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Finite-size effects on fluctuations in a fluid out of thermal equilibrium

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Abstract

In this paper, we consider a horizontal liquid layer in the presence of a stationary temperature gradient. Specifically, we calculate the structure factor neglecting gravity, but taking into account the finite height of the liquid layer. For this purpose, we consider the linearized Boussinesq equations, in the limit of negligible Rayleigh number, supplemented with Langevin noise terms and assuming free-slip boundary conditions. The nonequilibrium temperature fluctuations are obtained by expanding the solution in a complete set of orthogonal functions satisfying the boundary conditions. It is shown that the finite height of the system restricts the spatial range of the temperature fluctuations not only in the direction of the temperature gradient, but also in the horizontal direction away from the boundaries. It is demonstrated that the q^{-4} dependence of the structure factor in the absence of finite-size effects now crosses over to a q^2 dependence for very small values of the wave number q. Estimates of the wave numbers where light-scattering experiments will be affected by these finite-size effects are presented. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction and motivation

Questions concerning the nature of hydrodynamic fluctuations in fluids in stationary thermal nonequilibrium states are of current active interest. It turns out that the density or temperature fluctuations in such nonequilibrium states become long-ranged even in

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the absence of any convective instabilities [1]. As originally predicted by kinetic theory [2] and from fluctuating hydrodynamics [3–6], the structure factor, which determines the intensity of Rayleigh scattering, diverges as q^{-4} for small values of the scattering wave number q. This algebraic divergence of the correlation functions at small wave numbers has been confirmed in a number of experiments [7–9].

The divergence of the structure factor as q^{-4} cannot go on indefinitely up to wave numbers corresponding to macroscopic wavelengths. Specifically, one can identify two sources that will cause deviations from the q^{-4} behavior at very small wave numbers. Firstly, gravity causes the q^{-4} divergence to be quenched and the structure factor to reach a constant value in the limit $q \to 0$ as elucidated by Segrè et al. [10,11]. This gravitationally induced saturation of the q^{-4} divergence has been confirmed by Vailati and Giglio [12,13] in some ultra-low-angle light-scattering experiments. Secondly, since the temperature gradient is applied to a liquid layer with a finite height, finite-size effects will also cause a deviation from the q^{-4} divergence at very small wave numbers. However, such finite-size effects on the q dependence of the structure factor at small wave numbers have not yet been analyzed in detail and providing such an analysis of the finite-size effects is the goal of the present paper. We shall find that finite-size effects may be comparable to gravity effects in the interpretation of ultra-low-angle scattering experiments in liquids.

To focus on the effects of the boundaries, we shall evaluate the structure factor of a liquid in stationary thermal nonequilibrium states neglecting gravity effects. Neglecting gravity means that our results apply to fully stable thermal nonequilibrium states where convection is absent. For the sake of simplicity, we shall adopt free-slip boundary conditions [14]. Using stick boundary conditions would be more realistic [15], but we shall find that use of free-slip boundary conditions will yield physically plausible estimates for the wave numbers where deviations from the q^{-4} divergence will appear.

Our results complement some results obtained by Kirkpatrick and Cohen [16] and by Schmitz and Cohen [4]. Kirkpatrick and Cohen [16] analyzed the equal- and unequal-time correlation functions for free-slip boundary conditions close to the convective instability induced by gravity. We are studying here the same problem but in a different limit, namely, when the effect of gravity is negligible and the system is fully stable. Another difference is that Kirkpatrick and Cohen used kinetic theory whereas we are using here fluctuating hydrodynamics. Schmitz and Cohen [4] considered some aspects of the spatial dependence of the correlation function, but their discussion of finite-size effects again pertains to a situation close to the first convective instability.

Malek Mansour et al. [17,18] have considered the effects of the boundaries on some correlation functions in a fluid subjected to a stationary temperature gradient. They have used the same method as we do, namely, solving the linearized fluctuating hydrodynamic equations in terms of a complete set of orthogonal functions that fulfill the boundary conditions. But, to simplify the hydrodynamic equations, they made the assumption that the thermal expansion coefficient of the fluid vanishes. This is equivalent to assuming that the density fluctuations are caused only by pressure fluctuations. Hence, their calculations are concerned with Brillouin scattering, whereas here we shall investigate Rayleigh scattering. It is for the Rayleigh spectrum for which accurate experimental information on nonequilibrium fluctuations has been obtained [7–9,12,13]. Bena et al. [19] have recently published results from fluctuating hydrodynamics with boundary conditions in the case of Kolmogorov flow. It means that they have considered boundary modifications to the nonequilibrium velocity autocorrelation function. But as a consequence of the hydrodynamic simplifications adopted, this treatment again does not include the Rayleigh component of the structure factor.

We shall proceed as follows. In Section 2, we review the derivation of the well known expression for the structure factor in a liquid layer subjected to a stationary temperature gradient without taking into account the presence of boundaries. In Section 3, we then consider the modifications in the derivation needed to incorporate the effects of the finite height of the layer. In Section 4, we discuss the spatial decay of the structure factor as a result of the finite height of the liquid layer. We shall make a comparison with some spatial dependence of the correlation functions, reported by Schmitz and Cohen [4]. We shall also address the problem of the long-range nature of the spatial correlations resulting from the nonequilibrium heat diffusion equation [20–23]. Finally, in Section 5, we shall present a detailed analysis of the finite-size effects as they will appear in low-angle light-scattering experiments. Our conclusions are summarized in Section 6.

2. Structure factor of a liquid subjected to a stationary temperature gradient

We consider a liquid layer between two horizontal plates separated by a distance L. The liquid layer is subjected to a temperature gradient in the Z-direction by maintaining the plates at two different temperatures. The size of the system in the horizontal X- and Y-directions is much larger than the size L in the Z-direction.

To determine the structure factor of the liquid, we start from the linearized Boussinesq equations supplemented with Langevin noise terms, as first used by Swift and Hohenberg in studying the onset of Rayleigh–Bénard convection [24,25]. Use of the Boussinesq approximation to the hydrodynamic equations implies that we neglect the sound modes and consider only density fluctuations caused by temperature fluctuations or, equivalently, by entropy fluctuations [26]. While the fluctuating Boussinesq equations are commonly used to analyze fluctuations close to the Rayleigh–Bénard instability [24–27], we shall consider here a thermal nonequilibrium liquid that remains in a quiescent, fully stable, state for which the gravity term in the fluctuating hydrodynamics equations can be neglected.

Omitting the gravitational term, we can write the linearized fluctuating Boussinesq equations as

$$\frac{\partial}{\partial t}(\nabla^2 w) = \nu \nabla^2(\nabla^2 w) + F_1 ,$$

$$\frac{\partial \theta}{\partial t} = D_T \nabla^2 \theta + \beta w + F_2 , \qquad (1)$$

where, in the notation of Chandrasekhar [14], θ $(=\delta T)$ represents the local fluctuation of the temperature T and $w(=\delta v_z)$ denotes the fluctuation of the Z-component of the fluid velocity $\mathbf{v}$. The coefficient v is the kinematic viscosity and the coefficient D_T, as usual, is identified with the thermal diffusivity of the liquid. The coefficient $\beta = \mathrm{d}T/\mathrm{d}z$ represents the magnitude of the temperature gradient which, as mentioned above, is assumed to act in the Z-direction. Again following Chandrasekhar [14], we find it convenient to consider Eq. (1) for $\nabla^2 w$, rather than an equation for the fluctuating fluid velocity $\delta\mathbf{v}$. Finally, F_1 and F_2 represent the contributions from rapidly varying short-range fluctuations and are related to a random current tensor $\delta\mathsf{T}$ and a random heat flux $\delta\mathbf{Q}$ in such a way that [25]

$$F_1 = \frac{1}{\rho}\{\nabla \times [\nabla \times (\nabla \cdot (\delta\mathsf{T}))]\}_z \,,$$

$$F_2 = -\frac{D_T}{\lambda}\nabla \cdot (\delta\mathbf{Q}) \,, \tag{2}$$

where ρ and λ are the density and the thermal conductivity of the fluid, while the subscript z in Eq. (2) indicates that F_1 is to be identified with the Z-component of the vector between the curly brackets. In Eqs. (1) and (2), it is assumed that both v and D_T depend only weakly on temperature so that the variation of these properties as a function of z are negligibly small; in practice, this is a very good approximation [28]. Moreover, the Boussinesq approximation assumes the liquid to be incompressible [14,24], so that the coefficient D_T both in Eqs. (1) and (2) can indeed be identified with the thermal diffusivity $\lambda/\rho c_P$, where c_P is the specific isobaric heat capacity.

In the absence of any boundary conditions, a temporal and spatial Fourier transformation can be applied to Eq. (1) to obtain a set of equations for the fluctuations in the vertical component of the velocity $w(\omega, \mathbf{q})$ and for the fluctuations in the temperature $\theta(\omega, \mathbf{q})$ as a function of the frequency ω and the wavevector $\mathbf{q}$:

$$\begin{pmatrix} -q^2(\mathrm{i}\,\omega + v \cdot q^2) & 0 \\ -\beta & \mathrm{i}\,\omega + D_T \cdot q^2 \end{pmatrix} \cdot \begin{pmatrix} w(\omega, \mathbf{q}) \\ \theta(\omega, \mathbf{q}) \end{pmatrix} = \begin{pmatrix} F_1(\omega, \mathbf{q}) \\ F_2(\omega, \mathbf{q}) \end{pmatrix} . \tag{3}$$

The solution for $w(\omega, q)$ and $\theta(\omega, \mathbf{q})$ can be readily obtained by inverting the matrix appearing in Eq. (3). Rayleigh scattering probes density fluctuations caused by the temperature fluctuations and the relationship between the Rayleigh component of the structure factor $S(\omega, \mathbf{q})$ and the autocorrelation of temperature fluctuations is given by

$$\langle \theta^*(\omega, \mathbf{q}) \cdot \theta(\omega', \mathbf{q}')\rangle = \frac{1}{\alpha^2\rho^2} S(\omega, \mathbf{q})\,(2\pi)^4\delta(\omega - \omega')\delta(\mathbf{q} - \mathbf{q}') \,, \tag{4}$$

where α is the thermal expansion coefficient of the liquid. To deduce the correlation function $\langle \theta^*(\omega, \mathbf{q}) \cdot \theta(\omega', \mathbf{q}')\rangle$ of the temperature fluctuations from Eq. (3), we need the correlation functions for the Langevin noise terms F_1 and F_2. In nonequilibrium fluctuating hydrodynamics it is assumed that the correlation functions of the random current tensor and the random heat flux retain their local-equilibrium values [26,29,30]. This assumption has been verified experimentally even for temperature gradients in excess of 200 K cm^{-1} [28]. From the expressions for the correlation functions of the random current tensor $\delta\mathsf{T}$ and the random heat flux $\delta\mathbf{Q}$ as, for instance, given by Eqs. (3.12) in Ref. [26], and from the definition (2) of F_1 and F_2, we obtain

$$\langle F_1^*(\omega,\mathbf{q})\cdot F_1(\omega',\mathbf{q}')\rangle = 2k_\mathrm{B}T\frac{\nu}{\rho}\,q_\parallel^2\,q^4(2\pi)^4\delta(\omega-\omega')\delta(\mathbf{q}-\mathbf{q}')\,,$$

$$\langle F_2^*(\omega,\mathbf{q})\cdot F_2(\omega',\mathbf{q}')\rangle = \frac{2k_\mathrm{B}T^2\lambda}{\rho^2c_P^2}q^2(2\pi)^4\delta(\omega-\omega')\delta(\mathbf{q}-\mathbf{q}')\,,$$

$$\langle F_1^*(\omega,\mathbf{q})\cdot F_2(\omega',\mathbf{q}')\rangle = \langle F_2^*(\omega,\mathbf{q})\cdot F_1(\omega',\mathbf{q}')\rangle = 0\,, \tag{5}$$

where $q_\parallel$ represents the modulus of the component of the wavevector $\mathbf{q}$ in the XY plane: $\left(q_\parallel = \sqrt{q_x^2+q_y^2}\right)$, i.e., the component of $\mathbf{q}$ perpendicular to the temperature gradient. The symbol k_B represents Boltzmann's constant. From Eqs. (3)–(5) one obtains for the dynamic structure factor $S(\omega,\mathbf{q})$ of a nonequilibrium liquid in the Boussinesq approximation the following expression:

$$S(\omega,\mathbf{q}) = \rho^2\kappa_Tk_\mathrm{B}T\frac{\gamma-1}{\gamma}\,\frac{2D_Tq^2}{\omega^2+D_T^2q^4} + \frac{\alpha^2\rho k_\mathrm{B}T}{(\nu^2-D_T^2)}\,\frac{\beta^2q_\parallel^2}{q^6}\left[P\frac{2\,D_T\,q^2}{\omega^2+D_T^2q^4} - \frac{2\,\nu\,q^2}{\omega^2+\nu^2q^4}\right]\,, \tag{6}$$

where γ denotes the heat-capacity ratio c_P/c_V, κ_T the isothermal compressibility and $P=\nu/D_T$ the Prandtl number. In deriving Eq. (6), we have used the thermodynamic relation $\alpha^2D_T = [(\gamma-1)/\gamma]\lambda\kappa_T/T$. We note that in this paper the parallel and perpendicular directions are defined with respect to the horizontal plane, as was done by Cohen and coworkers [4,15,16,26], but unlike the notation used by Segrè et al. [10,11].

Eq. (6) for the Rayleigh spectrum was first obtained by Kirkpatrick et al. [2] and has been reproduced by many investigators [3,4,6]. The nonequilibrium dynamic structure factor $S(\omega,\mathbf{q})$ as given by Eq. (6), consists of an equilibrium contribution independent of the temperature gradient β, and two nonequilibrium contributions proportional to the square of the temperature gradient β. The nonequilibrium contributions to the structure factor are anisotropic and depend on the magnitude of the horizontal component of the wave vector $\mathbf{q}$.

In this paper, we focus our attention on the static structure factor, $S(\mathbf{q}) = (2\pi)^{-1}\times\int\mathrm{d}\omega\,S(\omega,\mathbf{q})$, which determines the total intensity of the Rayleigh scattering [12]. From Eq. (6) we obtain

$$S(\mathbf{q}) = \rho^2\kappa_Tk_\mathrm{B}T\frac{\gamma-1}{\gamma}\left\{1+\frac{(c_P/T)(P-1)}{(\nu^2-D_T^2)}\,\frac{\beta^2q_\parallel^2}{q^6}\right\}\,. \tag{7}$$

We note from Eq. (7) that the nonequilibrium enhancement of the structure factor is proportional to $q_\parallel^2/q^6$ and, hence, diverges as q^{-4} when $q\to 0$. Such an algebraic wave-number divergence is a general characteristic feature of the nonequilibrium fluctuations [1].

3. Finite-size effects on the nonequilibrium structure factor

As discussed in Section 1, modifications to the bulk expression (7) for the nonequilibrium structure factor are expected due to the presence of gravity and boundaries. The effects of gravity have already been considered in the literature, and we focus here on the modifications to Eq. (7) due to the presence of boundaries at $z=0$ and at $z=L$. As in Section 2, we introduce Fourier transforms in time and space but, to accommodate the effect of the boundary conditions in the Z-direction, we restrict the spatial Fourier transformation to the XY plane. Hence, from Eq. (1) we arrive at the following set of linear differential equations:

$$\begin{pmatrix} \mathrm{i}\,\omega\left[\dfrac{\mathrm{d}^2}{\mathrm{d}z^2}-q_{\parallel}^2\right]-\nu\left[\dfrac{\mathrm{d}^2}{\mathrm{d}z^2}-q_{\parallel}^2\right]^2 & 0 \\ -\beta & \mathrm{i}\,\omega-D_T\left[\dfrac{\mathrm{d}^2}{\mathrm{d}z^2}-q_{\parallel}^2\right] \end{pmatrix}\begin{pmatrix} w(\omega,\mathbf{q}_{\parallel},z) \\ \theta(\omega,\mathbf{q}_{\parallel},z)\end{pmatrix}$$

$$=\begin{pmatrix} F_1(\omega,\mathbf{q}_{\parallel},z) \\ F_2(\omega,\mathbf{q}_{\parallel},z)\end{pmatrix}, \tag{8}$$

where $\mathbf{q}_{\parallel}$ is now a wavevector in the XY plane. As is often done in the literature [16,24], we assume free-slip boundary conditions and perfectly conducting walls, so that

$$\begin{aligned} &\theta(\omega,\mathbf{q}_{\parallel},z)=0 \qquad \text{at } z=0,L\,, \\ &w(\omega,\mathbf{q}_{\parallel},z)=0 \qquad \text{at } z=0,L\,, \\ &\frac{\partial^2 w(\omega,\mathbf{q}_{\parallel},z)}{\partial z^2}=0 \quad \text{at } z=0,L\,. \end{aligned} \tag{9}$$

Note that these boundary conditions imply the absence of any possible fluctuations in the temperature and velocity of the fluid adjacent to the walls.

To search for a solution of Eq. (8), we represent $w(\omega,\mathbf{q}_{\parallel},z)$ and $\theta(\omega,\mathbf{q}_{\parallel},z)$ as a series expansion in a complete set of eigenfunctions of the differential operator satisfying the boundary conditions (9). An appropriate set of eigenfunctions is the Fourier sine basis in the $[0,L]$ interval [14]. We thus assume

$$\begin{pmatrix} w(\omega,\mathbf{q}_{\parallel},z) \\ \theta(\omega,\mathbf{q}_{\parallel},z)\end{pmatrix}=\sum_{N=1}^{\infty}\begin{pmatrix} A_N(\omega,q_{\parallel}) \\ B_N(\omega,q_{\parallel})\end{pmatrix}\sin\left(\frac{N\pi}{L}z\right)\,. \tag{10}$$

Since the differential operator in Eq. (8) depends only on the modulus of $\mathbf{q}_{\parallel}$, the problem has cylindrical symmetry and the solution will depend only on the magnitude $q_{\parallel}$ of the vector $\mathbf{q}_{\parallel}$.

To deduce the coefficients $A_N(\omega,q_{\parallel})$ and $B_N(\omega,q_{\parallel})$ from Eqs. (8), we also need to represent the random noise terms $F_1(\omega,q_{\parallel},z)$ and $F_2(\omega,q_{\parallel},z)$ in terms of a Fourier sine series:

$$\begin{pmatrix} F_1(\omega, q_{\|}, z) \\ F_2(\omega, q_{\|}, z) \end{pmatrix} = \sum_{N=1}^{\infty} \begin{pmatrix} F_{1,N}(\omega, q_{\|}) \\ F_{2,N}(\omega, q_{\|}) \end{pmatrix} \sin\left(\frac{N\pi}{L} z\right) , \tag{11}$$

with

$$\begin{pmatrix} F_{1,N}(\omega, q_{\|}) \\ F_{2,N}(\omega, q_{\|}) \end{pmatrix} = \frac{2}{L} \int_0^L \begin{pmatrix} F_1(\omega, q_{\|}, z) \\ F_2(\omega, q_{\|}, z) \end{pmatrix} \sin\left(\frac{N\pi}{L} z\right) \mathrm{d}z . \tag{12}$$

Representing the random noise terms by Eq. (11), one readily deduces from Eqs. (8),

$$A_N(\omega, q_{\|}) = -\frac{F_{1,N}(\omega, q_{\|})}{[N^2\pi^2/L^2 + q_{\|}^2]\,[\mathrm{i}\omega + v \cdot (N^2\pi^2/L^2 + q_{\|}^2)]} \tag{13}$$

and

$$B_N(\omega, q_{\|}) = \frac{1}{[\mathrm{i}\omega + D_T(\frac{N^2\pi^2}{L^2} + q_{\|}^2)]} \times \left\{ F_{2,N}(\omega, q_{\|}) - \frac{\beta F_{1,N}(\omega, q_{\|})}{\left[\frac{N^2\pi^2}{L^2} + q_{\|}^2\right]\left[\mathrm{i}\omega + v\left(\frac{N^2\pi^2}{L^2} + q_{\|}^2\right)\right]} \right\} . \tag{14}$$

In analogy to Eq. (4), the Rayleigh component of the structure factor is proportional to the autocorrelation function of the temperature fluctuations:

$$\langle \theta^*(\omega, \mathbf{q}_{\|}, z) \cdot \theta(\omega', \mathbf{q}_{\|}', z') \rangle = \frac{1}{\alpha^2 \rho^2} S(\omega, \mathbf{q}, z, z')(2\pi)^3 \delta(\omega - \omega')\delta(\mathbf{q} - \mathbf{q}') . \tag{15}$$

To compute this quantity we need to calculate the correlations between the different Fourier components of the random noise terms, which involve integrals like

$$\langle F_{1,N}^*(\omega, \mathbf{q}_{\|}) \cdot F_{1,M}(\omega', \mathbf{q}_{\|}') \rangle = \frac{4}{L^2} \int_0^L \int_0^L \langle F_1^*(\omega, \mathbf{q}_{\|}, \xi) \cdot F_1(\omega', \mathbf{q}_{\|}', \chi) \rangle \times \sin\left(\frac{N\pi}{L}\xi\right) \sin\left(\frac{M\pi}{L}\chi\right) \mathrm{d}\chi\, \mathrm{d}\xi \tag{16}$$

and similar integrals for the correlation functions $\langle F_{2,N}^* \cdot F_{2,M} \rangle$, $\langle F_{1,N}^* \cdot F_{2,M} \rangle$ and $\langle F_{2,N}^* \cdot F_{1,M} \rangle$. From Eqs. (2) and (12) we obtain the following expressions for these correlation functions:

$$\begin{aligned} &\langle F_{1,N}^*(\omega, \mathbf{q}_{\|}) \cdot F_{1,M}(\omega', \mathbf{q}_{\|}') \rangle \\ &\quad = 2k_{\mathrm{B}} T \frac{v}{\rho} \frac{2}{L} q_{\|}^2 \left(q_{\|}^2 + \frac{N^2\pi^2}{L^2} \right)^2 \delta_{NM} (2\pi)^3 \delta(\omega - \omega') \delta(\mathbf{q}_{\|} - \mathbf{q}_{\|}') , \\ &\langle F_{2,N}^*(\omega, \mathbf{q}_{\|}) \cdot F_{2,M}(\omega', \mathbf{q}_{\|}') \rangle \\ &\quad = \frac{2k_{\mathrm{B}} T^2 \lambda}{\rho^2 c_P^2} \frac{2}{L} \left(q_{\|}^2 + \frac{N^2\pi^2}{L^2} \right) \delta_{NM} (2\pi)^3 \delta(\omega - \omega') \delta(\mathbf{q}_{\|} - \mathbf{q}_{\|}') , \\ &\langle F_{1,N}^*(\omega, \mathbf{q}_{\|}) \cdot F_{2,M}(\omega', \mathbf{q}_{\|}') \rangle = \langle F_{2,N}^*(\omega, \mathbf{q}_{\|}) \cdot F_{1,M}(\omega', \mathbf{q}_{\|}') \rangle = 0 . \end{aligned} \tag{17}$$

In this calculation, because of the short-range nature of the random fluctuations, we continue to assume that the correlation functions of the random current tensor and the random heat flux retain their local-equilibrium values [26]. This assumption remains valid as long as L is a macroscopic distance much larger than the molecular distances in the liquid.

From Eqs. (13) to (15) and (17) we readily obtain an explicit expression for the dynamic structure factor $S(\omega, q_\parallel, z, z')$. Integration over the frequency ω then yields for the static structure factor $S(q_\parallel, z, z') = (2\pi)^{-1} \int \mathrm{d}\omega\, S(\omega, q_\parallel, z, z')$:

$$S(q_\parallel, z, z') = S_{\mathrm{E}}(q_\parallel, z, z') + S_{\mathrm{NE}}(q_\parallel, z, z')\,, \tag{18}$$

where

$$\begin{aligned} S_{\mathrm{E}}(q_\parallel, z, z') &= \rho^2 \kappa_T k_{\mathrm{B}} T\, \frac{\gamma - 1}{\gamma}\, \frac{2}{L} \sum_{N=1}^{\infty} \sin\left(\frac{N\pi}{L} z\right) \sin\left(\frac{N\pi}{L} z'\right) \\ &= \rho^2 \kappa_T k_{\mathrm{B}} T\, \frac{\gamma - 1}{\gamma}\, \delta(z - z') \end{aligned} \tag{19}$$

and

$$S_{\mathrm{NE}}(q_\parallel, z, z') = \rho^2 \kappa_T k_{\mathrm{B}} T\, \frac{\gamma - 1}{\gamma}\, \frac{(c_P/T)(P-1)\beta^2}{(v^2 - D_T^2)}\, \tilde{S}_{\mathrm{NE}}(q_\parallel, z, z') \tag{20}$$

with

$$\tilde{S}_{\mathrm{NE}}(q_\parallel, z, z') = 2L^3 \sum_{N=1}^{\infty} \frac{q_\parallel^2 L^2}{(q_\parallel^2 L^2 + N^2\pi^2)^3} \sin\left(\frac{N\pi}{L} z\right) \sin\left(\frac{N\pi}{L} z'\right)\,. \tag{21}$$

$S_{\mathrm{E}}(q_\parallel, z, z')$, given by Eq. (19), represents the equilibrium contribution to the structure factor and does not depend either on the temperature gradient β or the boundary conditions. As in the case of the bulk solution, S_{E} is short ranged (a delta function). The fact that the equilibrium structure factor is not affected by the presence of boundaries is well known and has been discussed in the literature (see, e.g., Ref. [16]).

$S_{\mathrm{NE}}(q_\parallel, z, z')$, given by Eq. (20), represents the nonequilibrium contribution to the structure factor and, as in the absence of boundaries, this contribution is again proportional to the square of the temperature gradient β. To determine the dependence of the nonequilibrium contribution to the structure factor on the height L, we need to sum the Fourier series (21). For this purpose, we start from the relation

$$\begin{aligned} &\sum_{N=0}^{\infty} \frac{1}{(N^2 + \mu^2)} \sin\left(\frac{N\pi}{L} z\right) \sin\left(\frac{N\pi}{L} z'\right) \\ &= \frac{\pi}{4\mu}\, \frac{1}{\sinh(\mu\pi)} \left\{ \cosh\left[\frac{\mu\pi}{L}(L - |z - z'|)\right] - \cosh\left[\frac{\mu\pi}{L}\left(L - (z + z')\right)\right] \right\} \end{aligned} \tag{22}$$

which is valid for $z, z' \in [0, L]$ and for real μ. Eq. (22) can be obtained by simple algebra from formula 1.445 in Ref. [31]. By differentiating Eq. (22) twice with respect to the variable μ, we implement the summation of the series in Eq. (21). The result is a long expression, not particularly informative, which can be easily obtained

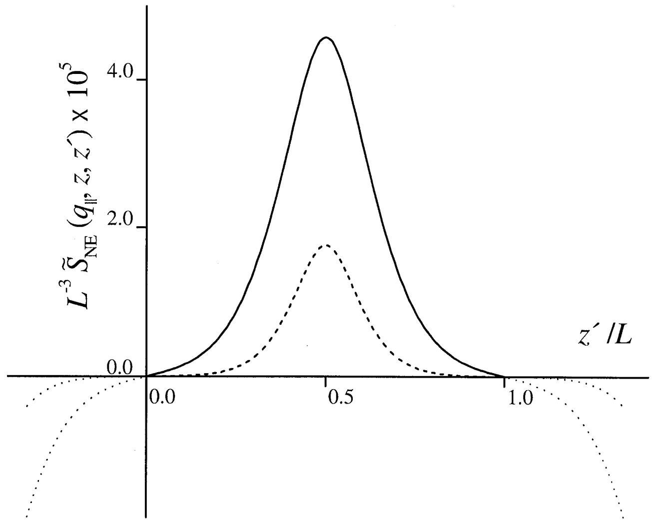

Fig. 1. Normalized nonequilibrium structure factor $L^{-3}\tilde{S}_{NE}(q_{\|}, z = L/2, z')$ as a function of z'/L for two different values of $q_{\|}$ (solid curve is for $q_{\|} = 16/L$ and dashed curve is for $q_{\|} = 22/L$). The dotted curves are extrapolations outside the [0, L] interval.

by the reader. We shall use the result thus obtained for $S_{NE}(q_{\|}, z, z')$ in the sequel, while explicit expressions to be obtained upon further integration will be presented in Sections 5 and 6.

The finite-size effects on the nonequilibrium structure factor are all contained in Eq. (21) for the normalized nonequilibrium structure factor $S_{NE}(q_{\|}, z, z')$. As an example, we show in Fig. 1 $L^{-3}\tilde{S}_{NE}(q_{\|}, z, z')$ as a function of z'/L at $z = L/2$ for two different values of the horizontal wave number $q_{\|}$. We see that $\tilde{S}_{NE}(q_{\|}, z, z')$ is peaked at $z = z'$. Two remarks about the behavior of $\tilde{S}_{NE}$ can be made. Firstly, $\tilde{S}_{NE}$ is continuous in the interval $[0, L]$ (actually it is so along the full real axis). Secondly, as a consequence of the boundary conditions, $\tilde{S}_{NE}$ goes to zero and has inflection points at both ends of the interval, i.e., at $z' = 0$ and L for any z. To indicate the behavior of $\tilde{S}_{NE}$ as a function of z' at the ends of the $[0, L]$ interval more clearly, we also show part of the extrapolated behavior (dotted curves) in Fig. 1.

Eqs. (20) and (21) are the actual expressions that we have obtained for the nonequilibrium structure factor in a liquid layer with finite height L using free-slip boundary conditions. The remaining part of this paper is concerned with a discussion of some physical consequences arising from the finite height of the system.

4. Correlations in real space

In order to elucidate how the correlation functions become long-ranged in real space, we need to consider the inverse Fourier transform of $S_{NE}(q_{\|}, z, z')$, which can be

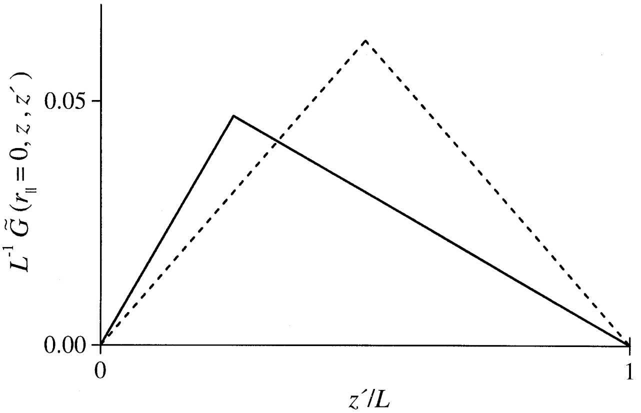

Fig. 2. Normalized correlation function $L^{-1}\tilde{G}_{\rm NE}(r_{\parallel}, z, z')$ in the Z-direction ($r_{\parallel}=0$) as a function of z'/L for $z=L/4$ (——) and for $z=L/2$ (- - - - -).

expressed as

$$G_{\rm NE}(r_{\parallel}, z, z') = \rho^2 \kappa_T k_{\rm B} T \, \frac{\gamma-1}{\gamma} \, \frac{(c_P/T)(P-1)\beta^2}{(v^2 - D_T^2)} \tilde{G}_{\rm NE}(r_{\parallel}, z, z') \,, \tag{23}$$

with

$$\tilde{G}_{\rm NE}(r_{\parallel}, z, z') = \int_0^{\infty} q_{\parallel} J_0(q_{\parallel} r_{\parallel}) \tilde{S}_{\rm NE}(q_{\parallel}, z, z') \, {\rm d}q_{\parallel} \,. \tag{24}$$

Here $r_{\parallel}$ is the cylindrical radial variable and $J_0(x)$ the Bessel function of the first kind and of order zero [31]. We have not been able to evaluate integral (24) exactly in the general case. Fortunately, there are two interesting particular cases for which integral (24) can be evaluated explicitly:

(i) The first case corresponds to $r_{\parallel}=0$, which yields the nonequilibrium equal-time correlation function along the Z-axis. After performing integration (24), we obtained in this case

$$\tilde{G}_{\rm NE}(r_{\parallel}=0, z, z') = \frac{L}{4} \left[\frac{|z+z'| - |z-z'|}{2L} - \frac{zz'}{L^2} \right] \,. \tag{25}$$

As an example, we show in Fig. 2, the normalized correlation function $L^{-1}\tilde{G}_{\rm NE}(r_{\parallel} = 0, z, z')$ as a function of z'/L, for two different values of z/L. This nonequilibrium real-space equal-time correlation function along the Z-axis is always positive, has a maximum at $z=z'$ and decreases monotonically from this maximum, reaching zero at both ends of the interval. The real-space correlation function in the Z-direction is nonlocal, long-ranged and does not involve any intrinsic length scale, i.e., the correlation encompasses the entire system only to be cut off by the finite size of the system itself. The algebraic exponent characterizing the long-range nature of the correlation in the direction coincident with the temperature gradient equals 1. We note that for points near the center of the liquid layer, where $z \simeq z' \simeq L/2$, expression (25) for

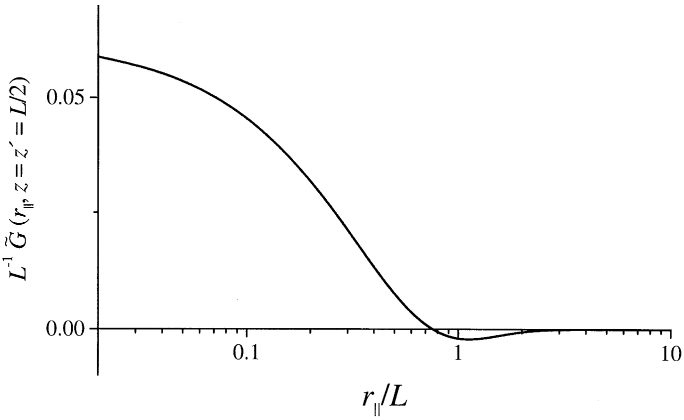

Fig. 3. Semi-logarithmic plot of the normalized correlation function $L^{-1}\tilde{G}_{\mathrm{NE}}(r_{\|}, z, z')$ in the central plane of the liquid layer ($z = z' = L/2$) as a function of $r_{\|}/L$.

$\tilde{G}_{\mathrm{NE}}(r_{\|} = 0, z, z')$ reduces to

$$\tilde{G}_{\mathrm{NE}}(r_{\|} = 0, z, z') = \frac{L}{16}\left[1 - 2\frac{|z - z'|}{L}\right] . \tag{26}$$

(ii) The second interesting case for which integral (24) can be evaluated exactly is for $z = z' = L/2$, in which case $\tilde{G}_{\mathrm{NE}}$ depends only on the radial variable $r_{\|}$. $\tilde{G}_{\mathrm{NE}}(r_{\|}, z = L/2, z' = L/2)$ represents the nonequilibrium equal-time correlation function in the plane parallel to the boundaries at mid-height of the cell, i.e., the plane at maximum distance from the boundaries. Integration of Eq. (24) in this case yields

$$\tilde{G}_{\mathrm{NE}}(r_{\|}, z = L/2, z' = L/2) = \frac{r_{\|}}{2\pi}\left\{\sum_{N=0}^{\infty}\frac{1}{2N+1}K_1\left(\frac{(2N+1)\pi r_{\|}}{L}\right) - \frac{\pi r_{\|}}{2L}\sum_{N=0}^{\infty}K_0\left(\frac{(2N+1)\pi r_{\|}}{L}\right)\right\} , \tag{27}$$

where K_0 and K_1 are modified Bessel functions of the second kind. In Fig. 3, we have plotted the normalized correlation function $L^{-1}\tilde{G}_{\mathrm{NE}}(r_{\|}, z = L/2, z' = L/2)$ as a function of $r_{\|}/L$. From Eq. (27) we conclude that for $r_{\|}/L \ll 1$ the real-space correlation function will vary with $r_{\|}$ as

$$\tilde{G}_{\mathrm{NE}} = \frac{L}{16}\left(1 - \frac{3r_{\|}}{L}\right) , \tag{28}$$

which confirms the existence of long-ranged correlations in the direction perpendicular to the temperature gradient, consistent with Eq. (7) for the nonequilibrium structure factor. On the other hand, for $r_{\|}/L \gg 1$, using the asymptotic expansion of the Bessel functions, we obtain

$$\tilde{G}_{\mathrm{NE}} = \frac{L}{4\pi^2}(2 - s)\sqrt{\frac{\pi s}{2}}\exp(-s) , \tag{29}$$

with $s = \pi r_{\|}/L$. Hence, the finite size of the liquid layer not only restricts the long-range nature of the correlations in the direction coincident with the temperature gradient, but also in the direction perpendicular to the temperature gradient. Fig. 3 shows how the correlations in a plane perpendicular to the temperature gradient rapidly vanish as the radial distance $r_{\|}$ approaches values of the order of L. This is also evident from the $r_{\|}$ dependence of the correlation function, which switches from a linear dependence in Eq. (28) for $r_{\|}/L \ll 1$ to an exponential dependence in Eq. (29) for $r_{\|}/L \gg 1$.

The temperature gradient not only induces long-range spatial correlations in the direction perpendicular to the temperature gradient (for $r_{\|}/L \ll 1$), but also in the direction coincident with the temperature gradient as has been elucidated by several previous investigators on the basis of the nonequilibrium heat-diffusion equation [17,23,32,33]. Considering only the heat-diffusion equation means neglecting any coupling between temperature and velocity fluctuations. Therefore, this approach only applies to nonequilibrium fluctuations with $q_{\|} = 0$, which is equivalent to considering real-space correlations along the direction of the gradient. The existence of long-range correlations in the direction of the temperature gradient has been confirmed by numerical integration [20], by computer simulations [34] and by a lattice-gas automaton approach [35]. Our expression (26) for the correlation function in the direction of the temperature gradient is in agreement with that obtained by Malek Mansour and coworkers [20,23], as is evident from a comparison of our Fig. 2 with Fig. 1 in Ref. [23].

We note that the long-range correlations in the direction perpendicular to the temperature gradient are caused by a coupling between the temperature fluctuations and the transverse momentum fluctuations [2–6]. This coupling vanishes in the direction of the temperature gradient, as is evident upon substituting $q_{\|} = 0$ in Eq. (7). The long-range correlations in the direction of the temperature gradient follow from solving the heat-diffusion equation in the presence of boundary conditions. The significance of our results is that we have obtained an expression, given by Eq. (21), which includes the effects of the boundary conditions in the correlations in all spatial directions.

It is worth mentioning that our results are consistent with the work of Schmitz and Cohen [4] regarding the spatial nature of the correlations in the absence of boundary conditions. If one substitutes $r_{\|} = 0$ into Eq. (3.13a) of Ref. [4], one obtains the result that the nonequilibrium part of the correlation function is directly proportional to $-2|z - z'|$ in agreement with the dependence on $|z - z'|$ in our Eq. (26) for the interior points of the liquid layer. However, our Eq. (26) differs from the result of Schmitz and Cohen by an additional term proportional to L which diverges in the limit $L \to \infty$ and, therefore, was not considered by Schmitz and Cohen. Furthermore, if one substitutes $z = z'$ into Eq. (3.13a) of Ref. [4], one obtains the result that the nonequilibrium part of the correlation function is proportional to $-3r_{\|}$ to be compared with our Eq. (28) for the correlations in the direction perpendicular to the temperature gradient and far from the boundaries, when $r_{\|}/L \ll 1$.

As can be seen from Fig. 3, the correlation function in the direction parallel to the boundaries has a minimum close to $r_{\|} = L$ (actually for our boundary conditions at $r_{\|}/L = 1.1542$). This value corresponds approximately to the size of the rolls that

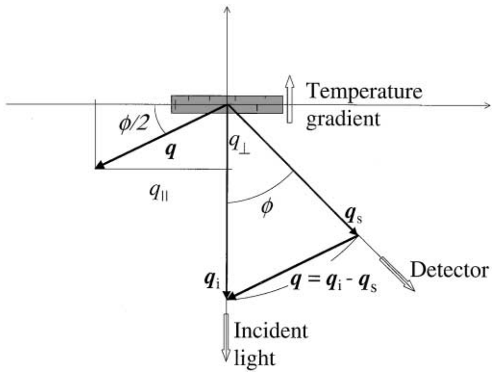

Fig. 4. Schematic representation of a nonequilibrium light-scattering experiment. $\mathbf{q}_i$ is the wave vector of the incident light and $\mathbf{q}_s$ is the wave vector of the scattered light. The magnitude $q = |\mathbf{q}_i - \mathbf{q}_s|$ of the scattering wave vector is related to the scattering angle ϕ by $q = 2q_0 \sin(\phi/2)$, where q_0 is the magnitude of the wave vector $\mathbf{q}_i$ of the incident light in the liquid.

appear at the first convective instability [27]. The fact that the correlation function has a horizontal structure on a length scale of order L is to be expected as a direct consequence of the boundary conditions with and without gravity.

5. Consequences for light-scattering experiments

In this section, we evaluate the effects due to the finite height of the fluid layer as they could be observed in light-scattering experiments. For this purpose we consider an experimental arrangement like the ones employed by Sengers and coworkers [7,8,28,36] or by Vailati and Giglio [12,13]. A schematic representation of such a light-scattering experiment is shown in Fig. 4. The scattering medium is a thin horizontal fluid layer bounded by two parallel plates whose temperatures can be controlled independently so as to establish a temperature gradient across the fluid layer. The horizontal plates are furnished with windows allowing laser light to propagate through the fluid in the direction (anti)parallel to the temperature gradient. Light scattered over an angle ϕ arises from fluctuations with a wave number such that [37]

$$q = 2q_0 \sin(\phi/2)\,, \tag{30}$$

where q_0 is the wave number of the incident light inside the fluid medium. To observe any finite-size effects one needs to observe the scattered-light intensity at small wave numbers q and, hence, at very small scattering angles.

From electromagnetic theory [37] it follows that the scattering intensity $S(\mathbf{q})$ is obtained from an integration of the structure factor (18) over the scattering volume, so that [4]

$$S(q_{||}, q_\perp) = \frac{1}{L}\int_0^L \int_0^L \mathrm{e}^{-\mathrm{i}q_\perp(z-z')}[S_\mathrm{E}(q_{||}, z, z') + S_\mathrm{NE}(q_{||}, z, z')]\,\mathrm{d}z\,\mathrm{d}z'\,. \tag{31}$$

In Eq. (31) we have assumed that the scattering volume extends over the full height of the fluid layer as is the case in small-angle light scattering from thin fluid layers. In this situation, scattered light received in the collecting pinhole of the detector indeed arises from all the points illuminated by the laser beam inside the fluid layer. From Eqs. (19), (20) and (31) it follows that the scattered-light intensity $S(q_{\|}, q_{\perp})$ will only depend on the magnitudes $q_{\|}$ and $q_{\perp}$ of the parallel and perpendicular components of the scattering wave vector $\mathbf{q}$. From Eq. (30) and the geometrical arrangement shown in Fig. 4, we note that $q_{\|}$ and $q_{\perp}$ are related to the scattering angle ϕ by

$$q_{\|} = q\cos(\phi/2) = 2q_0\sin(\phi/2)\cos(\phi/2)\,,$$

$$q_{\perp} = q\sin(\phi/2) = 2q_0\sin^2(\phi/2)\,. \tag{32}$$

Substitution of Eq. (19) into Eq. (31) yields for the equilibrium contribution $S_{\mathrm{E}}(q_{\|}, q_{\perp})$ to the scattered-light intensity

$$S_{\mathrm{E}}(q_{\|}, q_{\perp}) = \rho^2\kappa_T k_{\mathrm{B}} T\,\frac{\gamma-1}{\gamma}\,, \tag{33}$$

which is the traditional formula for the isotropic Rayleigh-scattering intensity [37]. Hence, the boundary conditions do not affect the Rayleigh scattering from a liquid in thermal equilibrium as long as the height L is large enough so that the correlation functions for the random noise terms retain the equilibrium values given by Eqs. (17). Eq. (33) for the equilibrium contribution to the Rayleigh-scattering intensity also remains valid in the presence of gravity, although gravity does affect the spectral distribution of the Rayleigh scattering [10].

Substituting Eq. (20) for $S_{\mathrm{NE}}(q_{\|}, z_1, z_2)$ into Eq. (31), after performing the summation in Eq. (21) and the integration in Eq. (31), we obtain for the total Rayleigh-scattering intensity (equilibrium plus nonequilibrium) $S(q_{\|}, q_{\perp})$

$$S(q_{\|}, q_{\perp}) = \rho^2\kappa_T k_{\mathrm{B}} T\,\frac{\gamma-1}{\gamma}\left[1 + \frac{(c_P/T)(P-1)}{(\nu^2 - D_T^2)}\beta^2\tilde{S}_{\mathrm{NE}}(q_{\|}, q_{\perp})\right]\,, \tag{34}$$

with

$$\tilde{S}_{\mathrm{NE}}(q_{\|}, q_{\perp}) = L^4\frac{\tilde{q}_{\|}^2}{\tilde{q}^6}[1 + H(\tilde{q}_{\|}, \tilde{q}_{\perp})] \tag{35}$$

and

$$\begin{aligned} H(\tilde{q}_{\|}, \tilde{q}_{\perp}) = &\left[\frac{15\tilde{q}_{\|}^4 - 10\tilde{q}_{\|}^2\tilde{q}_{\perp}^2 - \tilde{q}_{\perp}^4}{4\tilde{q}_{\|}^3(\tilde{q}_{\|}^2 + \tilde{q}_{\perp}^2)}\right]\frac{\cos(\tilde{q}_{\perp}) - \cosh(\tilde{q}_{\|})}{\sinh(\tilde{q}_{\|})} \\ &- \left[\frac{7\tilde{q}_{\|}^2 - \tilde{q}_{\perp}^2}{4\tilde{q}_{\|}^2}\right]\frac{1 - \cosh(\tilde{q}_{\|})\cos(\tilde{q}_{\perp})}{\sinh^2(\tilde{q}_{\|})} \\ &+ \left[\frac{\tilde{q}_{\|}^2 + \tilde{q}_{\perp}^2}{4\tilde{q}_{\|}}\right]\frac{[1 + \cosh^2(\tilde{q}_{\|})]\cos(\tilde{q}_{\perp}) - 2\cosh(\tilde{q}_{\|})}{\sinh^3(\tilde{q}_{\|})}\,. \end{aligned} \tag{36}$$

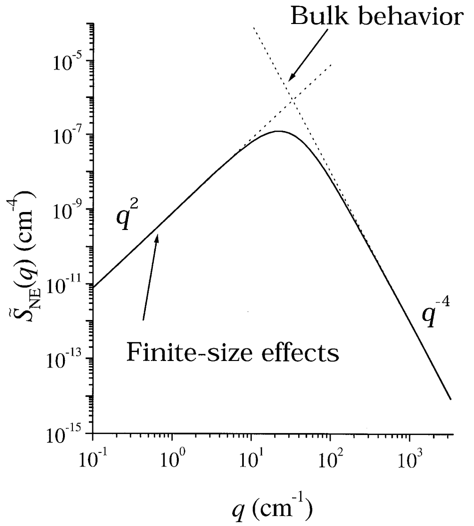

Fig. 5. Double-logarithmic plot of the wave number dependence of the nonequilibrium contribution $\tilde{S}_{NE}(q)$, given by Eq. (37), for a fluid layer with a height $L = 1$ mm.

In Eqs. (34)–(36) we have introduced $\tilde{q}_{\|} = q_{\|} L$ and $\tilde{q}_{\perp} = q_{\perp} L$ as dimensionless wave numbers.

The function $H(\tilde{q}_{\|}, \tilde{q}_{\perp})$ in Eq. (35) accounts for the finite-size effects on the scattering intensity. As $L \to \infty$, $H \to 0$ and we recover expression (7) for the Rayleigh-scattering intensity in the absence of boundary conditions. For low-angle scattering experiments, where the long-range nonequilibrium fluctuations can be investigated, we have $\tilde{q}_{\|} \simeq \tilde{q}$ and $\tilde{q}_{\perp} \simeq 0$. In this case, the normalized nonequilibrium contribution to the scattering intensity can be approximated by

$$\tilde{S}_{NE}(q) = \frac{L^4}{\tilde{q}^4} \left\{ 1 + \frac{\tilde{q}^2[\cosh(\tilde{q}) - 1] + \sinh(\tilde{q})[7\,\tilde{q} - 15\sinh(\tilde{q})]}{4\,\tilde{q}\sinh(\tilde{q})(\cosh(\tilde{q}) + 1)} \right\} . \quad (37)$$

Eq. (37) is valid up to an order $\sin^2(\phi/2)$ in terms of the scattering angle ϕ. The simplified form of the normalized structure factor $\tilde{S}_{NE}(q)$, as given by Eq. (37), is shown in Fig. 5 as a function of q on a double-logarithmic scale and for the case of $L = 0.1$ cm, which is the typical height of fluid layers in low-angle nonequilibrium Rayleigh-scattering experiments [9,12,36]. We have also evaluated the more complete expressions, Eqs. (35) and (36), using $q_0 = 1.5 \times 10^5$ cm^{-1}, which is a typical wavevector of the light sources employed in scattering experiments. The complete result, thus obtained, is indistinguishable from approximation (37) in the range of wave numbers displayed in Fig. 5. It can be shown that for large values of the wave number q, the term inside the curved brackets in Eq. (37) approaches unity and we recover the q^{-4} dependence of the scattering intensity in the absence of finite-size effects. However, such q^{-4} dependence cannot go on indefinitely with decreasing wave numbers and, as shown in Fig. 5, the finite size of the system causes a crossover to a q^2 dependence of the scattering function at very small wave numbers. For $q \to 0$ the function $H(\tilde{q})$ behaves as

$$H(\tilde{q}) \overset{q\to 0}{\to} -1 + \frac{17}{20160}\tilde{q}^6 , \tag{38}$$

indeed compensating the divergent q^{-4} dependence when finite-size effects are neglected, causing an asymptotic dependence on q^2 as shown in Fig. 5. From Eq. (38) we may define a characteristic wave number:

$$q_\times = \left(\frac{20160}{17}\right)^{1/6} \frac{1}{L} \simeq \frac{3.25}{L} , \tag{39}$$

which for $L = 0.1$ cm corresponds to $q_\times \simeq 33$ cm^{-1}. From Fig. 5, we see that $\tilde{S}_{\mathrm{NE}}(\tilde{q})$ exhibits a maximum at $q \simeq q_\times$, so that $q_\times$ may be interpreted as a "crossover" wave number separating the q^{-4} dependence and the q^2 dependence of the scattering function.

As mentioned in Section 1, not only the finite size of the system, but also gravity will cause deviations from the q^{-4} dependence of the scattering intensity. Segrè et al. [10] have predicted that the q^{-4} divergence will saturate to a constant value independent of q for small wave numbers. This prediction has been confirmed experimentally [12,13]. From Fig. 5, we conclude that the quenching of the q^{-4} divergence as a result of finite-size effects is even stronger, causing the nonequilibrium contribution to the scattering function to vanish as $q \to 0$. The result, that the crossover from the q^{-4} divergence to the q^2 dependence as a result of the finite size of the system occuring at wave numbers around $q_\times \simeq \pi/L$, seems intuitively plausible. The observation that the scattering function vanishes as $q \to 0$ is a consequence of the imposed condition of the absence of temperature and velocity fluctuations at the boundaries.

The gravitationally induced saturation of the q^{-4} divergence occurs at a "roll-off" wave number q_{RO} such that [10]

$$q_{\mathrm{RO}} = \left(\frac{g\alpha\beta}{\nu D_T}\right)^{1/4} , \tag{40}$$

where g is the gravitational acceleration constant. For toluene subjected to a temperature gradient $\beta = 100$ K cm^{-1}, we find that $q_{\mathrm{RO}} \simeq 70$ cm^{-1} [7,10]. From Fig. 5, we note that, at this wave number, deviations from the q^{-4} behavior due to finite-size effects are substantial. Thus, we conclude that, at least in one-component liquids, the finite-size effects may be equally important as the deviations from the q^{-4} divergence due to gravity.

Small-angle nonequilibrium scattering experiments so far performed in one component liquids (toluene and n-hexane) have probed wave numbers down to $q \simeq 1500$ cm^{-1} [28]. However, Vailati and Giglio [12] have demonstrated the feasibility of performing ultra-low-angle scattering experiments, probing wave numbers q down to values as small as 20 cm^{-1}.

Eq. (37) yields the scattering intensity as a function of $q \simeq q_\parallel$ for small scattering angles. Finite-size effects in nonequilibrium light-scattering experiments at any value of the scattering angle ϕ can be deduced from Eqs. (35) and (36). However, we note that Eq. (31) and hence Eq. (35) do not include any possible effects of the finite size of the scattering volume in the X- and Y-directions.

6. Conclusions

In this paper, we have evaluated the structure factor in a horizontal liquid layer of finite height L subjected to a vertical stationary temperature gradient. Rayleigh scattering, probes the density fluctuations that arise from temperature fluctuations (at constant pressure). We have shown that the finite height of the layer restricts the extent of the long-range nature of the correlations not only in the direction coincident with the temperature gradient, but also in the direction perpendicular to the temperature gradient. Specifically, we have elucidated how the well-known q^{-4} dependence of the structure factor in the presence of a temperature gradient is quenched by the finite size of the system, yielding a crossover to a q^2 dependence at very small scattering angles. We find that for a liquid like toluene, the deviations from the q^{-4} dependence at small wave numbers are just as important as deviations caused by the presence of gravity. Therefore, for a quantitative interpretation of ultra-low-angle light-scattering experiments, it may be important to account both for gravity and finite-size effects simultaneously. This will be considered in a future publication.

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References

[1] J.R. Dorfman, T.R. Kirkpatrick, J.V. Sengers, Annu. Rev. Phys. Chem. 45 (1994) 213.
[2] T.R. Kirkpatrick, E.G.D. Cohen, J.R. Dorfman, Phys. Rev. A 26 (1982) 995.
[3] D. Ronis, I. Procaccia, Phys. Rev. A 26 (1982) 1812.
[4] R. Schmitz, E.G.D. Cohen, J. Stat. Phys. 40 (1985) 431.
[5] R. Schmitz, Phys. Rep. 171 (1988) 1.
[6] B.M. Law, J.V. Sengers, J. Stat. Phys. 57 (1989) 531.
[7] B.M. Law, P.N. Segrè, R.W. Gammon, J.V. Sengers, Phys. Rev. A 41 (1990) 816.
[8] W.B. Li, P.N. Segrè, R.W. Gammon, J.V. Sengers, Physica A 204 (1994) 399.
[9] W.B. Li, K.J. Zhang, J.V. Sengers, R.W. Gammon, J.M. Ortiz de Zárate, Phys. Rev. Lett. 81 (1998) 5580.
[10] P.N. Segrè, R. Schmitz, J.V. Sengers, Physica A 195 (1993) 31.
[11] P.N. Segrè, J.V. Sengers, Physica A 198 (1993) 46.
[12] A. Vailati, M. Giglio, Phys. Rev. Lett. 77 (1996) 1484.
[13] A. Vailati, M. Giglio, Prog. Colloid. Polym. Sci. 104 (1997) 76.

[14] S. Chandrasekhar, Hydrodynamic and Hydromagnetic Stability, Clarendon, Oxford, 1961.
[15] H. Van Beijeren, E.G.D. Cohen, J. Stat. Phys. 53 (1988) 77.
[16] T.R. Kirkpatrick, E.G.D. Cohen, J. Stat. Phys. 33 (1983) 639.
[17] M. Malek Mansour, J.W. Turner, A.L. García, J. Stat. Phys. 48 (1987) 1157.
[18] M. Malek Mansour, A.L. García, J.W. Turner, M. Mareschal, J. Stat. Phys. 52 (1988) 295.
[19] I. Bena, M. Malek Mansour, F. Baras, Phys. Rev. E 59 (1999) 5503.
[20] A.L. García, M. Malek Mansour, G.C. Lie, E. Clementi, J. Stat. Phys. 47 (1987) 209.
[21] J.M. Rubí, A. Díaz-Guilera, L. Torner, Physica A 141 (1987) 220.
[22] C. Z.-W. Liu, I. Oppenheim, J. Stat. Phys. 86 (1997) 179.
[23] A.L. García, G. Sonnino, M. Malek Mansour, J. Stat. Phys. 90 (1998) 1489.
[24] J.B. Swift, P.C. Hohenberg, Phys. Rev. A 15 (1977) 319.
[25] P.C. Hohenberg, J.B. Swift, Phys. Rev. A 46 (1992) 4773.
[26] R. Schmitz, E.G.D. Cohen, J. Stat. Phys. 39 (1985) 285.
[27] M.C. Cross, P.C. Hohenberg, Rev. Mod. Phys. 65 (1993) 851.
[28] P.N. Segrè, R.W. Gammon, J.V. Sengers, B.M. Law, Phys. Rev. A 45 (1992) 714.
[29] L.D. Landau, E.M. Lifshitz, Fluid Mechanics, Addison-Wesley, Reading, MA, 1959.
[30] D. Ronis, I. Procaccia, J. Machta, Phys. Rev. A 22 (1980) 714.
[31] I.S. Gradstein, I.M. Ryzhik, Tables of Integrals, Series and Products, 5th Edition, Academic Press, New York, 1994.
[32] L. Torner, J.M. Rubí, Phys. Rev. A 44 (1991) 1077.
[33] I. Pagonabarraga, J.M. Rubí, L. Torner, Physica A 173 (1991) 111.
[34] M. Malek Mansour, M. Mareschal, G. Sonnino, E. Kestemont, in: M. Mareschal, B. Holian (Eds.), Microscopic Simulations of Complex Hydrodynamic Phenomena, NATO ASI Series, Vol. 292, Plenum, London, 1992, p. 87.
[35] A. Suárez, J.P. Boon, P. Grosfils, Phys. Rev. E 54 (1996) 1208.
[36] W.B. Li, K.J. Zhang, J.V. Sengers, R.W. Gammon, J.M. Ortiz de Zárate, J. Chem. Phys. 112 (2000) 9139.
[37] B.J. Berne, R. Pecora, Dynamic Light Scattering, Wiley, New York, 1976.