T \equiv \beta\rho + \alpha T \tag{2.12}$$

$$s = \left(\frac{\partial s}{\partial \rho}\right)_T^s \rho + \left(\frac{\partial s}{\partial T}\right)_\rho^s T \equiv \gamma\rho + \delta T . \tag{2.13}$$

In this chapter we will assume the transport coefficients η, η_v and λ and the thermodynamic derivatives α, β, γ and δ to be constants within the fluid layer. Hence they will not depend on the stationary state fields ρ_s

and T_s but only on some mean temperature and density for which we will choose the temperature and density in the middle of the layer, ρ_0 and T_0.

In eqs. (2.12) and (2.13) β is related to the isothermal compressibility by $\beta = -(\rho_0 \kappa_T)^{-1}$ and $T_0 \delta = c_v$, the specific heat at constant volume. Furthermore we have by the thermodynamic (Maxwell) relation $\gamma = -\alpha/\rho_0^2$.

The gradients of the stationary state fields ρ_s and s_s are, in terms of the gradients of p_s and T_s,

$$\vec{\nabla}\rho_s = \beta^{-1}\vec{\nabla}p_s - \alpha\beta^{-1}\vec{\nabla}T_s \tag{2.14}$$

$$\vec{\nabla}s_s = -\frac{1}{\rho_0^2}\alpha\beta^{-1}\vec{\nabla}p_s + \frac{c_p}{T_0}\vec{\nabla}T_s \tag{2.15}$$

where $c_p \equiv T_0(\partial s/\partial T)_p$ is the specific heat at constant pressure and where use has been made of the thermodynamic (Maxwell) relation $(\partial s/\partial p)_T = (1/\rho_0^2)(\partial\rho/\partial T)_p$.

The stationary state

Eqs. (2.7) and (2.8) together with the relations (2.5) and (2.14) determine the stationary state completely if boundary conditions at $z = -L/2$ and $z = L/2$ are specified. These boundary conditions are

$$\rho_s = \rho_1, \quad T_s = T_1 \quad \text{at } z = -L/2 \tag{2.16}$$

$$T_s = T_2 \quad \text{at } z = +L/2 . \tag{2.17}$$

Solving the differential equations (2.7) and (2.8) one obtains for the stationary temperature and density fields

$$T_s = T_0 - Az \tag{2.18}$$

$$\rho_s = \rho_0 \exp(-g\beta^{-1}z) + \frac{\alpha A}{g}(1 - \exp(-g\beta^{-1}z)) \tag{2.19}$$

where $T_0 \equiv (T_1+T_2)/2$, $A \equiv (T_1-T_2)/L$ and $\rho_0 \equiv \rho_1 \exp(-g\beta^{-1}L/2) + (\alpha A/g)(1 - \exp(-g\beta^{-1}L/2))$.

We will consider only systems in which the fluid layer thickness is not too large, $L \lesssim 1$ cm, and in which the temperature difference between the upper and lower boundary layer does not excede a few degrees Kelvin. In that case A is of order unity.

Expanding the exponential terms in ρ_s, eq. (2.19), to linear order

$(\beta^{-1}g|z| \le \beta^{-1}gL/2 \ll 1^{\dagger})$ and neglecting terms containing g $(g \ll \alpha A/\rho_0{}^{\dagger})$ one finds to a very good approximation

$$\rho_s(z) = \rho_0[1 + \frac{\alpha\beta^{-1}}{\rho_0} Az] . \tag{2.20}$$

Furthermore one obtains for the gradient of the stationary entropy field by inserting eqs. (2.7) and (2.18) into eq. (2.15)

$$\vec{\nabla}s_s = \frac{1}{\rho_0^2}\alpha\beta^{-1}g\rho_s\hat{z} - \frac{c_p}{T_0}A\hat{z} \simeq -\frac{c_p}{T_0}Az \ . \quad \left(\frac{c_p A}{T_0} \gg \frac{1}{\rho_0^2}\alpha\beta^{-1}g\rho_s{}^{\dagger} \right) \tag{2.21}$$

In the subsequent analysis we will use eqs. (2.6), (2.18), (2.20) and (2.21) for the stationary fluid fields.

3. Stochastic equations of motion

For an actual fluid in which the various fields fluctuate eqs. (2.9) - (2.11) together with (2.4) and (2.5) are only obeyed in the mean. The stochastic equations of motion are obtained by including random contributions to the pressure tensor and heat current.

The pressure tensor and heat current are then given by

$$\overleftrightarrow{P}(\vec{r},t) = p(\vec{r},t)\overleftrightarrow{U} - 2\eta\,\overline{\overleftrightarrow{\nabla}\vec{v}(\vec{r},t)} - \eta_v\vec{\nabla}\cdot\vec{v}(\vec{r},t)\overleftrightarrow{U} + \overleftrightarrow{\sigma}(\vec{r},t) \tag{3.1}$$

$$\vec{J}(\vec{r},t) = -\lambda\vec{\nabla}T(\vec{r},t) + \vec{J}_R(\vec{r},t) \tag{3.2}$$

where $\overleftrightarrow{\sigma}(\vec{r},t)$ is the random stress tensor and $\vec{J}_R(\vec{r},t)$ the random heat current.

The stochastic properties of $\overleftrightarrow{\sigma}$ and $\vec{J}_R$ are well known in equilibrium. We shall assume that these properties remain valid also in the steady state in view of the local nature of these random terms. In particular we assume that [6,9]

---

†) For an ideal gas (e.g. Ar, $T_0 \simeq 300$ K, $\rho_0 \simeq 10^{-3}$ g cm^{-3}):
$\beta \simeq 7.5 \times 10^8$ cm^{2}s^{-2}, $\alpha \simeq 2.5 \times 10^3$ g cm^{-1}s^{-2}K^{-1}, $\alpha\beta^{-1} \simeq 3 \times 10^{-7}$ g cm^{-3}K^{-1},
$c_p \simeq 6.4 \times 10^6$ cm^{2}s^{-2}K^{-1}.
For a liquid (e.g. H_2O, $T_0 \simeq 300$K, $\rho_0 \simeq 1$ g cm^{-3}):
$\beta \simeq 5 \times 10^{11}$ cm^{2}s^{-2}, $\alpha \simeq 2 \times 10^8$ g cm^{-1}s^{-2}K^{-1}, $\alpha\beta^{-1} \simeq 4 \times 10^{-4}$ g cm^{-3}K^{-1} ,
$c_p \simeq 4.2 \times 10^7$ cm^{2}s^{-2}K^{-1} .

$$\langle \vec{\vec{\sigma}}(\vec{r},t) \rangle = 0 \quad , \quad \langle \vec{J}_R(\vec{r},t) \rangle = 0 \tag{3.3}$$

$$\langle \sigma_{ij}(\vec{r},t)\sigma_{k\ell}(\vec{r}',t') \rangle = 2k_B T_0 (\eta\Delta_{ijk\ell} + \eta_v \delta_{ij}\delta_{k\ell})\delta(\vec{r}-\vec{r}')\delta(t-t') \tag{3.4}$$

$$\langle \sigma_{ij}(\vec{r},t)\vec{J}_{Rk}(\vec{r}',t') \rangle = \langle J_{Ri}(\vec{r},t)\sigma_{jk}(\vec{r}',t') \rangle = 0 \tag{3.5}$$

$$\langle J_{Ri}(\vec{r},t)J_{Rk}(\vec{r}',t') \rangle = 2k_B T_0^2 \lambda \delta_{ik} \delta(\vec{r}-\vec{r}')\delta(t-t') \tag{3.6}$$

where the brackets denote expectation values of fluctuations around the stationary state and $\Delta_{ijk\ell}$ is a symmetric traceless tensor of rank four

$$\Delta_{ijk\ell} = \delta_{ik}\delta_{j\ell} + \delta_{i\ell}\delta_{jk} - \frac{2}{3}\delta_{ij}\delta_{k\ell} \ . \tag{3.7}$$

In principle the temperature occurring in eqs. (3.4) and (3.6) should be the local stationary state temperature $T_s(z)$. However, since the gradients in the system are not large, e.g. since $A|z|/T_0 \lesssim 10^{-2}$, we may replace in first approximation T_s by T_0. In the next chapter we will study the consequences of taking also into account the coordinate dependence of T_s.

From eqs. (2.9) - (2.11) together with eqs. (3.1) and (3.2) and the stochastic properties (3.3) - (3.6) one can now determine in principle the correlation functions of the fluctuating fluid fields in the stationary state if one also specifies the boundary conditions at $z = L/2$ and $z = -L/2$.

4. Derivation of the hydrodynamic matrix

Substituting eqs. (2.12), (2.20) and (3.1) into eqs. (2.9) and (2.10) one obtains

$$\frac{\partial\rho}{\partial t} = -\rho_s \vec{\nabla}\cdot\vec{v} - \alpha\beta^{-1} A\, \vec{v}\cdot z \tag{4.1}$$

$$\rho_s \frac{\partial\vec{v}}{\partial t} = -\beta\vec{\nabla}\rho - \alpha\vec{\nabla}T + \eta\Delta\vec{v} + (\frac{1}{3}\eta + \eta_v)\vec{\nabla}\vec{\nabla}\cdot\vec{v} - g\rho\hat{z} + \vec{F}_R \tag{4.2}$$

where

$$\vec{F}_R \equiv -\vec{\nabla}\cdot\vec{\vec{\sigma}} \ . \tag{4.3}$$

Furthermore substitution of eqs. (2.13), (2.21) and (3.2) into eq. (2.11) and subsequent use of eq. (4.1) yields

$$\rho_s T_s \left(\frac{c_v}{T_0}\right) \frac{\partial T}{\partial t} = \lambda \Delta T - \rho_s^2 T_s \left(\frac{\alpha}{\rho_0^2}\right) \vec{\nabla}\cdot\vec{v} + \rho_s T_s \left(\frac{c_v}{T_0}\right) A\vec{v}\cdot\hat{z} + Q_R \qquad (4.4)$$

where

$$Q_R \equiv -\vec{\nabla}\cdot\vec{J}_R \qquad (4.5)$$

and use has been made of the thermodynamic relation

$$c_p = c_v + \alpha^2 T_0/\rho_0^2\beta \; . \qquad (4.6)$$

We now approximate the quantities ρ_s and T_s in eqs. (4.1), (4.2) and (4.4) by ρ_0 and T_0, since $\alpha\beta^{-1}A|z|/\rho_0 \lesssim 10^{-2}$ and $A|z|/T_0 \lesssim 10^{-2}$ (see note on page) so that a system of equations is obtained which is solvable by Fourier transformation.

We define, for a field $f(\vec{r},t)$, the Fourier transformed field $f(\vec{k},\omega)$ by

$$f(\vec{k},\omega) = \int_{-L/2}^{L/2} dz \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dt \; e^{i\omega t} e^{-i\vec{k}\cdot\vec{r}} f(\vec{r},t) \qquad (4.7)$$

$$f(\vec{r},t) = \frac{1}{(2\pi)^3} \frac{2}{L} \sum_{k_z} \int_{-\infty}^{\infty} dk_x \int_{-\infty}^{\infty} dk_y \int_{-\infty}^{\infty} e^{i\vec{k}\cdot\vec{r}} e^{-i\omega t} f(\vec{k},\omega) d\omega \qquad (4.8)$$

where k_z is a discrete parameter which assumes the values $\frac{2\pi n}{L}$, with n integer. This implies that we assume periodic boundary conditions for our fields (ρ, $\vec{v}$ and T). The behaviour of the system for $k_z L \gg 1$ will in good approximation be independent of this particular choice †). If one measures light scattering this condition is practically always fulfilled.

The above derived equations of motion for the fluid become in wave vector-frequency representation

$$-i\omega\rho = -\rho_0 i\vec{k}\cdot\vec{v} - \alpha\beta^{-1} A\,\vec{v}\cdot\hat{z} \qquad (4.9)$$

$$-i\omega\rho_0\vec{v} = -\beta i\vec{k}\rho - \alpha i\vec{k}T - \eta k^2\vec{v} - (\tfrac{1}{3}\eta + \eta_v)\vec{k}\vec{k}\cdot\vec{v} - g\rho\hat{z} + \vec{F}_R \qquad (4.10)$$

$$-i\omega\rho_0 c_v T = -\lambda k^2 T - \alpha T_0 i\vec{k}\cdot\vec{v} + \rho_0 c_v A\,\vec{v}\cdot\hat{z} + Q_R \qquad (4.11)$$

The fluid velocity field is conveniently specified by the following three variables [7]

---

†) For small values of k_z boundary conditions play a decisive role and may e.g. modify the spectrum of allowed k_z values [10,11].

$$\zeta \equiv (i\vec{k}\times\vec{v})_z \ , \qquad \xi \equiv (i\vec{k}\times i\vec{k}\times\vec{v})_z = \hat{z}\cdot(k^2-\vec{k}\vec{k})\cdot\vec{v} \tag{4.12}$$

and

$$D \equiv i\vec{k}\cdot\vec{v} \ . \tag{4.13}$$

From these definitions the following relation can be obtained

$$\vec{v}\cdot\hat{z} = \frac{1}{k^2}\,\xi - i\,\frac{k_z}{k^2}\,D \ . \tag{4.14}$$

Applying the operators $\hat{z}\cdot i\vec{k}\times$, $\hat{z}\cdot(k^2-\vec{k}\vec{k})\cdot$ and $i\vec{k}\cdot$ to eq. (4.10) and substituting eq. (4.14) into eqs. (4.9) and (4.11) a set of five equations with five unknown variables can be obtained. The variable ζ, which is the z-component of the vorticity, is completely decoupled from the other variables and satisfies the same equation as in equilibrium

$$(i\omega\rho_0 + \eta k^2)\zeta = (i\vec{k}\times\vec{F}_R)_z \ . \tag{4.15}$$

The remaining system of four equations can be written as

$$\overleftrightarrow{M}\cdot\vec{a} = \vec{F} \tag{4.16}$$

where $\vec{a}$ and $\vec{F}$ are vectors with components

$$\vec{a} = (\xi, D, T, \rho) \tag{4.17}$$

$$\vec{F} = (\hat{z}\cdot(k^2-\vec{k}\vec{k})\cdot\vec{F}_R,\ i\vec{k}\cdot\vec{F}_R,\ Q_R,\ 0) \equiv (F_{Tz},\ F_L,\ Q_R,\ 0) \ . \tag{4.18}$$

The hydrodynamic matrix $\overleftrightarrow{M}$ occurring in eq. (4.16) has the following form

$$\overleftrightarrow{M} = \begin{pmatrix} -i\omega\rho_0 + \eta k^2 & 0 & 0 & g(k^2-k_z^2) \\ 0 & -i\omega\rho_0 + \eta' k^2 & -\alpha k^2 & -\beta k^2 + gik_z \\ -\rho_0 c_v A/k^2 & \alpha T_0(1+i\gamma_1) & -i\omega\rho_0 c_v + \lambda k^2 & 0 \\ \alpha\beta^{-1}A/k^2 & \rho_0(1+i\gamma_2) & 0 & -i\omega \end{pmatrix} \tag{4.19}$$

where $\eta' \equiv (4/3)\eta + \eta_v$, $\gamma_1 \equiv (\rho_0 c_v/\alpha T_0)Ak_z/k^2$ and $\gamma_2 \equiv -(\alpha\beta^{-1}/\rho_0)Ak_z/k^2$.

Equilibrium fluctuating hydrodynamics of a uniform system follows then taking the limits $g\to 0$, $A\to 0$, in which case the variable ξ decouples from the other variables as it should.

From eq. (4.16) the fluctuating fluid fields (i.e. the vector $\vec{a}$) can be found by inverting the matrix $\overleftrightarrow{M}$. Subsequently the correlation functions may be obtained in the following way

$$\langle \vec{a}(\vec{k},\omega)\vec{a}^*(\vec{k}',\omega')\rangle = \overleftrightarrow{M}^{-1}(\vec{k},\omega)\cdot\langle\vec{F}(\vec{k},\omega)\vec{F}^*(\vec{k}',\omega')\rangle\cdot(\overleftrightarrow{M}^{-1}(\vec{k}',\omega'))^* \tag{4.20}$$

where $\tilde{\overleftrightarrow{M}}^{-1}$ denotes the transposed matrix of $\overleftrightarrow{M}^{-1}$.

As we will be interested in light scattering the correlation function of interest is the density autocorrelation function. In the next section we will study the matrix $\overleftrightarrow{M}^{-1}$, derive an explicit expression for the density autocorrelation and determine the corresponding light scattering spectrum.

5. The density-density correlation function and light scattering spectrum

By inverting eq. (4.16) one obtains for the fluctuating fluid density field

$$\rho(\vec{k},\omega) = (\overleftrightarrow{M}^{-1})_{41}F_{Tz} + (\overleftrightarrow{M}^{-1})_{42}F_L + (\overleftrightarrow{M}^{-1})_{43}Q_R \; . \tag{5.1}$$

Since all cross correlations between F_{Tz}, F_L and Q_R vanish (cf. the definitions (4.3), (4.5) and (4.18) together with eqs. (3.4) and (3.5)), while their autocorrelation functions are δ-correlated, one may write for the density autocorrelation function (cf. eq. (4.20))

$$\langle \rho(\vec{k},\omega)\rho^*(\vec{k}',\omega') \rangle = \frac{1}{|\det M|^2}\Big[|\det M_{41}|^2 \langle F_{Tz}(\vec{k},\omega)F_{Tz}^*(\vec{k}',\omega') \rangle + $$

$$+ |\det M_{42}|^2 \langle F_L(\vec{k},\omega)F_L^*(\vec{k}',\omega') \rangle + |\det M_{43}|^2 \langle Q_R(\vec{k},\omega)Q_R^*(\vec{k}',\omega') \rangle \Big] \tag{5.2}$$

where $(\det M_{ij})$ denotes the minor of the ij element of $\overleftrightarrow{M}$.
The determinant of the matrix $\overleftrightarrow{M}$ is given by

$$\det M = \rho_0^3 c_v \Big\{ (-i\omega+\nu k^2)\big((-i\omega)^3 + (-i\omega)^2(\nu'+\chi)k^2 + (-i\omega)[\nu'\chi k^4 + c_0^2k^2] + \frac{c_v}{c_p} c_0^2 \chi k^4\big)$$

$$- \frac{g\alpha\beta^{-1}}{\rho_0} A(1 - \frac{k_z^2}{k^2}) \; [\, (-i\omega)^2 + (-i\omega)(\nu'+\chi)k^2 + \nu'\chi k^4 + c_0^2 k^2 \,] \Big\} \tag{5.3}$$

where $\nu \equiv \eta/\rho_0$ is the kinematic viscosity, $\nu' \equiv \eta'/\rho_0$, $\chi \equiv \lambda/\rho_0 c_v$ is the thermal diffusivity and $c_0 \equiv \sqrt{(\partial p/\partial \rho)_s}$ is the adiabatic sound velocity. Use has also been made of the thermodynamic relations eq. (4.6) and

$$\frac{c_p}{c_v} = \frac{c_0^2}{\beta} \equiv \rho_0 \kappa_T c_0^2 \; . \tag{5.4}$$

The term gik_z has been neglected since $|gk_z| / \beta k^2 << 10^{-7}$ for $k >> L^{-1}$.

The physical behaviour of the density autocorrelation function is determined by the zeroes in the complex ω-plane of the determinant of the matrix $\overleftrightarrow{M}$. We define the dimensionless quantities $\epsilon \equiv \nu k^2/c_0 k$, $\epsilon b \equiv \nu' k^2/c_0 k$, $\epsilon c \equiv \chi k^2/c_0 k$ and $\epsilon d \equiv [gA\alpha\beta^{-1}(1-k_z^2/k^2)/\rho_0]^{\frac{1}{2}}/c_0 k$ and the dimensionless variable $t \equiv -i\omega/c_0 k$. The zeroes of det M are then the solutions of the equation

$$(t+\epsilon)[t^3 + \epsilon t^2(b+c) + t(\epsilon^2 bc + 1) + \frac{c_v}{c_p}\epsilon c] - \epsilon^2 d^2 [t^2 + \epsilon t(b+c) + \epsilon^2 bc + 1] = 0 \tag{5.5}$$

The quantity ε is for all fluids and for all physical values of k very small, $\epsilon << 1$, while b, c and d are at most of order unity. We can therefore expand the roots of eq. (5.5) in ε. One obtains in this way in good approximation (see Appendix A)

$$t_{1,2} = -\tfrac{1}{2}\epsilon \left[\left(1 + \frac{c_v}{c_p} c\right) \pm \left[\left(1 - \frac{c_v}{c_p} c\right)^2 + 4d^2\right]^{\frac{1}{2}}\right] \tag{5.6}$$

$$t_{3,4} = \pm i + \tfrac{1}{2}\epsilon\left[b + c\left(1 - \frac{c_v}{c_p}\right)\right] \tag{5.7}$$

From eq. (5.3) together with eqs. (5.6) and (5.7) and the definitions of ε, b, c, d and t it follows that $|\det M|^2$ can be written as

$$|\det M|^2 = (\rho_0^3 c_v)^2(\omega^2+\lambda_+^2)(\omega^2+\lambda_-^2)[(\omega-c_0 k)^2 + (\Gamma k^2)^2][(\omega+c_0 k)^2 + (\Gamma k^2)^2] \tag{5.8}$$

where

$$\Gamma \equiv \tfrac{1}{2}[\nu' + \chi(1 - \frac{c_v}{c_p})] \tag{5.9}$$

is the sound attenuation coefficient and λ_+, λ_- are given by

$$\lambda_\pm = -\tfrac{1}{2}\left(\nu + \frac{c_v}{c_p}\chi\right)k^2 \pm \tfrac{1}{2}\left[\left(\nu - \frac{c_v}{c_p}\chi\right)^2 k^4 + 4g\frac{\alpha\beta^{-1}}{\rho_0} A\left(1 - \frac{k_z^2}{k^2}\right)\right]^{\frac{1}{2}} . \tag{5.10}$$

These are the well known eigenvalues of the Bénard problem: for a positive thermal expansion coefficient and positive A, λ_+ may become zero for certain values of k, thus leading to unstable behaviour of the system.

The minors det M_{41}, det M_{42} and det M_{43} occurring in eq. (5.1) are

$$\det M_{41} = -\rho_0^3 c_v \frac{\alpha\beta^{-1}}{\rho_0 k^2} A[(-i\omega + \nu k^2)(-i\omega + \chi k^2) + c_0^2 k^2] \tag{5.11}$$

$$\det M_{42} = -\rho_0^3 c_v(-i\omega + \nu k^2)(-i\omega + \chi k^2)(1 + i\gamma_2) \tag{5.12}$$

and

$$\det M_{43} = -\rho_0^3 c_v \frac{\alpha k^2}{\rho_0 c_v} (-i\omega + \nu k^2)(1 + i\gamma_2) \ . \tag{5.13}$$

The density autocorrelation function, eq. (5.2), then becomes, using eqs. (3.4) and (3.6) and the definitions of F_{Tz}, F_L and Q_R, (cf. eqs. (4.3), (4.5) and (4.18)

$$\langle \rho(\vec{k},\omega)\rho^*(\vec{k}',\omega') \rangle = 2k_B T_0 L(2\pi)^3 \delta(k_x-k_x')\delta(k_y-k_y')\delta(\omega-\omega')\delta_{k_z,k_z'} S(\vec{k},\omega) \tag{5.14}$$

with the spectral density

$$S(\vec{k},\omega) = \left\{[\omega^2 + (\nu' k^2)^2][\omega^2 + (\chi k^2)^2]\eta' k^4 + \left(\frac{\alpha k^2}{\rho_0 c_v}\right)^2 [\omega^2 + (\nu k^2)^2]\lambda k^2 T_0\right\} \times$$

$$[(\omega^2+\lambda_+^2)(\omega^2+\lambda_-^2)\left((\omega-c_0 k)^2 + (\Gamma k^2)^2\right)\left((\omega+c_0 k)^2 + (\Gamma k^2)^2\right)]^{-1} \tag{5.15}$$

where we have consistently neglected small contributions to the amplitude of order $(\alpha\beta^{-1}Ak_z/\rho_0 k^2)^2$. The relative order of magnitude of these contributions is 10^{-4}.

Since $c_0 k >> \Gamma k^2$ eq. (5.15) can be rewritten in the form

$$S(\vec{k},\omega) = \rho_0^2 \kappa_T \left\{(1 - \frac{c_v}{c_p}) \frac{(\omega^2+\nu^2 k^4) c_v \chi k^2/c_p}{(\omega^2+\lambda_+^2)(\omega^2+\lambda_-^2)} + \right.$$

$$\left. + \tfrac{1}{2} \frac{c_v}{c_p} \left[\frac{\Gamma k^2}{(\omega-c_0 k)^2 + (\Gamma k^2)^2} + \frac{\Gamma k^2}{(\omega+c_0 k)^2 + (\Gamma k^2)^2}\right]\right\} \tag{5.16}$$

where use has been made of the thermodynamic relation eq. (5.4).

In the "equilibrium limit" ($A \to 0$, $g \to 0$) the first term reduces to

$$(1 - \frac{c_v}{c_p}) \frac{c_v \chi k^2/c_p}{\omega^2 + (c_v \chi k^2/c_p)^2} , \tag{5.17}$$

the usual form of the heat mode in equilibrium hydrodynamics.

We also note that, within the approximations of this chapter, the sound modes are essentially unaffected by the presence of a temperature gradient and the gravity field.

The only modification of the function $S(\vec{k},\omega)$ is contained in the first term of eq. (5.16) and is due to the simultaneous presence of the temperature gradient and the gravity field. This term may become anomalously large close to the Rayleigh-Bénard instability, i.e. when λ_+ approaches zero. From the general theory of light scattering in fluids it follows that the scattered intensity I at frequency ω is given by [12]

$$I(\vec{k},\omega) = BS(\vec{k}, \omega-\omega_0) \tag{5.18}$$

In eq. (5.18) ω_0 is the frequency of the incident monochromatic lightwave of wavevector $\vec{k}_0$. The wavevector $\vec{k}$ in this formula represents the difference vector between the wavevector $\vec{k}_0'$ of the scattered wave and the wavevector $\vec{k}_0$. The proportionality factor B is, averaging over the direction of polarisation of the incident lightwave, equal to

$$B = \frac{1}{2}\,\frac{V\,k_0^4 E_0^2}{16\pi^2 D^2 \varepsilon_0^2}\left(\frac{\partial\varepsilon_0}{\partial\rho_0}\right)_{T_0}^2 . \tag{5.19}$$

where E_0^2 is the intensity of the incident lightwave and ε_0 the dielectric constant of the medium, considered here to be a function of the mean density ρ_0 and the mean temperature T_0. Furthermore V is that portion of the fluid from which light is scattered and D is the distance from the scattering volume to the observer.

In light scattering experiments k values range from 10^5–10^3 cm^{-1}. Smaller values are as yet experimentally unaccessible. As a typical value for k we will take 10^4 cm^{-1}. In that case $\lambda_\pm$ can be approximated by

$$\lambda_+ = -\frac{c_v}{c_p}\chi k^2 \quad , \quad \lambda_- = -\nu k^2$$

$$4g\,\frac{\alpha\beta^{-1}}{\rho_0}\left(1-\frac{k_z^2}{k^2}\right) \le 4g\alpha\beta^{-1}/\rho_0 \ll \left(\nu-\frac{c_v}{c_p}\chi\right)^2 k^4 . \tag{5.20}$$

Inserting this result into eq. (5.18) one obtains the usual light scattering spectrum for equilibrium fluids. We thus see that in light scattering, if effects whose relative order of magnitude is 10^{-2} or smaller are neglected, no modification of the spectrum is found except at very small, experimentally unaccessible, scattering angles [7] ($\lesssim 10^{-4}$ rad).

6. Conclusion

We have found in this chapter that, on the basis of a set of approximations, the density autocorrelation function of a fluid at rest is not modified under the influence of a temperature gradient and gravity, except in the neighbourhood of the Rayleigh-Bénard instability point. The approximations made were the following.

1. The transport coefficients η, η_V and λ and also the thermodynamic derivatives, as e.g. $(\partial p/\partial \rho)_T$ etc., were assumed to be constant within the fluid layer.
2. The stationary density ρ_s and temperature T_s could be replaced by the "mean" density ρ_0 and temperature T_0, whenever they were not differentiated with respect to the z-coordinate in the original linearized hydrodynamic equations.

These approximations implied that effects whose relative order of magnitude is 10^{-2} were neglected. In addition a number of other effects with relative order of magnitude 10^{-4} or smaller (e.g. direct effects of gravity not coupled to the temperature gradient) were neglected.

We have also seen that the only remaining modification of the density autocorrelation function, due to the simultaneous presence of gravity and a temperature gradient is inaccessible to experimental observation by means of light scattering experiments.

In the next chapter we will take into account systematically effects whose relative order of magnitude is 10^{-2}. In order to simplify the analysis we will neglect the effects of gravity (i.e. we will consider systems far from the Rayleigh-Bénard instability) and of heat conduction.

Appendix A

In this appendix we derive the approximation to the roots of eq. (5.5) given by eqs. (5.6) and (5.7).

To zeroeth order in ε these roots can be found from the equation

$$t(t^3+t) = 0 \tag{A.1}$$

which yields

$$t^0_{1,2} = 0 \ , \qquad t^0_{3,4} = \pm i \ . \tag{A.2}$$

Up to second order in ε each of the roots t_j of the original equation can be written

$$t_j = t_j^0 + \varepsilon t_j' + \varepsilon^2 t_j'' \quad , \qquad j = 1,2,3,4 \ . \tag{A.3}$$

Inserting eq. (A.3) into eq. (5.5) and retaining terms up to second order in ε one obtains

$$\varepsilon t_j^0 \left[3(t_j^0)^2 t_j' + (t_j^0)^2(b+c) + t_j' + \frac{c_v}{c_p} c\right] +$$

$$\varepsilon^2 \Big\{ (t_j'+1)\left[3(t_j^0)^2 t_j' + (t_j^0)^2(b+c) + t_j' + \frac{c_v}{c_p} c\right] - d^2\left((t_j^0)^2 + 1\right)$$

$$+ t_j^0\left[3(t_j^0)^2 t_j'' + 3t_j^0 (t_j')^2 + 2t_j^0 t_j'(b+c) + t_j'' + bct_j^0\right] \Big\} \ . \tag{A.4}$$

We now consider the two different cases $j = 1,2$ and $j = 3,4$ (cf. eq. (A.2)).

(i) $j = 1,2$. In that case there are no first order terms and the second order term reduces to

$$(t_j'+1)(t_j' + \frac{c_v}{c_p} c) - d^2 = 0, \qquad j = 1,2. \tag{A.5}$$

The correction to the zeroeth order roots, eq. (A.2), are then found to be

$$t_j' = -\tfrac{1}{2}(1 + \frac{c_v}{c_p} c) \pm \tfrac{1}{2}[(1 - \frac{c_v}{c_p} c)^2 + 4d^2]^{\frac{1}{2}} \ , \qquad j = 1,2 \tag{A.6}$$

so that $t_{1,2}$ to order ε is given by eq. (5.6).

ii) $j = 3,4$. In that case we find from eq. (A.4)

$$-2t_j'' - (b+c) + \frac{c_v}{c_p} c = 0 \ , \qquad j = 3,4 \tag{A.7}$$

so that $t_{3,4}$ to order ε is given by eq. (5.7).
From eq. (A.4) one can also determine $t_{3,4}''$. It is seen that also to that order t_j is independent of d or in other words: the sound modes are not modified up to this order by the simultaneous presence of a temperature gradient and the gravity field.

References

1. T. Kirkpatrick, E.G.D. Cohen, J.R. Dorfman, Phys.Rev.Lett. 42 (1979) 862.
2. I. Procaccia, D. Ronis and I. Oppenheim, Phys.Rev.Lett. 42 (1979) 287, 614 (E).
3. I. Procaccia, D. Ronis, M.A. Collins, J. Ross, and I. Oppenheim, Phys.Rev. A19 (1979) 1290.
4. D. Ronis, I. Procaccia and I. Oppenheim, Phys.Rev. A19 (1979) 1307.
5. D. Ronis, I. Procaccia and I. Oppenheim, Phys.Rev. A19 (1979) 1324.
6. V.M. Zaĭtsev and M.I. Shliomis, Sov.Phys. JETP 32 (1971) 866.
7. H.N.W. Lekkerkerker and J.P. Boon, Phys.Rev. A10 (1974) 1355.
8. S.R. de Groot and P. Mazur, Non-equilibrium thermodynamics (North Holland, Amsterdam 1962).
9. L. Landau and E.M. Lifshitz, Fluid Mechanics (Pergamon Press, New York, 1959).
10. S. Chandrasekhar, Hydrodynamic and hydromagnetic instability (Clarendon Press, Oxford, 1961).
11. F. Garisto and P. Mazur, Physica 94A (1978) 365.
12. See e.g. M. Fixman, J.Chem.Phys. 23 (1955) 2074.
    P. Mazur, in Advances of chemical physics, Ed. I. Prigogine (Interscience publishers, New York, 1958).

IV. EFFECTS LINEAR IN AN APPLIED TEMPERATURE GRADIENT

1. Introduction

In this chapter we again consider the fluid system described in section 2 of chapter III. We will take, however, the direction of the gravitational field opposite to the direction of the temperature gradient, so that, for positive thermal expansion coefficient, λ_+ will be negative for all values of A and k (cf. eq. (III. 5.10)). In such a system no convective (Rayleigh-Bénard) instability can occur. We have shown in the previous chapter that the direct effects of gravity on the density-density correlation function are in general very small (of relative order 10^{-7}). We may therefore in this chapter neglect altogether effects due to the gravitational field and omit the term $-g\rho\hat{z}$ in eq. (III. 2.2). The stationary state is then characterized by the set of equations (cf. eqs. (III. 2.6) - (III. 2.8))

$$\vec{v}_s = 0 \tag{1.1}$$

$$\vec{\nabla} p_s = 0 \tag{1.2}$$

$$\vec{\nabla}\cdot\vec{J}_s = 0 \tag{1.3}$$

As a consequence of eq. (1.2) the stationary pressure $p_s = p_0$ is constant throughout the system.

For simplicity's sake we will neglect the temperature dependence of η and η_v at constant pressure, and consider these quantities to be constant throughout the fluid layer. Moreover we will put $\lambda = 0$ †). In equilibrium this last simplification implies that the fluid behaves adiabatically. All other effects due to the presence of a temperature gradient will be taken into account up to linear order *). These effects are related to the dependence of thermodynamic quantities $\psi(T_s,p_s)$ on the stationary state temperature field $T_s(z)$. If the temperature gradient A is sufficiently small (A of order unity) we may write for any quantity ψ

$$\psi(T_s,p_s) = \psi(T_0,p_0) - \left(\frac{\partial\psi}{\partial T}\right)_p Az \tag{1.4}$$

---

†) In fact λ is considered to be exceedingly small so that we may neglect its contribution once the steady state is established.

*) An extension of the theory presented in this chapter to the case that also the temperature dependence of η, η_v and λ is taken into account is straightforward but quite cumbersome.

where $(\partial\psi/\partial T)_p$ has to be evaluated at the mean temperature T_0, i.e. at $z = 0$. For all quantities of interest here the relative order of magnitude of the terms occurring in eq. (1.4) turns out to be smaller than 10^{-2}.

Under the conditions stated above the system can then be described by the following set of linear stochastic equations (cf. eqs. (III. 2.9) - (III. 2.11))

$$\frac{\partial\rho}{\partial t} = -\rho_s \vec{\nabla}\cdot\vec{v} - \vec{v}\cdot\vec{\nabla}\rho_s \tag{1.5}$$

$$\rho_s \frac{\partial\vec{v}}{\partial t} = -\vec{\nabla}p + \eta\Delta\vec{v} + (\frac{1}{3}\eta + \eta_v)\vec{\nabla}\vec{\nabla}\cdot\vec{v} + \vec{F}_R \tag{1.6}$$

$$\frac{\partial s}{\partial t} = -\vec{v}\cdot\vec{\nabla}s_s \ . \tag{1.7}$$

The pressure fluctuations are related to the density and entropy fluctuations by

$$p = \left[c_0^2 - \left(\frac{\partial c_0^2}{\partial T}\right)_p Az\right]\rho + \left[\frac{\alpha T_0}{c_v} - \left(\frac{\partial}{\partial T}\alpha T/c_v\right)_p Az\right]s \tag{1.8}$$

where use has been made of the thermodynamic relations $(\partial p/\partial\rho)_s = c_0^2$, $(\partial p/\partial s)_\rho = \alpha T/c_v$ and of relation (1.4).

The properties of the random force $\vec{F}_R$ can be derived from eqs. (III. 3.3) and (III. 3.4) where we now have to replace the temperature T_0 by the stationary temperature T_s.

In the next section we shall obtain from eqs. (1.2) - (1.4) an expression valid to linear order in A for the fluid density field in terms of $\vec{F}_R$.

2. The fluid density field

Since we will be interested in light scattering from a volume with linear dimensions larger than the wave length of light but much smaller than the width L of the fluid layer and far removed from its boundaries we may assume in very good approximation the fluid layer to be of infinite extension in the z-direction and eqs. (1.5) - (1.8) to hold for z in the interval $(-\infty,\infty)$. This implies that we replace our fluid layer by an infinite fictive fluid for which eq. (1.4) for all relevant functions $\psi(T_s,p_s)$ holds everywhere and not only in the interval (-L/2, L/2).

We then define the Fourier transform of a function $f(\vec{r},t)$ by

$$f(\vec{k},\omega) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dt\; e^{-i\vec{k}\cdot\vec{r}+i\omega t}\; f(\vec{r},t) \tag{2.1}$$

$$f(\vec{r},t) = \frac{1}{(2\pi)^4} \int_{-\infty}^{\infty} dk_x \int_{-\infty}^{\infty} dk_y \int_{-\infty}^{\infty} dk_z \int_{-\infty}^{\infty} d\omega\; e^{i\vec{k}\cdot\vec{r}-i\omega t}\; f(\vec{k},\omega)\; . \tag{2.2}$$

In $\vec{k},\omega$ representation eq. (1.5) becomes

$$-i\omega\rho = -\left(\rho_0 + \alpha\beta^{-1} A\, i \frac{\partial}{\partial k_z}\right) D - \alpha\beta^{-1} A\; \vec{v}\cdot\hat{z} \tag{2.3}$$

where use has been made of the definitions of D, eq. (III. 4.13), and of eq. (III. 2.20). Inserting relation (III. 4.14) into eq. (2.3) one obtains

$$-i\omega\rho = -\left(\rho_0 - \alpha\beta^{-1} A\, i \frac{k_z}{k^2} + \alpha\beta^{-1} A\, i \frac{\partial}{\partial k_z}\right) D - \alpha\beta^{-1} \frac{A\xi}{k^2} = -\rho_0 \hat{O} D - \alpha\beta^{-1} \frac{A\xi}{k^2} \tag{2.4}$$

where the operator $\hat{O}$ is defined as

$$\hat{O} \equiv \left(1 - \frac{\alpha\beta^{-1}}{\rho_0} A\, i \frac{k_z}{k^2} + \frac{\alpha\beta^{-1}}{\rho_0} A\, i \frac{\partial}{\partial k_z}\right) . \tag{2.5}$$

In the same way we obtain from eq. (1.6)

$$\begin{aligned} -i\omega\left(\rho_0 + \alpha\beta^{-1} A\, i \frac{\partial}{\partial k_z}\right) \vec{v} &= -i\vec{k}\left\{c_0^2 - \left(\frac{\partial c_0^2}{\partial T}\right)_p A\, i \frac{\partial}{\partial k_z}\right\}\rho \\ &- i\vec{k}\left[\frac{\alpha T_0}{c_v} - \left(\frac{\partial \alpha T/c_v}{\partial T}\right)_p A\, i \frac{\partial}{\partial k_z}\right] s - \eta k^2 \vec{v} - \left(\frac{1}{3}\eta + \eta_v\right)\vec{k}\vec{k}\cdot\vec{v} + \vec{F}_R \end{aligned} \tag{2.6}$$

where eqs. (III. 2.20) and (1.8) have been used.

Applying the operators $\hat{z}\cdot(k^2 - \vec{k}\vec{k})\cdot$ and $i\vec{k}\cdot$ to eq. (2.6) one obtains two equations for ξ and D (cf. the derivation of eq. (III. 4.16)):

$$(-i\omega\rho_0\hat{O} + \eta k^2)\xi - i\omega\alpha\beta^{-1} A\left(1 - \frac{k_z^2}{k^2}\right) D = F_{Tz} \tag{2.7}$$

$$\begin{aligned} (-i\omega\rho_0\hat{O} + \eta' k^2) D - i\omega\alpha\beta^{-1} \frac{A\xi}{k^2} &= k^2 \left\{c_0^2 - \left(\frac{\partial c_0^2}{\partial T}\right)_p A\, i \frac{\partial}{\partial k_z}\right\}\rho \\ &+ k^2 \left[\frac{\alpha T_0}{c_v} - \left(\frac{\partial \alpha T/c_v}{\partial T}\right)_p A\, i \frac{\partial}{\partial k_z}\right] s + F_L \end{aligned} \tag{2.8}$$

where use has been made of the definitions of F_{Tz} and F_L eq. (III. 4.18). Finally, Fourier transformation of eq. (1.7) and subsequent use of eq. (III. 4.14) yields

$$-i\omega s = -\left(\frac{\partial s}{\partial T}\right)_p A\, i\,\frac{k_z}{k^2}\, D + \left(\frac{\partial s}{\partial T}\right)_p \frac{A\xi}{k^2} \quad . \tag{2.9}$$

The set of equations (2.4), (2.7), (2.8) and (2.9) can be solved for $\rho(\vec{k},\omega)$ in terms of F_{Tz} and F_L. In appendix A we show that up to linear order in A one obtains

$$\rho(\vec{k},\omega) = \left[G_0(\vec{k},\omega) + AG_1(\vec{k},\omega)i\,\frac{k_z}{k^2} + AG_2(\vec{k},\omega)i\,\frac{\partial}{\partial k_z}\right]F_L(\vec{k},\omega)$$

$$-\frac{\alpha\beta^{-1}}{\rho_0}\,\frac{A}{k^2}\,\frac{c_0^2k^2 - i\omega\nu' k^2}{-i\omega(-i\omega+\nu k^2)}\,G_0(\vec{k},\omega)F_{Tz}(\vec{k},\omega) \tag{2.10}$$

where

$$G_0(\vec{k},\omega) = [\omega^2 - c_0^2k^2 + i\omega\nu' k^2]^{-1} \tag{2.11}$$

$$G_1(\vec{k},\omega) = \frac{\alpha\beta^{-1}}{\rho_0}\,(c_0^2k^2 - i\omega\nu' k^2)G_0^2(\vec{k},\omega) \tag{2.12}$$

$$G_2(\vec{k},\omega) = -\left[\left(\frac{\partial c_0^2}{\partial T}\right)_p k^2 - i\omega\nu' k^2\,\frac{\alpha\beta^{-1}}{\rho_0}\right]G_0^2(\vec{k},\omega) \quad . \tag{2.13}$$

The function $G_0(\vec{k},\omega)$ is the propagator for the fluctuating density field in equilibrium. The three functions G_0, G_1 and G_2 satisy the following condition

$$G_i(\vec{k},\omega) = G_i^*(\vec{k},-\omega) \qquad i=0,1,2 \quad . \tag{2.14}$$

These relations will be of use in the next section in connection with symmetry properties of the density-density correlation function.

3. The density-density correlation function

The density-density correlation function can now be calculated consistently to linear order in the temperature gradient A. Since the cross correlation between F_{Tz} and F_L vanishes in equilibrium, i.e. for A=0, the density-density correlation function up to terms linear in A is given by

$$\langle \rho(\vec{k},\omega)\rho^*(\vec{k}',\omega') \rangle = G_0(\vec{k},\omega)G_0^*(\vec{k}',\omega') \langle F_L(\vec{k},\omega)F_L^*(\vec{k}',\omega') \rangle +$$

$$+ A\left[G_1(\vec{k},\omega)G_0^*(\vec{k}',\omega')\, i\frac{k_z}{k^2} - G_0(\vec{k},\omega)G_1^*(\vec{k}',\omega')\, i\frac{k_z'}{k'^2}\right] \langle F_L(\vec{k},\omega)F_L^*(\vec{k}',\omega') \rangle_{A=0}$$

$$+ A\left[G_2(\vec{k},\omega)G_0^*(\vec{k}',\omega')\, i\frac{\partial}{\partial k_z} - G_0(\vec{k},\omega)G_2^*(\vec{k}',\omega')\, i\frac{\partial}{\partial k_z'}\right] \langle F_L(\vec{k},\omega)F_L^*(\vec{k}',\omega') \rangle_{A=0}. \tag{3.1}$$

The correlation function of the random force must now be evaluated in the presence of a temperature gradient. For the random stress tensor we have here (cf. eq. (III. 3.4) and after eq. (1.8))

$$\langle \sigma_{ij}(\vec{r},t)\sigma_{k\ell}(\vec{r}',t') \rangle = 2k_BT_S(\eta\Delta_{ijk\ell} + \eta_v\delta_{ij}\delta_{k\ell})\delta(\vec{r}-\vec{r}')\delta(t-t')$$

$$= 2k_B(T_0 - Az)(\eta\Delta_{ijk\ell} + \eta_v\delta_{ij}\delta_{k\ell})\delta(\vec{r}-\vec{r}')\delta(t-t'). \tag{3.2}$$

Upon Fourier transformation this correlation function becomes

$$\langle \sigma_{ij}(\vec{k},\omega)\sigma_{k\ell}^*(\vec{k}',\omega') \rangle = 2k_B(\eta\Delta_{ijk\ell} + \eta_v\delta_{ij}\delta_{k\ell})(2\pi)^4(T_0 - Ai\frac{\partial}{\partial k_z})\delta(\vec{k}-\vec{k}')\delta(\omega-\omega') \tag{3.3}$$

so that, cf. eqs. (III. 4.3), (III. 4.18)

$$\langle F_L(\vec{k},\omega)F_L^*(\vec{k}',\omega') \rangle = \sum_{i=1}^{3}\sum_{j=1}^{3}\sum_{k=1}^{3}\sum_{\ell=1}^{3} k_ik_jk_k'k_\ell' \langle \sigma_{ij}^*(\vec{k},\omega)\sigma_{k\ell}(\vec{k}',\omega') \rangle =$$

$$(2\pi)^4 2k_BT_0\eta' k^4\delta(\vec{k}-\vec{k}')\delta(\omega-\omega')$$

$$-(2\pi)^4 2k_BA\,\delta(\vec{k}_\parallel-\vec{k}_\parallel')\delta(\omega-\omega')\left[2\eta(\vec{k}\cdot\vec{k}')^2 + (\eta_v - \frac{2}{3}\eta)k^2k'^2\right] i\frac{\partial}{\partial k_z}\,\delta(k_z-k_z') \tag{3.4}$$

where $\vec{k}_\parallel$ is the vector parallel to the xy-plane with components k_x, k_y.

From eq. (3.1) together with eq. (3.3) it follows that the density-density correlation function can be written as

$$\langle \rho(\vec{k},\omega)\rho^*(\vec{k}',\omega') \rangle = (2\pi)^4 2k_BT_0\left[S_0(\vec{k},\omega) + AS_1(\vec{k},\omega)\right]\delta(\vec{k}-\vec{k}')\delta(\omega-\omega')$$

$$+ (2\pi)^4 2k_BT_0AS_2(k_z,k_z';\vec{k}_\parallel,\omega)\delta(\vec{k}_\parallel-\vec{k}_\parallel')\delta(\omega-\omega')\, i\frac{\partial}{\partial k_z}\,\delta(k_z-k_z') \tag{3.5}$$

where

$$S_0(\vec{k},\omega) = \eta' k^4 |G_0(\vec{k},\omega)|^2 \tag{3.6}$$

$$S_1(\vec{k},\omega) = i\,\frac{k_z}{k^2}\left[G_1(\vec{k},\omega)G_0^*(\vec{k},\omega) - G_1^*(\vec{k},\omega)G_0(\vec{k},\omega)\right] \tag{3.7}$$

$$S_2(k_z,k_z';\vec{k}_\parallel,\omega) =$$

$$-\frac{1}{T_0}\,G_0(\vec{k}_\parallel,k_z,\omega)G_0^*(\vec{k}_\parallel,k_z',\omega)\left[2\eta(k_\parallel^2-k_zk_z')^2 + (\eta_v-\frac{2}{3}\eta)(k_\parallel^2+k_z^2)(k_\parallel^2+k_z'^2)\right]$$

$$+\left[G_2(\vec{k}_\parallel,k_z,\omega)G_0^*(\vec{k}_\parallel,k_z',\omega)\eta'(k_\parallel^2+k_z'^2)^2 + G_0(\vec{k}_\parallel,k_z,\omega)G_2^*(\vec{k}_\parallel,k_z',\omega)\eta'(k_\parallel^2+k_z^2)^2\right] \tag{3.8}$$

By definition the density-density correlation function is Hermitian

$$\langle \rho(\vec{k},\omega)\rho^*(\vec{k}',\omega')\rangle = \langle \rho(\vec{k}',\omega')\rho^*(\vec{k},\omega)\rangle^*. \tag{3.9}$$

As a consequence the functions S_0, S_1 and S_2 must satisfy the relations (cf. eq. (3.5))

$$S_0(\vec{k},\omega) = S_0^*(\vec{k},\omega) \tag{3.10}$$

$$S_1(\vec{k},\omega) = S_1^*(\vec{k},\omega) \tag{3.11}$$

$$S_2(k_z,k_z';\vec{k}_\parallel,\omega) = S_2^*(k_z',k_z;\vec{k}_\parallel,\omega)\ . \tag{3.12}$$

This may also be verified explicitly from eqs. (3.6) - (3.8).

If we write for the function S_2

$$S_2 = S_2' + iS_2''\ , \tag{3.13}$$

where S_2' and S_2'' are the real and imaginary parts of S_2 respectively, the symmetry relation (3.12) becomes

$$S_2'(k_z,k_z';\vec{k}_\parallel,\omega) = S_2'(k_z',k_z;\vec{k}_\parallel,\omega) \tag{3.14}$$

$$S_2''(k_z,k_z';\vec{k}_\parallel,\omega) = -S_2''(k_z',k_z;\vec{k}_\parallel,\omega)\ . \tag{3.15}$$

It follows furthermore from equations (3.6) - (3.8), using the property (2.14) that

$$S_0(\vec{k},\omega) = S_0(\vec{k},-\omega) \tag{3.16}$$

$$S_1(\vec{k},\omega) = -S_1(\vec{k},-\omega) \tag{3.17}$$

$$S_2(k_z,k_z';\vec{k}_\parallel,\omega) = S_2^*(k_z,k_z';\vec{k}_\parallel,-\omega) \tag{3.18}$$

For S_2' and S_2'' the last relation implies that

$$S_2'(k_z,k_z';\vec{k}_\parallel,\omega) = S_2'(k_z,k_z';\vec{k}_\parallel,-\omega) \quad (3.19)$$

$$S_2''(k_z,k_z';\vec{k}_\parallel,\omega) = -S_2''(k_z,k_z';\vec{k}_\parallel,-\omega) \ . \quad (3.20)$$

Thus S_0 and S_2' are even functions of ω while S_1 and S_2'' are odd.

In the next section we shall derive from eq. (3.5) the light scattering spectrum and the equal time density-density correlation function, making use of the symmetry properties derived above.

4. Light scattering spectrum and equal time density-density correlation function

From the general theory of light scattering it follows that the intensity of scattered light is given by

$$I(\vec{k},\omega) = \frac{B}{V}\int_V d\vec{r}\int_V d\vec{r}\,'\int_{-\infty}^{\infty} d\tau \,\langle \rho(\vec{r})\rho(\vec{r}\,',\tau)\rangle\, e^{-ik\cdot(\vec{r}-\vec{r}\,')}\, e^{i(\omega_0-\omega)\tau} \quad (4.1)$$

where B, V, ω_0, ω and k are defined in section 5 of the previous chapter.

From this expression and eq. (3.5) one can derive (see appendix B) the following formula for the spectrum of light scattered from a volume centered at z=0, i.e. in the middle of the fluid layer :

$$I(\vec{k},\omega) = B2k_BT_0\left\{S_0(\vec{k},\omega-\omega_0) + AS_1(\vec{k},\omega-\omega_0) + A\left(\frac{\partial}{\partial k_z}S_2''(k_z,k_z';\vec{k}_\parallel,\omega-\omega_0)\right)_{k_z'=k_z}\right\} . \quad (4.2)$$

Here S_2'' is the imaginary part of S .

Inserting S_0, S_1 and S_2 (eqs. (3.6) - (3.8)) into eq. (4.2) one obtains

$$\begin{aligned} I(\vec{k},\omega) = {} & 2Bk_BT_0\eta'k^4|G_0(\vec{k},\omega-\omega_0)|^2\left\{1 + A|G_0(\vec{k},\omega-\omega_0)|^2\left[\frac{2}{T_0}(\omega-\omega_0)^3\nu'k_z\right.\right. \\ & + 4\frac{\alpha\beta^{-1}}{\rho_0}(\omega-\omega_0)\nu'k_z\left(2(\omega-\omega_0)^2 - c_0^2k^2\right) + 4(\omega-\omega_0)\nu'k_z\left(\frac{\partial c_0^2}{\partial T}\right)_p k^2 - \\ & - 8(\omega-\omega_0)^2\left((\omega-\omega_0)^2 - c_0^2k^2\right)|G_0(\vec{k},\omega-\omega_0)|^2\left[(\omega-\omega_0)^3\nu'k_z\alpha\beta^{-1}/\rho_0 + \right. \\ & \left.\left.\left. + (\omega-\omega_0)\nu'c_0^2k^2k_z\left[\frac{1}{c_0^2}\left(\frac{\partial c_0^2}{\partial T}\right)_p - \frac{\alpha\beta^{-1}}{\rho_0}\right]\right]\right]\right\} . \end{aligned} \quad (4.3)$$

For $|G_0(\vec{k},\omega-\omega_0)|^2$ we can write to a very good approximation, since $c_0 k \gg \Gamma k^2$,

$$|G_0(\vec{k},\omega-\omega_0)|^2 = \frac{1}{4c_0^2k^2\Gamma k^2}\left[\frac{\Gamma k^2}{(\omega-\omega_0-c_0k)^2+(\Gamma k^2)^2}+\frac{\Gamma k^2}{(\omega-\omega_0+c_0k)^2+(\Gamma k^2)^2}\right] \tag{4.4}$$

where the sound attenuation coefficient Γ is given by

$$\Gamma = \tfrac{1}{2}\nu' \tag{4.5}$$

(cf. eq. (III. 4.5), $\lambda=0$).

Inserting eq. (4.4) into eq. (4.3) and using the fact that the function $|G_0|^2$ is sharply peaked around $\omega = \omega_0+c_0k$ and $\omega = \omega_0-c_0k$, and that $c_0k \gg \Gamma k^2$, one obtains for the intensity

$$I(k,\omega) = B\ 2k_BT_0\rho_0^2\frac{c_v}{2c_p}\kappa_T \times$$
$$\left[\frac{\Gamma k^2\left(1+(c_0A\ k_z/kT_0)\varepsilon(k,\omega)\right)}{(\omega-\omega_0-c_0k)^2+(\Gamma k^2)^2}+\frac{\Gamma k^2\left(1-(c_0A\ k_z/kT_0)\varepsilon(-k,\omega)\right)}{(\omega-\omega_0+c_0k)^2+(\Gamma k^2)^2}\right] \tag{4.6}$$

where

$$\varepsilon(k,\omega) = \frac{\Gamma k^2[1+2\alpha\beta^{-1}\ T_0/\rho_0+4(T_0/c_0)(\partial c_0/\partial T)_p]}{(\omega-\omega_0-c_0k)^2+(\Gamma k^2)^2} - $$
$$2kT_0\left(\frac{\partial c_0}{\partial T}\right)_p\frac{\Gamma k^2(\omega-\omega_0-c_0k)}{[(\omega-\omega_0-c_0k)^2+(\Gamma k^2)^2]^2}\ . \tag{4.7}$$

At frequency $\omega = \omega_0+c_0k$ this factor becomes

$$\varepsilon(k,\ \omega{=}\omega_0+c_0k) = \left(1+2\alpha\beta^{-1}\ T_0/\rho_0+4(T_0/c_0)(\partial c_0/\partial T)_p\right)/\Gamma k^2\ . \tag{4.8}$$

In the limit $A\to 0$ the terms with ε vanish, thus leading to the equilibrium expression for the Brillouin lines of the light scattering spectrum.

Eq. (4.6) illustrates the phenomenon previously found [1,2] that under the influence of a stationary temperature gradient the spectrum becomes asymmetric around $\omega=\omega_0$. For values of k of the order 10^4 this effect is of the order of a few percent. In the next section we will give a more detailed discussion of eq. (4.6).

A quantity of special interest (related to the total intensity of scattered light) is the equal time density-density correlation function which is equal to

$$\langle \rho(\vec{r},t)\rho(\vec{r}', t) \rangle =$$

$$\frac{1}{(2\pi)^8} \int d\omega \int d\omega' \int d\vec{k} \int d\vec{k}'\, e^{i\vec{k}\cdot\vec{r}-i\vec{k}'\cdot\vec{r}'}\, e^{i(\omega-\omega')t} \langle \rho(\vec{k},\omega)\rho^*(\vec{k}',\omega') \rangle \tag{4.9}$$

(cf. eq. (2.2)).

If one introduces eq. (3.5) into the right-hand side of this equation one obtains (see appendix C)

$$\langle \rho(\vec{r},t)\rho(\vec{r}',t) \rangle = \frac{1}{(2\pi)^4} 2k_B T_0 \int d\vec{k}\, e^{i\vec{k}\cdot(\vec{r}-\vec{r}')} \left\{ \int_{-\infty}^{\infty} d\omega\, S_0(\vec{k},\omega) + \right.$$

$$\left. + \tfrac{1}{2}(z+z') \int_{-\infty}^{\infty} d\omega\, S_2'(k_z,k_z;\vec{k}_\parallel,\omega) \right\} \tag{4.10}$$

where S_2' is the real part of S_2, cf. eq. (3.13).

Inserting S_2 and S_2', eqs. (3.6) and (3.8), into eq. (4.10) one obtains by complex integration (see appendix C)

$$\langle \rho(\vec{r},t)\rho(\vec{r}',t) \rangle = k_B \frac{T_0\rho_0}{c_0^2} \left[1 - \frac{Az}{T_0} + \frac{\alpha\beta^{-1}}{\rho_0} Az + \frac{1}{c_0^2} \left(\frac{\partial c_0^2}{\partial T}\right)_p Az \right] \delta(\vec{r}-\vec{r}'). \tag{4.11}$$

The coefficient of the δ-function at the right-hand side of this equation corresponds to the expansion up to linear order in A of the quantity $k_B T_s \rho_s/(c_0^2)_s$. Indeed using eq. (1.4) we have up to linear order

$$\frac{T_s\rho_s}{(c_0^2)_s} = \frac{T_0\rho_0}{c_0^2} \left[1 - \frac{Az}{T_0} + \frac{\alpha\beta^{-1}}{\rho_0} Az + \frac{1}{c_0^2} \left(\frac{\partial c_0^2}{\partial T}\right)_p Az \right]. \tag{4.12}$$

The equal time density-density correlation function is therefore given by

$$\langle \rho(\vec{r},t)\rho(\vec{r}',t) \rangle = k_B \frac{T_s\rho_s}{(c_0^2)_s} \delta(\vec{r}-\vec{r}') = k_B\Big(T\rho^2(c_v/c_p)\kappa_T\Big)_s \delta(\vec{r}-\vec{r}') \ . \tag{4.14}$$

This correlation function has exactly the same form as in equilibrium: *no long range correlation exists and the usual coefficient of the δ-function has the steady state value at position $\vec{r}$.*

5. Discussion

In the previous section we have established that under the influence of a steady temperature gradient the spectrum of scattered light becomes asymmetric around $\omega = \omega_0$, the frequency of the incident lightwave. As has been mentioned above this fact is in agreement with results recently obtained by various authors within a different theoretical framework. Quantitatively, however, our result does not agree with previous predictions.

Thus Procaccia, Ronis and Oppenheim find an expression for $I(\vec{k},\omega)$ of the form (4.6) but with a different function $\varepsilon(k,\omega)$. Their result for the factor ε introduced above is [2)]

$$\varepsilon^{P.R.O.}(k,\omega) = \tfrac{1}{2}\,\frac{1}{\Gamma k^2} \quad . \tag{5.1}$$

This is in contrast to our result which leads to a frequency dependent factor ε. Our result at $\omega = \omega_0 + c_0 k$, eq. (4.8), still differs from eq.(5.1) since we find a factor 1 instead of the factor $\frac{1}{2}$ and in addition contributions due to the thermal expansion coefficient $-\alpha/\rho_0\beta$ and the temperature dependence of the velocity of sound.

Procaccia, Ronis and Oppenheim conclude from their results (cf. eq.(5.1) and (4.6)) that long-range correlations exist for the static (equal time) correlation function in the steady state. We find that such an effect does not exist if the frequency dependence of ε is properly taken into account.

Kirkpatrick, Cohen and Dorfman derive an expression of the form (4.6) from kinetic theory taking also into account the temperature dependence of η, η_v and λ. They do indeed find that ε is frequency dependent. They have however, as yet only published their result for $\omega = \omega_0 \pm c_0 k$ which is in our notation [1)†)]

$$\varepsilon^{K.C.D.}(k,\omega=\omega_0+c_0k) = \varepsilon^{K.C.D.}(-k,\omega=\omega_0-c_0k) =$$

$$= \left(\frac{1}{4} - \alpha\beta^{-1}T_0/\rho_0 - (T_0/\Gamma)(\partial\Gamma/\partial T)_\rho - \frac{1}{3}\,\frac{\lambda/\rho_0 c_v}{\Gamma}\right)\Big/\Gamma k^2 \tag{5.2}$$

---

†) Kirkpatrick, Cohen and Dorfman use a sound attenuation factor Γ_s which is equal to 2Γ, the sound attenuation coefficient used by Procaccia, Ronis and Oppenheim. When comparing results obtained by various authors this fact must not be overlooked.

In order to compare this expression to eq. (4.8) we must put $\lambda=0$ and $(\partial\Gamma/\partial T)_\rho = 0$ so that $\varepsilon^{K.C.D}$ then reduces to

$$\varepsilon^{K.C.D.} = (\tfrac{1}{4} - \alpha\beta^{-1}T_0/\rho_0)\Big/\Gamma k^2 \quad . \tag{5.3}$$

Although this result has a structure similar to ours we find different numerical factors (1 instead of $\frac{1}{4}$, and +2 instead of −1 for the coefficient of $\alpha\beta^{-1}T_0/\rho_0$) and in addition the contribution from $(\partial c_0/\partial T)_p$. Kirkpatrick, Cohen and Dorfman also find effects due to this last temperature dependence which disappear, however, completely for $\omega=\omega_0+c_0k$. [3)]

To summarize, we find from an analysis based on fluctuating hydrodynamics results qualitatively in agreement with those of previous authors but differing as to the precise form of the corrections to the Brillouin lines in the presence of a stationary temperature gradient. Our results are somewhat more closely related to those found on the basis of kinetic theory.

The theory presented should be extended in such a way that also the temperature dependence of the transport coefficients is taken into account. It is to be expected that certain additional contributions of the type found by Kirkpatrick, Cohen and Dorfman will be obtained.

Appendix A

In this appendix we derive from eqs. (2.4), (2.7), (2.8) and (2.9) the equation for the fluctuating fluid density field to linear order in A, eq. (2.10).

In equilibrium there is no coupling between the fields ξ and the other fluid fields D, T and ρ. Hence wherever ξ occurs in eqs. (2.4), (2.8) and (2.9) it is multiplied by A. Therefore we may substitute in these equations the zeroeth order (in A) solution of eq. (2.7)

$$\xi = (-i\omega\rho_0 + \eta k^2)^{-1}F_{Tz} \quad . \tag{A.1}$$

The equations then become

$$-i\omega\rho = -\rho_0\hat{O}D - \alpha\beta^{-1}A(-i\omega\rho_0 + \eta k^2)^{-1}F_{Tz} \tag{A.2}$$

$$(-i\omega\rho_0 + \eta' k^2 \hat{O}^{-1})\hat{O}D = k^2\left[c_0^2 - \left(\frac{\partial c_0^2}{\partial T}\right)_p A\, i \frac{\partial}{\partial k_z}\right]\rho \, +$$

$$+ \, k^2\left[\frac{\alpha T_0}{c_v} - \left(\frac{\partial \alpha T/c_v}{\partial T}\right)_p A\, i \frac{\partial}{\partial k_z}\right] s + F_L + i\omega\alpha\beta^{-1} A(-i\omega\rho_0 + \eta k^2)k^{-2}F_{Tz} \quad \text{(A.3)}$$

$$-i\omega s = -(\partial s/\partial T)_p \, A\, i \frac{k_z}{k^2} D + (\partial s/\partial T)_p A k^{-2}\xi \; . \quad \text{(A.4)}$$

To linear order in A the inverse operator $\hat{O}^{-1}$ is given by (cf. eq. (2.5))

$$\hat{O}^{-1} = \left(1 + \frac{\alpha\beta^{-1}}{\rho_0} A\, i \frac{k_z}{k^2} - \frac{\alpha\beta^{-1}}{\rho_0} A\, i \frac{\partial}{\partial k_z}\right) . \quad \text{(A.5)}$$

From the above equations one obtains (again to linear order in A) the following equation for ρ in terms of F_L and F_{Tz}

$$G^{-1}(\vec{k},\omega)\rho(\vec{k},\omega) = F_L + \frac{i\omega\alpha\beta^{-1}Ak^{-2}}{-i\omega\rho_0 + \eta k^2} F_{Tz} + \frac{1}{i\omega}\alpha\beta^{-1}Ak^{-2}G_0^{-1}(\vec{k},\omega)F_{Tz} \quad \text{(A.6)}$$

where

$$G^{-1}(\vec{k},\omega) = G_0^{-1}(\vec{k},\omega)\left[1 - (c_0^2k^2 - i\omega\nu' k^2)G_0(\vec{k},\omega)\frac{\alpha\beta^{-1}}{\rho_0} A\, i \frac{k_z}{k^2} + \right.$$

$$\left. + \left\{\left(\frac{\partial c_0^2}{\partial T}\right)_p k^2 - i\omega\nu' k^2 \frac{\alpha\beta^{-1}}{\rho_0}\right\} G_0(\vec{k},\omega) A\, i \frac{\partial}{\partial k_z}\right] . \quad \text{(A.7)}$$

The equilibrium propagator $G_0(\vec{k},\omega)$ is defined in eq. (2.11).
Solving for $\rho(\vec{k},\omega)$ one obtains

$$\rho(\vec{k},\omega) = G(\vec{k},\omega)F_L(\vec{k},\omega) - \frac{\alpha\beta^{-1}A}{\rho_0 k^2}\,\frac{c_0^2k^2 - i\omega\nu' k^2}{-i\omega(-i\omega+\nu k^2)}\, G_0(\vec{k},\omega)F_{Tz} \; . \quad \text{(A.8)}$$

From eq. (A.7) we find for the propagator $G(\vec{k},\omega)$ to linear order in A

$$G(\vec{k},\omega) = G_0(\vec{k},\omega)\left[1 + (c_0^2k^2 - i\omega\nu' k^2)G_0(\vec{k},\omega)\frac{\alpha\beta^{-1}}{\rho_0} A\, i\frac{k_z}{k^2} - \right.$$

$$\left. - \left\{\left(\frac{\partial c_0^2}{\partial T}\right)_p k^2 - i\omega\nu' k^2 \frac{\alpha\beta^{-1}}{\rho_0}\right\} G_0(\vec{k},\omega) A\, i\frac{\partial}{\partial k_z}\right] \quad \text{(A.9)}$$

so that eq. (A.8) becomes eq. (2.10) which we set out to derive.

Appendix B

Formula (4.1) for the scattering intensity may be rewritten as

$$I(\vec{k},\omega) = \frac{B}{V}\frac{1}{(2\pi)^8}\int_V d\vec{r}\int_V d\vec{r}\,'\int_{-\infty}^{\infty} d\tau\int d\vec{k}_1\int d\vec{k}_2\, e^{i\vec{k}_1\cdot\vec{r}}\, e^{-i\vec{k}_2\cdot\vec{r}\,'}\int_{-\infty}^{\infty} d\omega_1\int_{-\infty}^{\infty} d\omega_2\, e^{i\omega_2\tau}\times$$

$$\times\langle\rho(\vec{k}_1,\omega_1)\rho^*(k_2,\omega_2)\rangle\, e^{-i\vec{k}\cdot(\vec{r}-\vec{r}\,')}\, e^{i(\omega_0-\omega)\tau} \quad . \tag{B.1}$$

Substitution of eq. (3.5) into eq. (B.1) yields

$$I(\vec{k},\omega) = \frac{B}{V}\frac{k_BT_0}{(2\pi)^4}\left\{\int_V d\vec{r}\int_V dr'\int_{-\infty}^{\infty} d\tau\int d\vec{k}_1\int d\omega_1\, e^{i(\vec{k}_1-\vec{k})\cdot(\vec{r}-\vec{r}\,')}\, e^{i(\omega_0-\omega+\omega_1)\tau}\times\right.$$

$$\times[S_0(\vec{k}_1,\omega_1)+AS_1(\vec{k}_1,\omega_1)] + \int_V d\vec{r}\int_V d\vec{r}\,'\int_{-\infty}^{\infty} d\tau\int d\vec{k}_1\int d\vec{k}_2\int_{-\infty}^{\infty} d\omega_1\, e^{i\vec{k}_1\cdot\vec{r}}\, e^{-i\vec{k}_2\cdot\vec{r}\,'}\times$$

$$\left.\times\, e^{i\vec{k}\,(\vec{r}-\vec{r}\,')}\, e^{i(\omega_0-\omega+\omega_1)\tau}\, AS_2(k_{1z},k_{2z};\vec{k}_{1\parallel},\omega_1)\,(\vec{k}_{1\parallel}-\vec{k}_{2\parallel})\, i\frac{\partial}{\partial k_{1z}}\,\delta(k_{1z}-k_{2z})\right\}. \tag{B.2}$$

We will assume the scattering volume V to be a cube of linear dimension 2a centered around the origin of the coordinate system.
Using the relating

$$\int_{-\infty}^{\infty} d\tau\, e^{i(\omega_0-\omega+\omega_1)\tau} = 2\pi\,\delta(\omega_0-\omega+\omega_1) \tag{B.3}$$

and subsequently performing the integratin over ω_1, $\vec{r}$ and $\vec{r}\,'$ one obtains

$$I(\vec{k},\omega) = BV\frac{k_BT_0}{(2\pi)^3}\left\{\int d\vec{k}_1 F^2(k_{1x}-k_x)F^2(k_{1y}-k_y)F^2(k_{1z}-k_z)\,[S_0(\vec{k}_1,\omega-\omega_0)+AS_1(\vec{k}_1,\omega-\omega_0)]\right.$$

$$\left.+\int d\vec{k}_{1\parallel}F^2(k_{1x}-k_x)F^2(k_{1y}-k_y)Ag(\vec{k}_{1\parallel},\omega-\omega_0)\right\}. \tag{B.4}$$

In eq. (B.4) the functions F(x) and $g(\vec{k}_{1\parallel},\omega-\omega_0)$ are defined as

$$F(x) = \frac{\sin ax}{ax} \tag{B.5}$$

and

$$g(\vec{k}_{1\parallel},\omega-\omega_0) = \int dk_{1z} \int dk_{2z}\, F(k_{1z})F(k_{2z})S_2(k_{1z},k_{2z};\vec{k}_{1\parallel},\omega-\omega_0)\, i\frac{\partial}{\partial k_{1z}}\, \delta(k_{1z}-k_{2z})$$

$$= \int dk_{1z} \int dk_{2z}\, F(k_{1z})F(k_{2z})\Big[S_2'(k_{1z},k_{2z};\vec{k}_{1\parallel},\omega-\omega_0) + iS_2''(k_{1z},k_{2z};k_{1\parallel},\omega-\omega_0)\Big] \times$$

$$\times\, i\frac{\partial}{\partial k_{1z}}\, \delta(k_{1z}-k_{2z}) \qquad \text{(B.6)}$$

where S_1' and S_2'' are the real and imaginary part of S_2, cf. eq. (3.13). Due to the symmetry property (3.14) the integral over S_2' vanishes. Partial integration of eq. (B.6) and use of the symmetry property (3.15) of S_2'' then lead to

$$g(\vec{k}_{1\parallel},\omega-\omega_0) = \int dk_{1z}\, F^2(k_{1z}) \left(\frac{\partial}{\partial k_{1z}}\, S_2''(k_{1z},k_{2z};\vec{k}_{1\parallel},\omega-\omega_0)\right)_{k_{2z}=k_{1z}} \qquad \text{(B.7)}$$

Inserting eq. (B.7) into eq. (B.4) one obtains for the scattering intensity

$$I(\vec{k},\omega) = BV\,\frac{k_B T_0}{(2\pi)^3} \int dk_1\, F^2(k_{1x}-k_x)F^2(1_{1y}-k_y)F^2(k_{1z}-k_z)\Big[S_0(\vec{k}_1,\omega-\omega_0) +$$

$$+ AS_1(\vec{k}_1,\omega-\omega_0) + A\left(\frac{\partial}{\partial k_{1z}}\, S_2''(k_{1z},k_{2z};\vec{k}_{1\parallel},\omega-\omega_0)\right)_{k_{2z}=k_{1z}}\Big] . \qquad \text{(B.8)}$$

The function $F^2(x)$ is sharply peaked around $x=0$. We may therefore replace in good approximation $\vec{k}_1$ in S_0, S_1 and S_2'' by $\vec{k}$ and subsequently perform the integration over $\vec{k}_1$ [4].

Using the relation

$$\int_{-\infty}^{\infty} \left(\frac{\sin ax}{ax}\right)^2 dx = \frac{\pi}{a}$$

we then obtain formula (4.2) for the scattering intensity $I(\vec{k},\omega)$.

Appendix C

Inserting eq. (3.5) into eq. (4.9) one obtains

$$\langle \rho(\vec{r},t)\rho(\vec{r}',t)\rangle = \frac{1}{(2\pi)^4} k_B T_0 \Bigg\{ \int_{-\infty}^{\infty} d\omega \int d\vec{k}\, e^{i\vec{k}\cdot(\vec{r}-\vec{r}')} [S_0(\vec{k},\omega) + AS_1(\vec{k},\omega)] +$$

$$+ \int_{-\infty}^{\infty} d\omega \int d\vec{k}_\parallel \int dk_z \int dk_z'\, e^{i\vec{k}_\parallel\cdot(\vec{r}_\parallel-\vec{r}_\parallel')}\, e^{ik_z z}\, e^{-ik_z' z'}\, S_2(k_z,k_z';\vec{k}_\parallel,\omega)\, i\frac{\partial}{\partial k_z}\delta(k_z-k_z')\Bigg\}. \tag{C.1}$$

From the symmetry relation (3.17) it follows that

$$\int_{-\infty}^{\infty} d\omega\, S_1(\vec{k},\omega) = 0\ . \tag{C.2}$$

Consider now the integral

$$H = \int_{-\infty}^{\infty} d\omega \int dk_z \int dk_z'\, e^{-ik_z' z'}\, e^{ik_z z}\, S_2(k_z,k_z';\vec{k}_\parallel,\omega)\, i\frac{\partial}{\partial k_z}\ (k_z-k_z') =$$

$$= -\int_{-\infty}^{\infty} d\omega \int dk_z \int dk_z'\, e^{-ik_z' z'} \left[i\frac{\partial}{\partial k_z}\, e^{ik_z z}\, S_2(k_z,k_z';\vec{k}_\parallel,\omega) \right] \delta(k_z-k_z') \tag{C.3}$$

where we performed a partial integration over k_z.
If we use the fact that

$$i\,\frac{\partial}{\partial k_z}\,\delta(k_z-k_z') = -i\,\frac{\partial}{\partial k_z'}\,\delta(k_z-k_z') \tag{C.4}$$

we may also write for H

$$H = -\int_{-\infty}^{\infty} d\omega \int dk_z \int dk_z'\, e^{-ik_z' z'}\, e^{ik_z z}\, S_2(k_z,k_z';\vec{k}_\parallel,\omega)\, i\frac{\partial}{\partial k_z'}\,\delta(k_z-k_z') =$$

$$= \int_{-\infty}^{\infty} d\omega \int dk_z \int dk_z'\, e^{ik_z z} \left[i\frac{\partial}{\partial k_z'}\, e^{-ik_z' z'}\, S_2(k_z,k_z';\vec{k}_\parallel,\omega) \right] \delta(k_z-k_z') \tag{C.5}$$

where we performed a partial integration over k_z'.

Upon the transformation $k_z \to k_z'$, $k_z' \to k_z$, we obtain from eq. (C.5)

$$H = \int_{-\infty}^{\infty} d\omega \int dk_z \int dk_z' \, e^{ik_z z} \left[i \frac{\partial}{\partial k_z} e^{-ik_z z'} S_2(k_z', k_z; \vec{k}_\parallel, \omega) \right] \delta(k_z - k_z'). \quad (C.6)$$

From eqs. (C.3) and (C.6) it then follows that

$$H = \frac{1}{2} \int_{-\infty}^{\infty} d\omega \int dk_z \int dk_z' \left\{ -e^{-ik_z z'} \left(i \frac{\partial}{\partial k_z} e^{ik_z z} S_2(k_z, k_z'; \vec{k}_\parallel, \omega) \right) \right.$$

$$\left. + e^{ik_z z} \left(i \frac{\partial}{\partial k_z} e^{-ik_z z'} S_2(k_z', k_z; \vec{k}\ , \omega) \right) \right\} \delta(k_z - k_z') =$$

$$= \frac{1}{2} \int_{-\infty}^{\infty} d\omega \int dk_z \int dk_z' \left[(z+z') S_2(k_z, k_z; \vec{k}_\parallel, \omega) \right.$$

$$\left. - i \frac{\partial}{\partial k_z} \left(S_2(k_z, k_z'; \vec{k}_\parallel, \omega) - S_2(k_z', k_z; \vec{k}_\parallel, \omega) \right) \right] e^{ik_z(z-z')} \delta(k_z - k_z') . \quad (C.7)$$

Using eq. (3.13) together with the symmetry relation eq. (3.15) eq. (C.6) may be written as

$$H = \frac{1}{2} \int_{-\infty}^{\infty} d\omega \int dk_z \left[(z+z') S_2'(k_z, k_z; \vec{k}_\parallel, \omega) + 2 \left(\frac{\partial}{\partial k_z} S_2''(k_z, k_z', \vec{k}_\parallel, \omega) \right)_{k_z' = k_z} \right] e^{ik_z(z-z')} . \quad (C.8)$$

From eq. (3.20) it follows that the integral over ω of S_2'' vanishes. Inserting eqs. (C.2) and (C.8) into eq. (C.1) one obtains eq. (4.10) for the equal time density-density correlation function.

Consider next the integrals

$$I_1 = \int_{-\infty}^{\infty} d\omega \; S_0(\vec{k}, \omega) = \eta' k^4 \int_{-\infty}^{\infty} d\omega |G_0(\vec{k}, \omega)|^2 \quad (C.9)$$

where we have used eq. (3.6), and

$$I_2 = \int_{-\infty}^{\infty} d\omega \; S_2(k_z, k_z; \vec{k}_\parallel, \omega) \quad . \quad (C.10)$$

With eq. (2.11) the integral I_1 becomes

$$I_1 = \eta' k^4 \int_{-\infty}^{\infty} d\omega \frac{1}{(\omega-\omega_1)(\omega-\omega_2)(\omega+\omega_1)(\omega+\omega_2)} \tag{C.11}$$

where

$$\omega_{1,2} = -\tfrac{1}{2} i\nu' k^2 \pm \left[c_0^2 k^2 - \tfrac{1}{4}(\nu' k^2)^2\right]^{\frac{1}{2}} . \tag{C.12}$$

The poles ω_1 and ω_2 are in the lower half of the complex ω-plane. By complex integration (closing the contour in the upper half plane) one finds

$$I_1 = \eta' k^4 \, 2\pi i \frac{1}{2\omega_1\omega_2(\omega_1+\omega_2)} = \frac{\pi\rho_0}{c_0^2} . \tag{C.13}$$

The integral I_2 becomes with eq. (3.8)

$$I_2 = -\frac{\eta' k^4}{T_0} \int_{-\infty}^{\infty} d\omega \, |G_0(\vec{k},\omega)|^2$$

$$+ \eta' T_0 k^4 \int_{-\infty}^{\infty} d\omega [G_2(\vec{k},\omega) G_0^*(\vec{k},\omega) + G_0(\vec{k},\omega) G_2^*(\vec{k},\omega)] = -\frac{1}{T_0} I_1 + I_3 + I_3^* \tag{C.14}$$

where

$$I_3 = \eta' T_0 k^4 \int_{-\infty}^{\infty} d\omega \, G_2(\vec{k},\omega) G_0^*(\vec{k},\omega) . \tag{C.15}$$

Inserting eq. (2.13) for $G_2(\vec{k},\omega)$ one has

$$I_3 = \eta' T_0 k^4 \int_{-\infty}^{\infty} d\omega \frac{(\partial c_0^2/\partial T)_p \, k^2 - i\omega\nu' k^2 \alpha\beta^{-1}/\rho_0}{(\omega-\omega_1)^2(\omega-\omega_2)^2(\omega+\omega_1)(\omega+\omega_2)} \tag{C.16}$$

where $\omega_{1,2}$ are given by eq. (C.12).

By complex integration, closing the contour in the upper half plane, one obtains

$$I_3 = 2\pi i \left[\frac{(\partial c_0^2/\partial T)_p k^2}{4\omega_1^2\omega_2^2(\omega_1+\omega_2)} + \frac{i\nu' k^2 \alpha\beta^{-1}/\rho_0}{4\omega_1\omega_2(\omega_1+\omega_2)^2} \right] \eta' T_0 k^4 = \frac{\pi\rho_0}{2c_0^2} \left[\frac{1}{c_0^2} \left(\frac{\partial c_0^2}{\partial T}\right)_p + \frac{\alpha\beta^{-1}}{\rho_0} \right] . \tag{C.17}$$

Combining expressions (C.13), (C.14) and (C.17) and using the relation

$$\int d\vec{k}\ e^{i\vec{k}\cdot(\vec{r}-\vec{r}\,')} = (2\pi)^3\delta(\vec{r}-\vec{r}\,') \tag{C.18}$$

we obtain eq. (4.11) from eq. (4.10).

References

1. T. Kirkpatrick, E.G.D. Cohen, J.R. Dorfman, Phys.Rev.Lett. 42 (1979) 862.
2. I. Procaccia, D. Ronis and I. Oppenheim, Phys.Rev.Lett. 42 (1979) 287, 614E.

   I. Procaccia, D. Ronis, M.A. Collins, J. Ross and I. Oppenheim, Phys.Rev. A19 (1979) 1290.

   D. Ronis, I. Procaccia and I. Oppenheim, Phys.Rev. A19 (1979) 1307.

   D. Ronis, I. Procaccia and I. Oppenheim, Phys.Rev. A19 (1979) 1324.
3. E.G.D. Cohen, private communication.
4. G.B. Benedek in Statistical Physics, Phase Transitions and Superfluidity, Brandeis University summer institute in theoretical physics, 1966 vol. 2, eds. M. Chrétien, E.P. Gross and S. Deser (Gordon and Breach, New York 1968).

SAMENVATTING

Op een lengteschaal die veel groter is dan moleculaire afmetingen kan een klassiek fluïdum dat uit één component bestaat beschreven worden door zijn snelheidsveld en twee onafhankelijke thermodynamische grootheden b.v. het dichtheidsveld en het temperatuurveld. Het gedrag van deze velden wordt bepaald door een stelsel niet-lineaire (hydrodynamische) vergelijkingen. Deze vergelijkingen kunnen worden afgeleid uit de behoudswetten voor massa, impuls en totale energie door gebruik te maken van de thermodynamische Gibbs relatie en phenomenologische wetten die een verband geven tussen de warmtestroom en de temperatuurgradiënt (wet van Fourier) en tussen de visceuze druktensor en de gradiënt van het snelheidsveld (wet van Newton). Het is in het algemeen niet mogelijk deze niet-lineaire vergelijkingen op te lossten. Ze kunnen echter gelineariseerd worden rond de evenwichtstoestand of een andere stationaire toestand, waarbij aangenomen wordt dat de afwijkingen van de verschillende vloeistofvelden uit die referentietoestand voldoende klein zijn. Deze procedure levert een stelsel lineaire vergelijkingen in de vloeistofvelden dat in principe oplosbaar is bij gegeven randcondities en beginwaarden.

In de fluctuerende hydrodynamica is de fundamentele aanname dat de hierboven besproken lineaire vergelijkingen voor de regressie van macroscopische afwijkingen gelden voor de gemiddelde regressie van kleine fluctuaties rond de referentietoestand. Deze kleine fluctuaties worden opgewekt door gegeneraliseerde "random-krachten" die opgenomen worden in de lineaire vergelijkingen. De verwachtingswaarden van deze "random-krachten" zijn nul terwijl de correlatiefuncties ervan gerelateerd zijn aan de dissipatieve verschijnselen in het fluïdum door zgn. fluctuatie-dissipatie-stellingen. Het is dan mogelijk de eigenschappen van de fluctuerende vloeistofvelden, zoals hun correlatiefuncties, uit de stochastische eigenschappen van de "random-krachten" af te leiden.

De methode van de fluctuerende hydrodynamica heeft bewezen zeer bruikbaar te zijn voor het beschrijven van fluctuaties in fluïda als de processen die ermee bestudeerd worden plaatsvinden op een lengteschaal tussen 10^{-5} cm en 10^{-2} cm. Dit is erg klein vergeleken met macroscopische lengtes maar toch nog veel groter dan moleculaire afmetingen van 10^{-8} cm. Bij Brownse beweging is de karakteristieke lengte de straal van het Brownse deeltje, die van de orde 10^{-3} - 10^{-5} cm is. Bij lichtverstrooiïng is dat de golflengte van het licht, die van de orde 10^{-5} cm is. Zowel Browse deeltjes als licht kunnen daarom gebruikt worden als middel om de fluctuaties in het fluïdum, die geanalyseerd kunnen worden met behulp van fluctuerende hydrodynamica, te bestuderen.

In het eerste deel van dit proefschrift wordt Brownse beweging dicht bij het evenwichts-kritisch punt bestudeerd. Het is bekend dat dicht bij een vloeistof-gas kritisch punt de isotherme compressibiliteit oneindig groot wordt, terwijl tegelijkertijd de dichtheidsfluctuaties gecorreleerd worden over lange afstanden. Het is te verwachten dat deze correlaties over lange afstanden invloed zullen uitoefenen op de beweging van Brownse deeltjes,in het bijzonder wanneer de correlatielengte van de dichtheidsfluctuaties groter wordt dan de straal van het Brownse deeltje.

In hoofdstuk I wordt een uitdrukking afgeleid, met behulp van fluctuerende hydrodynamica, voor de frictiecoëfficiënt van een bolvormig Browns deeltje. Daartoe gaat men uit van het stelsel lineaire vergelijkingen, verkregen door linearisering van de hydrodynamische vergelijkingen rond de evenwichtstoestand van het fluïdum. Dicht bij het kritisch punt divergeert ook de specifieke warmte. De beweging van het fluïdum is daarom vrijwel isotherm zodat temperatuurfluctuaties verwaarloosd mogen worden. Dientengevolge is het voldoende om een gereduceerd stelsel lineaire hydrodynamische vergelijkingen te beschouwen. Ook moet men beschikken over een relatie tussen de druk- en dichtsheidsfluctuaties in het fluïdum, waarvoor de niet-lokale Ornstein-Zernike relatie genomen kan worden. Het bestaan van de lange-afstandscorrelaties van de dichtheidsfluctuaties in het fluïdum is in deze relatie vervat.

Om uit het bovenbeschreven stelsel vergelijkingen, samen met de bewegingsvergelijking van de bol, de frequentie-afhankelijke frictiecoëfficiënt te vinden wordt gebruik gemaakt van de methode van geïnduceerde krachten, die ontwikkeld werd door Mazur en Bedeaux. Op die manier vindt men een uitdrukking (Hoofdstuk I, § 3) voor de kracht, uitgeoefend door het fluïdum op het Brownse deeltje. Deze uitdrukking is een uitbreiding van de bekende stelling van Faxén tot het geval van een bolvormig deeltje, vastgehouden in een fluïdum dicht bij het kritisch punt, in niet-stationaire, niet-homogene stroming. Uit deze algemene stelling kunnen de frictiecoëfficiënt en de random-kracht op het deeltje worden afgeleid.

Voor het lage frequentiegedrag wordt inderdaad een modificatie gevonden dicht bij het kritisch punt ten opzichte van het gedrag buiten het kritisch gebied. Op grond van de uitdrukking voor de random-kracht op het deeltje kan men voor deze grootheid een fluctuatie-dissipatie-stelling afleiden. Deze stelling wordt op een meer formele manier verkregen in hoofdstuk II. De fluctuatie-dissipatie-stelling kan dan gebruikt worden om een uitdrukking te vinden voor de snelheids-autocorrelatiefunctie van het Brownse deeltje. Het blijkt dat er een kleine negatieve bijdrage is tot het gebruikelijke $t^{-3/2}$ lange-tijdsgedrag van deze snelheids-autocorrelatiefunctie als de correlatielengte van de dichtheidsfluctuaties groter wordt dan de straal van de Brownse deeltjes, i.e. voldoende dicht bij het kritische punt.

In hoofdstuk II wordt een formele afleiding gegeven van de fluctuatie-dissipatie-stelling voor de random-kracht op het Brownse deeltje, waarbij ook rekening wordt gehouden met de temperatuurfluctuaties in het fluïdum. De gebruikte methode is oorspronkelijk ontwikkeld door Fox en Uhlenbeck voor een deeltje in een incompressibele vloeistof. Deze methode is gebaseerd op een systematisch gebruik van Greense identiteiten voor de fluctuerende en gemiddelde vloeistofvelden samen met randcondities voor deze velden op het oppervlak van het Brownse deeltje. De in hoofdstuk I gebruikte stelling is een speciaal geval van de stelling die in dit hoofdstuk wordt afgeleid.

In het tweede deel van dit proefschrift wordt de lichtverstrooiïng aan een fluïdum dat in een niet-evenwichts-stationaire toestand verkeert, bestudeerd.

Het lichtverstrooiïngsspectrum wordt bepaald door de dichtheids-dichtheids-correlatiefunctie in het fluïdum, die verkregen kan worden uit de fluctuerende hydrodynamica. In evenwicht is dit spectrum, als functie van de frequentie, symmetrisch rond de frequentie ω_0 van de invallende, monochromatische, lichtgolf en bestaat uit drie Lorentz lijnen: de centrale, of Rayleigh, lijn, die ontstaat door verstrooiïng aan entropiefluctuaties, en twee symmetrisch verschoven lijnen, het Brillouin doublet, die ontstaan door verstrooiïng aan geluidsgolven. De breedte van de centrale lijn wordt bepaald door de thermische diffusiviteit en de breedte van de Brillouin lijnen door de geluidsabsorptiecoëfficiënt.

Mogelijke modificaties van dit evenwichtsspectrum in aanwezigheid van stationaire gradiënten in het fluïdum zullen bestudeerd worden in de hoofdstukken III en IV. Om het lichtverstrooiïngsspectrum te verkrijgen is het eerst noodzakelijk een uitdrukking af te leiden voor de dichtheids-dichtheids-correlatiefunctie onder die omstandigheden.

In hoofdstuk III wordt een gas- of vloeistoflaag onder invloed van het zwaartekrachtsveld, waarin bovendien een stationaire temperatuurgradiënt aanwezig is, beschouwd. Om dit systeem te bestuderen worden de hydrodynamische vergelijkingen rond de stationaire toestand gelineariseerd. Zoals bekend is het mogelijk dat bij een zekere waarde van het temperatuurverschil tussen de grenzen van de laag een convectieve instabiliteit, de Rayleigh-Bénard instabiliteit, optreedt. Indien men aanneemt dat de stochastische eigenschappen van de "random-krachten" in de lineaire vergelijkingen dezelfde zijn als in evenwicht, is het mogelijk de fluctuatiespectra in het systeem te bestuderen in het prekritische regime.

Dicht bij de Rayleigh-Bénard instabiliteit worden de temperatuurfluctuaties anomaal groot. Dit leidt tot een modificatie van de dichtheids-dichtheids-correlatiefunctie. Deze modificatie leidt echter niet tot een experimenteel waarneembare verandering in het lichtverstrooiïngsspectrum tengevolge van het lage golfgetal waarbij de corresponderende verandering in de dichtheids-dichtheids-correlatiefunctie optreedt. Dit is in overeenstemming met eerder gevonden resultaten.

In hoofdstuk IV wordt een vloeistoflaag, waarin alleen een temperatuurgradiënt aanwezig is, bestudeerd. Daarbij wordt opnieuw uitgegaan van een stelsel gelineariseerde vergelijkingen waaruit een uitdrukking wordt afgeleid voor de dichtheids-dichtheids-correlatiefunctie die correct is tot op eerste orde in de aangelegde temperatuurgradiënt. In deze uitdrukking wordt nu de temperatuurafhankelijkheid van de stationaire waarden van thermodynamische grootheden meegenomen. Deze laatste afhankelijkheden werden verwaarloosd in hoofdstuk III. Om de behandeling te vereenvoudigen werd de temperatuurafhankelijkheid van de viscositeit verwaarloosd. Verder is aangenomen dat het warmtegeleidingsvermogen voldoende klein is en nul gesteld mag worden.

In het lichtverstrooiïngsspectrum vindt men dan een modificatie van de Brillouin lijnen. Deze lijnen hebben nu ongelijke amplitude en niet meer de vorm van Lorentz lijnen. Modificaties van het spectrum zijn recent ook gevonden door enerzijds Kirkpatrick, Cohen en Dorfman, die gebruik maken van kinetische theorie, en anderzijds door Procaccia, Ronis en Oppenheim die een niet-lineaire responstheorie gebruiken. De expliciete uitdrukkingen voor het lichtverstrooiïngsspectrum die werden gevonden door bovenstaande auteurs zijn niet in overeenstemming met elkaar en ook niet met het resultaat dat hier verkregen is met behulp van de meer directe methode van de fluctuerende hydrodynamica.

STUDIEOVERZICHT

21 juni 1969	eindexamen HBS-B; Christelijke scholengemeenschap Leiden Zuid-West, Leiden
september 1969	aanvang scheikundestudie, Rijksuniversiteit Leiden
19 januari 1973	kandidaatsexamen scheikunde en natuurkunde met bijvak wiskunde
eerste halfjaar 1975	experimentele stage in de metalengroep van Dr. G.J. van den Berg; onderzoek naar warmtegeleiding in kristallen tijdens de kristalgroei
14 december 1976	doctoraalexamen natuurkunde met bijvak wiskunde
1 februari 1977	indiensttreding bij de Stichting F.O.M., aanvang van het onderzoek voor dit proefschrift onder leiding van Prof.dr. P. Mazur

De Stichting F.O.M. stelde mij in staat in 1977 deel te nemen aan de Nuffic-zomerschool te Jadwisin, Polen over fundamentele problemen in de statistische mechanica.

Gedurende het gehele onderzoek heb ik mogen profiteren van de levendige interesse en de vele suggesties van Dr. D. Bedeaux, als ook van zijn grote kennis op het gebied van de statistische fysica.

Het typewerk werd verzorgd door mevrouw M. de C. Bridgen en door mevrouw S. Hélant Muller-Soegies.

STELLINGEN

en

ERRATA

behorende bij het proefschrift van

G. van der Zwan

Leiden

23 januari 1980

STELLINGEN

1. Met behulp van de in dit proefschrift ontwikkelde methode kan de dichtheid-dichtheids correlatiefunctie, en het daarmee corresponderende lichtverstrooiingsspectrum, ook worden berekend voor systemen waarin een stationaire snelheidsgradiënt aanwezig is.

   Dit proefschrift, Hoofdstuk III en IV.
   J. Machta, I. Oppenheim, I. Procaccia, Phys.Rev.Lett. 42 (1979) 1368.

2. De in hoofdstuk IV van dit proefschrift gevonden symmetrierelaties voor de functies S_0, S_1 en S_2 volgen ook algemeen uit de realiteit, stationariteit en de ruimtelijke symmetrieeigenschappen van de dichtheid-dichtheids correlatiefunctie.

3. Met behulp van de methode van geïnduceerde krachten kan ook bij lage frequenties, en niet slechts bij frequentie nul, de stelling van Faxén worden afgeleid voor deeltjes van ellipsoïdale vorm.

   R. Berker, in: Encyclopedia of Physics Vol. VIII/2, Fluid dynamics II Springer (Berlijn, 1963).

4. De theoretische analyse die door Mountain wordt gegeven van het spectrum van licht verstrooid aan een één-component fluïdum dicht bij het kritisch punt is onjuist.

   R. Mountain, Rev.Mod.Phys. 38 (1966) 205.

5. Bij de berekening van remstralingsamplitudes voor processen waaraan longitudinaal gepolariseerde spin-$\frac{1}{2}$ deeltjes deelnemen is het, ook bij hoge energieen, in het algemeen niet toegestaan de benadering te gebruiken waarbij de spinor-projectieoperator wordt uitgedrukt in de heliciteitsoperator.

   Y.S. Tsai, Phys.Rev. D12 (1975) 3533.

6. Ten onrechte suggereren Graham en Haken dat het principe van "detailed balance" algemeen geldt voor systemen in stationaire niet-evenwichts toestanden.

   R. Graham, H. Haken, Z.Phys. 243 (1971) 289.

7. De door Lebon en Jou gegeven continuümtheorie van vloeibaar Helium II, gebaseerd op de invoering van een vectorgrootheid $\vec{\xi}$ in de Gibbs-relatie, leidt tot inconsistente resultaten.

G. Lebon, D. Jou, J.Non-Equilib.Thermodyn. 4 (1979) 259.

8. De warmtegeleidingsmetingen van Boon, Allain en Lallemand vinden plaats bij dermate hoge Rayleigh-getallen dat geen overeenstemming verwacht mag worden met de resultaten van de volledig gelineariseerde hydrodynamische theorie.

J.P. Boon, C. Allain, P. Lallemand, Phys.Rev.Lett. 43 (1979) 199.

9. De bewering van Schulman en Seiden dat, bij de door hen ingevoerde "temperatuur"-(T)-afhankelijkheid van de overlevings- en geboortekans van een cel in Conway's spel "Life", een dichtheid die bij T=0 stationair is, dat ook is voor T>0, is aanvechtbaar.

L.S. Schulman, P.E. Seiden, J.Stat.Phys. 19 (1978) 293.

ERRATA

p. 18,	eq. (2.19)	$\omega^2 - \frac{\eta'}{\rho_e} k^2 + c_0^2 k^2 (1+\xi^2 k^2)$	$\rightarrow \omega^2 + i\omega \frac{\eta'}{\rho_e} k^2 - c_0^2 k^2 (1+\xi^2 k^2)$
p. 20,	eq. (3.5)	$\vec{F}_{ind}(\vec{k}\omega,\omega)$	$\rightarrow \vec{F}_{ind}(k\vec{\Omega},\omega)$
p. 28,	eq. (A.6)	$d\vec{\Omega}$	$\rightarrow d\vec{\Omega}'$
p. 62		page)	→ page 60)
p. 84,	eq. (B.2)	$e^{i\vec{k}(\vec{r}-\vec{r}')}$	$\rightarrow e^{i\vec{k}\cdot(\vec{r}-\vec{r}')}$
p. 84,	eq. (B.2)	$(\vec{k}_{1\parallel} - \vec{k}_{2\parallel})$	$\rightarrow \delta(\vec{k}_{1\parallel} - \vec{k}_{2\parallel})$