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Light scattering from suspensions under external gradients

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We analyze the light-scattering spectrum of a suspension in a viscoelastic fluid under density and velocity gradients. When a density gradient is present, the dynamic structure factor exhibits universality in the sense that its expression depends only on the reduced frequency and the reduced density gradient. For a velocity gradient, however, the universality breaks down. In this last case we have found a transition point from one to three characteristic frequencies in the spectrum, which is governed by the value of the external gradient. The presence of the viscoelastic time scales introduces a shift in the "critical" point.

I. INTRODUCTION

Modern developments in optical technology have made light-scattering techniques a powerful tool in the investigation of the dynamic properties of a variety of complex systems such as suspensions,[1] colloidal dispersions,[2] or viscoelastic liquids.[3] Although light scattering occurs as a result of correlations over space and time in the fluctuations of the dielectric tensor of a condensed medium, the origin of these fluctuations strongly depends on both the specific features of the system and the nature of its state. For instance, it is well known that the light scattered in simple fluids in equilibrium arises from density fluctuations. The theory of this phenomenon was developed long ago, and its validity has been confirmed many times.[4,5] On the other hand, in the case of complex fluids the fluctuations of the local density as well as the anisotropy of the dielectric tensor give rise to the scattering properties of the system.[6] As a result, the scattered light is, for specific geometries, a superposition of two components, namely, an isotropic one due to the density fluctuations and an anisotropic contribution arising from orientational fluctuations.

Actually, the theoretical treatment of light scattering from complex fluids has taken two basic approaches. On the one hand, statistical-mechanical formulations of the Mori-Zwanzig[7] type have been extensively used to describe light scattering from viscoelastic liquids.[8] On the other hand, from a macroscopic point of view, different phenomenological theories have been formulated for the same purpose. In fact, one of the first approaches within this latter class of theories treats liquids consisting of anisotropic molecules as relaxing solids.[9] In this theory, the fluctuations of the dielectric tensor are due to deformations, temperature fluctuations, and to the internal relaxation of parameters in the system. Other phenomenological descriptions are built upon irreversible thermodynamics and consider that in order to describe highly dispersive systems additional variables should be introduced to characterize the relaxing processes occurring in them.[10–13]

Although the hydrodynamical theory describing the observed spectra generated by equilibrium fluctuations is well established,[5,14] the corresponding theory for nonequilibrium fluctuations in simple and complex media is still being developed. A large variety of approaches has been used to study fluctuations away from equilibrium,[14,15] however, among these, fluctuating hydrodynamics has been particularly fruitful in describing those processes near equilibrium for many physical systems.[16] The main purpose of this paper is to use this latter approach to study the light-scattering properties of a dilute suspension of spherical particles immersed in a viscoelastic (Maxwell) solvent. The system is driven to a nonequilibrium steady state through the action of a hydrodynamic flow and a concentration gradient separately. More specifically, we first calculate the nonequilibrium density correlation function for the suspension and, in terms of it, we subsequently evaluate the dynamic structure factor of the isotropic component of the spectrum. We find that in the case of a density gradient, the Rayleigh central line is no longer symmetric, with a maximum shifted with respect to its equilibrium position by an amount determined by the magnitude of the density gradient and the viscoelastic relaxation time scales. We will also show that in the case in which the distribution of particles is spatially homogeneous but the system is subjected to a stationary Couette flow,[17,18] the central line may also display a dip whose depth and width depend on the magnitude of the velocity gradient generating the flow as well as the viscoelastic characteristic of the suspension.

The paper is organized as follows. In Sec. II the model is defined and the equations governing the stochastic dynamics of the suspended particles and the solvent are set up. The specific nonequilibrium states generated by the externally imposed gradients are identified as stationary states of these dynamical equations. Then, in Sec. III the density correlation functions are calculated to different orders in the magnitude of these gradients and the corresponding structure factor is evaluated. In Sec. IV the features of the obtained spectra are analyzed for the case of Brownian particles moving through a Maxwell viscoelastic fluid.

II. GOVERNING EQUATIONS

Consider a dilute suspension of noninteracting identical particles of mass m and radius a moving through a viscoelastic solvent which itself may flow with velocity $\mathbf{v}(\mathbf{r},t)$. Furthermore, since in general a fluid may be regarded as incompressible if the temperature perturbations are sufficiently small,[19] under isothermal conditions we may consider the solvent to be incompressible. Hence, if the suspension is so diluted that the presence of the particles does not appreciably perturb the motion of the fluid, the dynamics of the latter is described by

$$\nabla\cdot\mathbf{v}=0 \tag{2.1}$$

and

$$\rho\left[\frac{\partial\mathbf{v}}{\partial t}+\mathbf{v}\cdot\nabla\mathbf{v}\right]=-\nabla p+\int_{-\infty}^{t}\eta(t-t')\nabla^2\mathbf{v}(\mathbf{r},t')dt' . \tag{2.2}$$

Here $\rho(\mathbf{r},t)$ and $p(\mathbf{r},t)$ denote, respectively, the mass density and the hydrodynamic pressure of the fluid and $\eta(t)$ is the time-dependent shear viscosity.

Let us now turn our attention to the suspended particles. If no chemical reaction occurs, the number of particles is conserved and their local number density $n(\mathbf{r},t)$ obeys the conservation equation

$$\frac{\partial n(\mathbf{r},t)}{\partial t}+\nabla\cdot\mathbf{J}(\mathbf{r},t)=0 , \tag{2.3}$$

where $\mathbf{J}(\mathbf{r},t)$ is the flux of particles given by

$$\mathbf{J}(\mathbf{r},t)=-\int_{-\infty}^{t}D(t-t')\nabla n(\mathbf{r},t')dt'+n(\mathbf{r},t)\mathbf{v}(\mathbf{r},t) . \tag{2.4}$$

The first term on the right-hand side is the diffusive flux, which generalizes the usual Fick's law by allowing the diffusion coefficient $D(t)$ to depend on the previous times, $t'<t$, due to the viscoelasticity of the suspension. Clearly, the explicit time dependence of D is determined by both, the properties of the suspended particles and the type of viscoelasticity of the fluid. On the other hand, the second term on the right-hand side of (2.4) is the convective flux of particles due to the state of flow of the solvent. Thus from Eqs. (2.1), (2.3), and (2.4) the diffusion equation describing the time evolution of $n(\mathbf{r},t)$ is

$$\frac{\partial n(\mathbf{r},t)}{\partial t}+\mathbf{v}(\mathbf{r},t)\cdot\nabla n(\mathbf{r},t)=\int_{-\infty}^{t}D(t-t')\nabla^2 n(\mathbf{r},t')dt' . \tag{2.5}$$

The stationary solutions of Eqs. (2.1), (2.2), and (2.5) correspond to nonequilibrium steady states determined by the boundary conditions imposed on the system. Here we shall only analyze those nonequilibrium states corresponding to the following stationary solutions, that is, a concentration gradient ∇n_s in a fluid at rest for which

$$\begin{aligned} n_s(\mathbf{r})&=n_0+\mathbf{r}\cdot\nabla n_s , \\ \mathbf{v}_s(\mathbf{r})&=0 , \end{aligned} \tag{2.6}$$

and Couette flow for the unperturbed solvent with homogeneous distribution of particles n_0,

$$\begin{aligned} n_s(\mathbf{r})&=n_0 , \\ \mathbf{v}_s(\mathbf{r})&=\mathbf{r}\cdot\nabla\mathbf{v}_s , \end{aligned} \tag{2.7}$$

with constant pressure

$$p_s(\mathbf{r},t)=\text{const} , \tag{2.8}$$

where $\nabla\mathbf{v}_s$ is defined as

$$\nabla\mathbf{v}_s=\beta\begin{bmatrix}0&0&0\\1&0&0\\0&0&0\end{bmatrix} , \tag{2.9}$$

β being the constant shear rate. The deviations from this steady state will be denoted by δ,

$$\delta n(\mathbf{r},t)=n(\mathbf{r},t)-n_s(\mathbf{r}) , \tag{2.10}$$

$$\delta\mathbf{v}(\mathbf{r},t)=\mathbf{v}(\mathbf{r},t)-\mathbf{v}_s(\mathbf{r}) . \tag{2.11}$$

Within the framework of Landau-Lifshitz fluctuating hydrodynamics,[19] we shall now introduce fluctuations into the dynamic equations (2.2) and (2.5). This is accomplished just by adding a momentum-fluctuating source $\overleftrightarrow{\Pi}^R(\mathbf{r},t)$ into (2.2) and a stochastic current $\mathbf{J}^R(\mathbf{r},t)$ to the flux (2.4). If in addition we linearize the resulting equations with respect to the deviations (2.10) and (2.11), we arrive at the Navier-Stokes-Langevin equation

$$\rho\left[\frac{\delta\delta\mathbf{v}}{\partial t}+\mathbf{v}_s\cdot\nabla\delta\mathbf{v}+\delta\mathbf{v}\cdot\nabla\mathbf{v}_s\right] =-\nabla p+\int_{-\infty}^{t}\eta(t-t')\nabla^2\delta\mathbf{v}(\mathbf{r},t')dt'+\nabla\cdot\overleftrightarrow{\Pi}^R(\mathbf{r},t) , \tag{2.12}$$

together with the incompressibility condition

$$\nabla\cdot\delta\mathbf{v}=0 \tag{2.13}$$

and at the fluctuating diffusion equation

$$\frac{\partial \delta n}{\partial t}+\mathbf{v}_s\cdot\nabla\delta n+\delta\mathbf{v}\cdot\nabla n_s =\int_{-\infty}^{t} D(t-t')\nabla^2\delta n(\mathbf{r},t')dt'-\nabla\cdot\overleftrightarrow{J}^R(\mathbf{r},t) \ . \tag{2.14}$$

Notice that $D(t-t')$ represents the bare diffusion coefficient; consequently, $\mathbf{J}^R$ and $\delta\mathbf{v}$ are not coupled. The influence of the convective term, however, can be considered in a renormalized diffusion coefficient.[20] When particles are Brownian the bare diffusion coefficient is zero; therefore diffusion comes from velocity fluctuations.[21] The fluctuating sources are stochastic processes with zero mean

$$\begin{aligned}&\langle \overleftrightarrow{\Pi}^R(\mathbf{r},t)\rangle=0 \ ,\\ &\langle \mathbf{J}^R(\mathbf{r},t)\rangle=0 \ ,\end{aligned} \tag{2.15}$$

and satisfy the following fluctuation-dissipation theorems:

$$\langle \Pi^R_{ij}(\mathbf{r},t)\Pi^R_{lm}(\mathbf{r}',t')\rangle=2k_BT\eta(|t-t'|)\delta(\mathbf{r}-\mathbf{r}')\Delta_{ijlm} \ , \tag{2.16}$$

$$\langle \mathbf{J}^R(\mathbf{r},t)\mathbf{J}^R(\mathbf{r}',t')\rangle=2n_s(\mathbf{r})D(|t-t'|)\delta(\mathbf{r}-\mathbf{r}')\overleftrightarrow{1} \ , \tag{2.17}$$

where T is the equilibrium temperature $\overleftrightarrow{1}$ the unit tensor, and

$$\Delta_{ijlm}=\delta_{il}\delta_{jm}+\delta_{im}\delta_{jl}-\tfrac{2}{3}\delta_{ij}\delta_{lm} \ . \tag{2.18}$$

In order to calculate, in Sec. III, the density correlation functions, it is convenient to recast the stationary solutions (2.6) and (2.7) in the form[16]

$$\begin{aligned}&n_s(\mathbf{r})=n_0+\tilde{n}\sin(\mathbf{q}_1\cdot\mathbf{r}) \ ,\\ &\mathbf{v}_s(\mathbf{r})=\tilde{\mathbf{v}}\sin(\mathbf{q}_2\cdot\mathbf{r}) \ ,\end{aligned} \tag{2.19}$$

where we have identified

$$\begin{aligned}&\mathbf{q}_1\tilde{n}=\nabla n_s \ ,\\ &\mathbf{q}_2\tilde{\mathbf{v}}=\nabla\mathbf{v}_s \ .\end{aligned} \tag{2.20}$$

It is clear that up to first order in $\mathbf{q}_1$ and $\mathbf{q}_2$, Eqs. (2.19) reduce to (2.6) and (2.7), respectively. However, it is easier to carry out the calculations using (2.19) and to take the above limit at the end. Furthermore, if we define the Fourier transform of an arbitrary field $A(\mathbf{r},t)$ as

$$A(\mathbf{k},\omega)=\int d\mathbf{r}\int_{-\infty}^{\infty} dt\, e^{-\mathbf{k}\cdot\mathbf{r}}e^{i\omega t}A(\mathbf{r},t) \tag{2.21}$$

in $(\mathbf{k},\omega)$ space Eqs. (2.19) read

$$n_s(\mathbf{k})=(2\pi)^3\left[n_0\delta(\mathbf{k})+\frac{\tilde{n}}{2i}[\delta(\mathbf{k}-\mathbf{q}_1)-\delta(\mathbf{k}+\mathbf{q}_1)]\right] \ , \tag{2.22}$$

$$\mathbf{v}_s(\mathbf{k})=(2\pi)^3\frac{\tilde{\mathbf{v}}}{2i}[\delta(\mathbf{k}-\mathbf{q}_2)-\delta(\mathbf{k}+\mathbf{q}_2)] \ . \tag{2.23}$$

Similarly, the Fourier transforms of Eqs. (2.12), (2.13), and (2.14) are, respectively,

$$\delta\mathbf{v}(\mathbf{k},\omega)=G^{v}(\mathbf{k},\omega)(\overleftrightarrow{1}-\hat{\mathbf{k}}\hat{\mathbf{k}})\cdot\{i\mathbf{k}\cdot\overleftrightarrow{\Pi}^R(\mathbf{k},\omega)-\rho\nabla n_s\cdot\delta\mathbf{v}(\mathbf{k},\omega)+\tfrac{1}{2}\rho\tilde{\mathbf{v}}\cdot\mathbf{k}[\delta\mathbf{v}(\mathbf{k}+\mathbf{q}_2,\omega)-\delta\mathbf{v}(\mathbf{k}-\mathbf{q}_2,\omega)]\} \ , \tag{2.24}$$

$$\mathbf{k}\cdot\delta\mathbf{v}(\mathbf{k},\omega)=0 \ , \tag{2.25}$$

$$\delta n(\mathbf{k},\omega)=G(\mathbf{k},\omega)\{\tfrac{1}{2}\tilde{\mathbf{v}}\cdot\mathbf{k}[\delta n(\mathbf{k}+\mathbf{q}_2,\omega)-\delta n(\mathbf{k}-\mathbf{q}_2,\omega)]-\nabla n_s\cdot\delta\mathbf{v}(\mathbf{k},\omega)-i\mathbf{k}\cdot\mathbf{J}^R(\mathbf{k},\omega)\} \ . \tag{2.26}$$

Here $\hat{\mathbf{k}}$ is the unit vector along the direction of $\mathbf{k}$ and

$$G^{v}(\mathbf{k},\omega)=[-i\omega\rho+\eta(\omega)k^2]^{-1} \ , \tag{2.27}$$

$$G(\mathbf{k},\omega)=[-i\omega+D(\omega)k^2]^{-1} \tag{2.28}$$

are the Green functions in Fourier space associated with Eqs. (2.12) and (2.14). Also, from Eqs. (2.16) and (2.17) it follows that the fluctuation-dissipation theorems read in Fourier space

$$\langle \mathbf{J}^R(\mathbf{k},\omega)\mathbf{J}^R(\mathbf{k}',\omega')\rangle =2(2\pi)\mathrm{Re}[D(\omega)]\,n_s(\mathbf{k}+\mathbf{k}')\,\delta(\omega+\omega')\overleftrightarrow{1} \ , \tag{2.29}$$

$$\langle \Pi^R_{ij}(\mathbf{k},\omega)\Pi^R_{lm}(\mathbf{k}',\omega')\rangle =2(2\pi)^4k_BT\,\mathrm{Re}[\eta(\omega)]\delta(\omega+\omega')\delta(\mathbf{k}+\mathbf{k}')\Delta_{ijlm} \ . \tag{2.30}$$

It should be pointed out that to arrive at Eq. (2.24) we have applied the operator $(\overleftrightarrow{1}-\hat{\mathbf{k}}\hat{\mathbf{k}})$ to the equation obtained after Fourier transforming (2.12). Furthermore, use has been made of the fact that $\tilde{\mathbf{v}}\cdot\mathbf{q}_2=0$, which follows from the incompressible nature of the solvent.

III. NONEQUILIBRIUM CORRELATION FUNCTIONS AND DYNAMIC STRUCTURE FACTOR

Our purpose in this section is to calculate the density correlation functions in three different situations, corresponding to equilibrium and to the stationary states given by Eqs. (2.6) and (2.7), respectively. From these correlation functions we will proceed to obtain the dynamic structure factor which becomes the relevant quantity when dealing with nonequilibrium fluctuation theories, because it can be compared with the experiments.

A. Dynamic Structure Factor in equilibrium

Equilibrium can be reached when all the gradients are zero (in our notation $\tilde{\mathbf{v}}=0$ and $\tilde{n}=0$), then (2.26) transforms into

$$\delta n(\mathbf{k},\omega)=G(\mathbf{k},\omega)[-i\mathbf{k}\cdot\mathbf{J}^R(\mathbf{k},\omega)] \ , \tag{3.1}$$

with

$$\langle \mathbf{J}^R(\mathbf{k},\omega)\mathbf{J}^R(\mathbf{k}',\omega')\rangle =2(2\pi)^4n_0\mathrm{Re}[D(\omega)]\delta(\mathbf{k}+\mathbf{k}')\delta(\omega+\omega')\overleftrightarrow{1} \ . \tag{3.2}$$

Squaring and averaging (3.1) we obtain

$$\langle \delta n(\mathbf{k},\omega)\delta n(\mathbf{k}',\omega')\rangle = 2(2\pi)^4 \mathrm{Re}[D(\omega)] n_0(-\mathbf{k}\cdot\mathbf{k}')G(\mathbf{k},\omega)G(\mathbf{k}',\omega') \times \delta(\mathbf{k}+\mathbf{k}')\delta(\omega+\omega) \; . \tag{3.3}$$

The only nonzero contribution of Eq. (3.3) to the structure factor is given by $\mathbf{k}'=-\mathbf{k}$ and $\omega'=-\omega$. We then obtain

$$S_{\mathrm{eq}}(\mathbf{k},\omega)\langle \delta n(\mathbf{k},\omega)\delta n(-\mathbf{k},-\omega)\rangle = 2(2\pi)^4 n_0 \delta^4(0) k^2 \mathrm{Re}[D(\omega)]G(\mathbf{k},\omega)G^*(\mathbf{k},\omega) \; , \tag{3.4}$$

where $S_{\mathrm{eq}}(\mathbf{k},\omega)$ is the dynamic structure factor in equilibrium and the asterisk denotes the complex conjugate.

B. Dynamic structure factor in the case of a density gradient

In this case the density fluctuations follows from Eq. (2.26) by setting $\tilde{\mathbf{v}}$ equal to zero. Then one arrives at

$$\delta n(\mathbf{k},\omega) = G(\mathbf{k},\omega)[-i\mathbf{k}\cdot\mathbf{J}^R(\mathbf{k},\omega) - \nabla n_s \cdot \delta\mathbf{v}(\mathbf{k},\omega)] \; . \tag{3.5}$$

The fluctuation-dissipation theorem given in (2.29) is now

$$\langle \mathbf{J}^R(\mathbf{k},\omega)\mathbf{J}^R(\mathbf{k}',\omega')\rangle = 2(2\pi)^4 \mathrm{Re}[D(\omega)]\delta(\omega+\omega')\overleftrightarrow{1}\left[n_0\delta(\mathbf{k}+\mathbf{k}') + \frac{\tilde{n}}{2i}[\delta(\mathbf{k}+\mathbf{k}'-\mathbf{q}_1) - \delta(\mathbf{k}+\mathbf{k}'+\mathbf{q}_1)]\right] \; , \tag{3.6}$$

where use has been made of (2.22). The nonequilibrium density correlation function is obtained following the same procedure outlined in Sec. III A. Using the fact that $\mathbf{J}^R$ and $\delta\mathbf{v}$ are uncoupled, we obtain

$$\langle \delta n(\mathbf{k},\omega)\delta n(\mathbf{k}',\omega')\rangle = G(\mathbf{k},\omega)G(\mathbf{k}',\omega')[-\mathbf{k}\cdot\langle \mathbf{J}^R(\mathbf{k},\omega)\mathbf{J}^R(\mathbf{k}',\omega')\rangle\cdot\mathbf{k}' + \nabla n_s\cdot\langle \delta\mathbf{v}(\mathbf{k},\omega)\delta\mathbf{v}(\mathbf{k}',\omega)\rangle\cdot\nabla n_s] \; . \tag{3.7}$$

Clearly, in the case of tagged particles the nonequilibrium state of the system introduces a coupling between δn and $\delta\mathbf{v}$ through ∇n_s. However, as shown in (3.6), $\langle \delta n(\mathbf{k},\omega)\delta n(\mathbf{k}',\omega')\rangle$ also depends on ∇n_s through the correlation of the stochastic fluxes. This dependence is of first order in the density gradient, while the coupling with the velocity fluctuations is of second order. For small gradients, this last term turns out to be negligible in front of the first-order contribution. Then we obtain

$$\langle \delta n(\mathbf{k},\omega)\delta n(\mathbf{k}',\omega')\rangle = -G(\mathbf{k},\omega)G(\mathbf{k}',\omega')\left[2(2\pi)^4\mathrm{Re}[D(\omega)]\delta(\omega+\omega')\mathbf{k}\cdot\mathbf{k}'\left[n_0\delta(\mathbf{k}+\mathbf{k}') + \frac{\tilde{n}}{2i}\sum_{\epsilon=\pm 1}\epsilon\,\delta(\mathbf{k}+\mathbf{k}'-\epsilon\mathbf{q}_1\right]\right] \; . \tag{3.8}$$

Notice that the first term on the right-hand side (rhs) yields an equilibrium contribution identical to (3.3). Then, in this section we will calculate only the nonequilibrium contributions, that is, those proportional to ∇n_s through $\tilde{n}$. In order to arrive at the spectral density, we have to substitute

$$\mathbf{k}\to\mathbf{k}+\frac{\epsilon\mathbf{q}_1}{2} \; , \quad \mathbf{k}'\to\mathbf{k}'+\frac{\epsilon\mathbf{q}_1}{2} \tag{3.9}$$

in the nonequilibrium part of (3.8). We then get the nonequilibrium part

$$\langle \delta n(\mathbf{k},\omega)\delta n(\mathbf{k}',\omega')\rangle_{\nabla n} = -\sum_{\epsilon=\pm 1}\epsilon 2(2\pi)^4\mathrm{Re}[D(\omega)]\delta(\omega+\omega')\delta(\mathbf{k}+\mathbf{k}')\frac{\tilde{n}}{2i}\left[\mathbf{k}+\frac{\epsilon\mathbf{q}_1}{2}\right]\cdot\left[\mathbf{k}'+\frac{\epsilon\mathbf{q}_1}{2}\right] \times G\left[\mathbf{k}+\frac{\epsilon\mathbf{q}_1}{2},\omega\right]G\left[\mathbf{k}'+\frac{\epsilon\mathbf{q}_1}{2},\omega'\right] \; . \tag{3.10}$$

From Eq. (3.10) one can see that the nonzero contributions to the structure factor verify $\mathbf{k}+\mathbf{k}'=0$ and $\omega+\omega'=0$. Making use of Eq. (2.28), Eqs. (3.4) and (3.10), we finally arrive at the dynamic structure factor

$$S(\mathbf{k},\omega) = \langle \delta n(\mathbf{k},\omega)\delta n(-\mathbf{k},-\omega)\rangle_{\mathrm{eq}} + \langle \delta n(\mathbf{k},\omega)\delta n(-\mathbf{k},-\omega)\rangle_{\nabla n} = \frac{2(2\pi)^4\mathrm{Re}[D(\omega)]n_0\delta^4(0)k^2}{[-i\omega+D(\omega)k^2][i\omega+D^*(\omega)k^2]}\left[1-\frac{2\omega\,\mathrm{Re}[D(\omega)]\mathbf{k}\cdot\nabla n_s/n_0}{[-i\omega+D(\omega)k^2][i\omega+D^*(\omega)k^2]}\right] \; . \tag{3.11}$$

This last expression is analogous with the one corresponding to the case in which a temperature gradient is present in the system.[16] Our result (3.11) deserves some comments. Due to the fact that $D(t)$ has to be a real quantity, $D(-\omega)=D^*(\omega)$; then, $\mathrm{Re}[D(-\omega)] = \mathrm{Re}[D(\omega)]$, that is, $\mathrm{Re}[D(\omega)]$ is an even function of the frequency. Using the same kind of arguments one can see that $G(\mathbf{k},\omega)G^*(\mathbf{k},\omega)$ also is an even function of ω. According to this, we can conclude that the nonequilibrium correction is an odd function of ω that introduces an asymmetry in the shape of the structure factor, shifting the maximum to the region of negative frequencies. The shape and the magnitude of this shift depends, clearly, on the density gradient and the viscoelastic time scales involved in $D(\omega)$.

C. Dynamic structure factor in the case of a velocity gradient

The case in which the fluid is under flow is a much more interesting situation. To single out the effect of the external gradient let us consider the steady state given in Eqs. (2.7). In this case, the density fluctuations can be obtained from (2.26) with $\nabla n_s=0$,

$$\delta n(\mathbf{k},\omega)=-G(\mathbf{k},\omega)\left[\frac{1}{2}\mathbf{k}\cdot\tilde{\mathbf{v}}\sum_{\epsilon=\pm1}\epsilon\,\delta n(\mathbf{k}-\epsilon\mathbf{q}_2,\omega)+i\mathbf{k}\cdot\mathbf{J}^R(\mathbf{k},\omega)\right]. \tag{3.12}$$

Setting $\tilde{n}=0$ in Eq. (2.22) and substituting it in the fluctuation-dissipation theorem given in Eq. (2.29), it reduces to

$$\langle\mathbf{J}^R(\mathbf{k},\omega)\mathbf{J}^R(\mathbf{k}',\omega')\rangle=2(2\pi)^4 n_0\mathrm{Re}[D(\omega)]\delta(\omega+\omega')\delta(\mathbf{k}+\mathbf{k}')\overleftrightarrow{1}\,. \tag{3.13}$$

Notice from Eq. (3.12) that $\delta n(\mathbf{k},\omega)$ is coupled with the shifted modes $\delta n(\mathbf{k}-\epsilon\mathbf{q}_2,\omega)$ through the velocity gradient. In this situation we can formally solve Eq. (3.12) as an expansion in powers of the velocity gradient[22] $\nabla\mathbf{v}_s$ through $\tilde{\mathbf{v}}$. Up to second order, we have

$$\delta n^{(0)}(\mathbf{k},\omega)=-G(\mathbf{k},\omega)i\mathbf{k}\cdot\mathbf{J}^R(\mathbf{k},\omega)\,, \tag{3.14}$$

$$\delta n^{(1)}(\mathbf{k},\omega)=-\frac{\mathbf{k}\cdot\tilde{\mathbf{v}}}{2i}\sum_{\epsilon=\pm1}\epsilon G(\mathbf{k},\omega)G(\mathbf{k}-\epsilon\mathbf{q}_2,\omega)(\mathbf{k}-\epsilon\mathbf{q}_2)\cdot\mathbf{J}^R(\mathbf{k}-\epsilon\mathbf{q}_2,\omega)\,, \tag{3.15}$$

$$\delta n^{(2)}(\mathbf{k},\omega)=-\frac{i}{4}\sum_{\epsilon,\epsilon'=\pm1}\epsilon\epsilon'\{G(\mathbf{k},\omega)G(\mathbf{k}-\epsilon'\mathbf{q}_2,\omega)G(\mathbf{k}-(\epsilon+\epsilon')\mathbf{q}_2,\omega)(\mathbf{k}\cdot\tilde{\mathbf{v}})^2[\mathbf{k}-(\epsilon+\epsilon')\mathbf{q}_2]\cdot\mathbf{J}^R(\mathbf{k}-(\epsilon+\epsilon')\mathbf{q}_2,\omega)\}\,. \tag{3.16}$$

From these formal solutions one may obtain the density correlation functions. Up to quadratic order in $\tilde{\mathbf{v}}$ one has

$$\begin{aligned}\langle\delta n(\mathbf{k},\omega)\delta n(\mathbf{k}',\omega')\rangle={}&\langle\delta n^{(0)}(\mathbf{k},\omega)\delta n^{(0)}(\mathbf{k}',\omega')\rangle+\langle\delta n^{(0)}(\mathbf{k},\omega)\delta n^{(1)}(\mathbf{k}',\omega')\rangle+\langle\delta n^{(1)}(\mathbf{k},\omega)\delta n^{(0)}(\mathbf{k}',\omega)\rangle\\&+\langle\delta n^{(1)}(\mathbf{k},\omega)\delta n^{(1)}(\mathbf{k}',\omega')\rangle+\langle\delta n^{(0)}(\mathbf{k},\omega)\delta n^{(2)}(\mathbf{k}',\omega')\rangle+\langle\delta n^{(2)}(\mathbf{k},\omega)\delta n^{(0)}(\mathbf{k}',\omega')\rangle+O(\tilde{\mathbf{v}})^3\,.\end{aligned} \tag{3.17}$$

The first term on the rhs corresponds to the equilibrium density correlation function which was given by Eq. (3.3). Its contribution to the structure factor is identical to (3.4). The second and third terms are the first-order contribution to the structure factor. They can be calculated by following a similar procedure to that leading to Eq. (3.11). We find that these first-order terms vanish. The second-order contributions are represented by the fourth, fifth, and sixth terms on the rhs of (3.17). It turns out that from Eqs. (3.14)–(3.16) all the second-order contributions occurring in (3.17) are proportional to $\delta(\mathbf{k}+\mathbf{k}'-(\epsilon+\epsilon')\mathbf{q}_2)$. In order to obtain the contributions of these density correlation functions to the nonequilibrium structure factor, we follow the standard procedure introduced in Sec. III B. We substitute

$$\begin{aligned}\mathbf{k}&\to\mathbf{k}+\frac{(\epsilon+\epsilon')}{2}\mathbf{q}_2\,,\\ \mathbf{k}'&\to\mathbf{k}'+\frac{(\epsilon+\epsilon')}{2}\mathbf{q}_2\end{aligned} \tag{3.18}$$

into the terms of Eq. (3.17) that we are analyzing. The nonzero contribution to the structure factor is

$$\begin{aligned}S_\beta={}&\langle\delta n^{(1)}(\mathbf{k},\omega)\delta n^{(1)}(-\mathbf{k},-\omega)\rangle\\&+\langle\delta n^{(0)}(\mathbf{k},\omega)\delta n^{(2)}(-\mathbf{k},-\omega)\rangle\\&+\langle\delta n^{(2)}(\mathbf{k},\omega)\delta n^{(0)}(-\mathbf{k},-\omega)\rangle\,.\end{aligned} \tag{3.19}$$

To evaluate the above correlation functions we have to develop all the expressions up to second order in $\mathbf{q}_2$. An important simplification can be made if we specialize to the case in which $\mathbf{k}\cdot\mathbf{q}_2=0$. Using the definition of $G(\mathbf{k},\omega)$ given in Eq. (2.28) and denoting by c an unspecified constant coefficient, one obtains up to second order in $\mathbf{q}_2$,

$$G(\mathbf{k}\pm c\mathbf{q}_2,\omega)\to G(\mathbf{k},\omega)[1-c^2q_2^2D(\omega)G(\mathbf{k},\omega)]\,, \tag{3.20}$$

$$G(-\mathbf{k}\pm c\mathbf{q}_2,-\omega)\to G^*(\mathbf{k},\omega)[1-c^2q_2^2D^*(\omega)G^*(\mathbf{k},\omega)]\,.$$

Taking all of these considerations into account, the first contribution gives

$$\langle\delta n^{(1)}(\mathbf{k},\omega)\delta n^{(1)}(-\mathbf{k},-\omega)\rangle=(2\pi)^4\mathrm{Re}[D(\omega)]n_0\delta^4(0)|G(\mathbf{k},\omega)|^4\beta^2k^2\,, \tag{3.21}$$

whereas the second contribution yields

$$\begin{aligned}\langle\delta n^{(0)}(\mathbf{k},\omega)\delta n^{(2)}(-\mathbf{k},-\omega)\rangle&=(2\pi)^4\mathrm{Re}[D(\omega)]n_0\delta^4(0)\beta^2k^2|G(\mathbf{k},\omega)|^2[G^*(\mathbf{k},\omega)]^2\\&\quad\times\{1-2k^2\mathrm{Re}[D(\omega)]G(\mathbf{k},\omega)\}\,.\end{aligned} \tag{3.22}$$

One can easily show that the remaining nonequilibrium term also is given from Eq. (3.22) replacing $\mathbf{k}$ by $-\mathbf{k}$ and

ω by $-\omega$. Since this amounts to conjugate the propagator $G(\mathbf{k},\omega)$, we have that

$$\langle \delta n^{(2)}(\mathbf{k},\omega)\delta n^{(0)}(-\mathbf{k},-\omega)\rangle = \langle \delta n^{(0)}(\mathbf{k},\omega)\delta n^{(2)}(-\mathbf{k},-\omega)\rangle^* . \tag{3.23}$$

Thus, putting together all the contributions given by Eqs. (3.4), (3.21), (3.22), and (3.23), we arrive at the final expression for the dynamic structure factor

$$\begin{aligned} S(\mathbf{k},\omega) &= S_{\mathrm{eq}}(\mathbf{k},\omega)+S_{\beta}(\mathbf{k},\omega) \\ &= 2(2\pi)^4 n_0 \mathrm{Re}[D(\omega)]\delta^4(0)k^2|G(\mathbf{k},\omega)|^2 \\ &\quad \times[1+\tfrac{1}{2}\beta^2(|G(\mathbf{k},\omega)|^2+2\,\mathrm{Re}[G^{*2}(\mathbf{k},\omega)] \\ &\quad \times\{1-2k^2\mathrm{Re}[D(\omega)G(\mathbf{k},\omega)]\})] . \end{aligned} \tag{3.24}$$

Expression (3.24) is general because it does not depend on the form of $D(\omega)$. A discussion of a particular case corresponding to a simple viscoelastic model will be included in Sec. IV.

IV. DISCUSSION OF THE RESULTS

In order to analyze the effect of the external gradients in the suspensions we will specialize to the case in which the suspended particles are Brownian and the viscoelastic fluid follows Maxwell's rheological equation of state, characterized by a single relaxation time. This case is interesting because one can obtain a simple expression for $D(\omega)$ which depends on the frequency through both the nonstationary motion of the particles and the viscoelasticity of the fluid.

Our first goal will be the obtention of $D(\omega)$ for a dilute suspension of spherical identical Brownian particles. It is possible to show that the hydrodynamic force exerted by a viscoelastic fluid of frequency-dependent viscosity $\eta(\omega)$ on a spherical particle of radius a moving with velocity $\mathbf{u}(\omega)$ is given by

$$\begin{aligned} \mathbf{F}^H(\omega) &= 6\pi\eta(\omega)a[1+\alpha(\omega)a+\tfrac{1}{9}\alpha^2(\omega)a^2]\mathbf{u}(\omega) \\ &= \xi(\omega)\mathbf{u}(\omega) , \end{aligned} \tag{4.1}$$

where $\xi(\omega)$ defines the frequency-dependent friction coefficient and α is the inverse penetration length

$$\alpha(\omega)=\left[\frac{-i\omega\rho}{\eta(\omega)}\right]^{1/2} . \tag{4.2}$$

Our result (4.1) constitutes a generalization for the expression of the force exerted by a Newtonian fluid on a particle.[23]

Now, we are able to write a Langevin equation for one isolated particle (provided that the suspension is diluted). As is well known, the forces acting on the particle are, on the one hand, the friction with the fluid due to the motion of the sphere and, on the other hand, the random force which originates in the internal fluctuations of the fluid. We then obtain

$$m\frac{d\mathbf{u}}{dt}=\mathbf{F}^H(t)+\mathbf{F}^R(t) , \tag{4.3}$$

or, in frequency representation,

$$-i\omega m\,\mathbf{u}(\omega)=\mathbf{F}^H(\omega)+\mathbf{F}^R(\omega) . \tag{4.4}$$

The random force $\mathbf{F}^R$ satisfies the fluctuation-dissipation theorem

$$\langle \mathbf{F}^R(t)\mathbf{F}^R(t')\rangle = 2k_B T\xi(|t-t'|)\overleftrightarrow{1} \tag{4.5}$$

or

$$\langle \mathbf{F}^R(\omega)\mathbf{F}^R(\omega')\rangle = 2(2\pi)k_B T\,\mathrm{Re}[\xi(\omega)]\delta(\omega+\omega')\overleftrightarrow{1} . \tag{4.6}$$

If we define the time-dependent diffusion coefficient as

$$D(t)=\tfrac{1}{3}\mathrm{Tr}[\langle \mathbf{u}(t)\mathbf{u}(0)\rangle]\Theta(t) , \tag{4.7}$$

where $\Theta(t)$ stands for the Heaviside function and the symbol Tr for the trace of the tensor, then, from Eqs. (4.3)–(4.7), making use of the causality principle, we obtain for $D(\omega)$

$$\begin{aligned} D(\omega) &= \tfrac{1}{3}\mathrm{Tr}\left[\int_0^\infty dt\, e^{i\omega t}\langle \mathbf{u}(t)\mathbf{u}(0)\rangle\right] \\ &= \frac{k_B T}{-i\omega m+\xi(\omega)} . \end{aligned} \tag{4.8}$$

At this point we will consider the viscoelastic model for the fluid, introduced through Maxwell's rheological equation of state[24]

$$\eta(t)=\frac{\eta_0}{\tau}e^{-t/\tau}\Theta(t) , \tag{4.9}$$

η_0 being the zero-frequency shear viscosity and τ the relaxation time characterizing the relaxation of the internal degrees of freedom of the fluid particles. The Fourier transform of Eq. (4.9) yields

$$\eta(\omega)=\frac{\eta_0}{1-i\omega\tau} . \tag{4.10}$$

For low frequencies (of the order of the relaxation of diffusion modes), the leading contribution to the frequency dependence of $D(\omega)$ is given by the viscoelastic nature of the solvent, the reason being the fact that in Eq. (4.1) αa is much smaller than 1 and, in Eq. (4.8), the term $i\omega m$ is smaller than $\xi(\omega)$. In other words, the time scale introduced by the relaxation of the perturbations of the fluid and the time scale due to the inertia of the particle are negligible compared with the time scales we are interested in. According to this, we finally arrive at

$$D(\omega)=\frac{k_B T}{6\pi\eta_0 a}(1-i\omega\tau)\equiv D_0(1-i\omega\tau) . \tag{4.11}$$

For future calculations it will be convenient to introduce the dimensionless quantities

$$\tilde{\omega}=\omega\frac{1+D_0k^2\tau}{D_0k^2}\equiv\frac{\omega}{\omega_0} , \tag{4.12}$$

$$\tilde{S}(\tilde{\omega})=S(\mathbf{k},\omega)\frac{D_0k^2}{2(2\pi)^4\delta^4(0)n_0} , \tag{4.13}$$

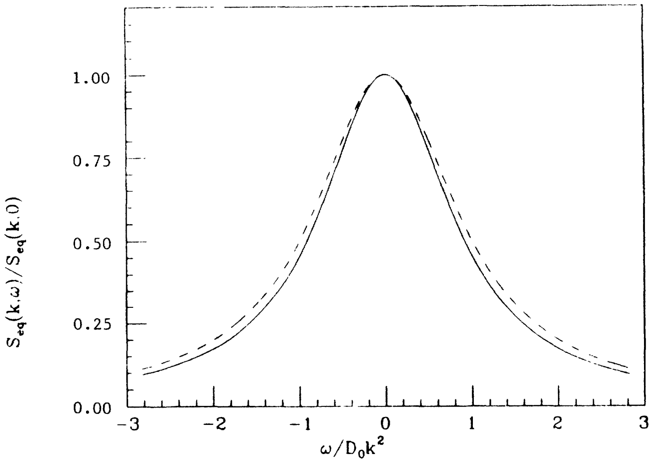

FIG. 1. Equilibrium dynamic structure factor is plotted vs frequency. The solid line corresponds to liquid salol at 80.2 °C ($\eta_0=11.54\times10^{-4}$ g cm^{-3}, and $\tau=89.9\times10^{-6}$ s, at the same temperature), $a=10^{-7}$ cm, and $k=10^{-5}$ cm. The dashed line gives the result for the Newtonian case ($\tau=0$).

$$|\nabla v_{\parallel}|=\frac{\mathbf{k}\cdot\nabla n_s/n_0}{k^2(1+D_0k^2\tau)} , \tag{4.14}$$

$$\tilde{\beta}=\frac{\beta}{D_0k^2} , \tag{4.15}$$

which will be useful to analyze the results obtained in Sec. III.

A. Equilibrium

The dynamic structure factor obtained in Eq. (3.4) can be expressed in terms of the quantities given in (4.12) and (4.13) as

$$\tilde{S}_{\rm eq}(\tilde{\omega})=\frac{1}{\tilde{\omega}^2+1} . \tag{4.16}$$

Clearly, in this case the presence of the viscoelastic time scale does not change the essential behavior of the suspension. In fact, the dynamic structure factor is a Lorentzian with a modified relaxation frequency for the diffusion modes: $D_0k^2\rightarrow D_0k^2/(1-D_0k^2\tau)$. If τ is much smaller than D_0k^2, no effect will be seen, but in the opposite case, the relaxation frequency of the diffusion modes will be slowed due to the coupling with the internal degrees of freedom of the fluid particles through τ. Notice that the maximum of the spectrum is placed at $\tilde{\omega}=0$ and any modification due to the new time scales can be found due to the fact that the viscoelasticity disappears when the frequency goes to zero (see Fig. 1).

B. Density gradient

The dynamic structure factor given in Eq. (3.11) can be also expressed in this case in terms of the dimensionless quantities introduced in Eqs. (4.12)–(4.14). We then obtain

$$\tilde{S}(\tilde{\omega})=\frac{1}{\tilde{\omega}^2+1}\left[1-2|\nabla v_{\parallel}|\frac{\tilde{\omega}}{\tilde{\omega}^2+1}\right] . \tag{4.17}$$

Thus we also conclude that (4.17) has the same form as in the case in which the carrier fluid is Newtonian. Due to the asymmetry introduced by the gradient, it is expected that the maximum of the dynamic structure factor is displaced with respect to its equilibrium position. To calculate the magnitude of this shift up to the lowest order in the density gradient we must derive $\tilde{S}(\omega)$ with respect to $\tilde{\omega}$ and equate it to zero. We then obtain the equation for the position of the maximum as a function of the dimensionless density gradient (see Fig. 2)

$$\tilde{\omega}\left[1-2|\nabla v_{\parallel}|\frac{\tilde{\omega}}{\tilde{\omega}^2+1}\right]+|\nabla v_{\parallel}|\left[\frac{1-\tilde{\omega}^2}{\tilde{\omega}^2+1}\right]=0 . \tag{4.18}$$

Up to first order in the density gradient one gets

$$\tilde{\omega}=-|\nabla v_{\parallel}| . \tag{4.19}$$

Therefore the maximum is shifted due to the presence of the density gradient by an amount proportional to this quantity, towards the region of negative frequencies. In order to see the effect of the viscoelastic time scales, we write (4.19) in terms of the old quantities

$$\omega=\frac{D_0\mathbf{k}\cdot\nabla n_s/n_0}{(1+D_0k^2\tau)^2} . \tag{4.20}$$

From (4.20) one can see that in the case in which $\tau\ll 1/D_0k^2$ the viscoelastic effect will be negligible and the maximum will be located at the same point as if the fluid were Newtonian. When $\tau\sim 1/D_0k^2$, however, the shift of the maximum is lowered because the relaxation time of the diffusion modes increases due to the presence of the viscoelastic time scale.

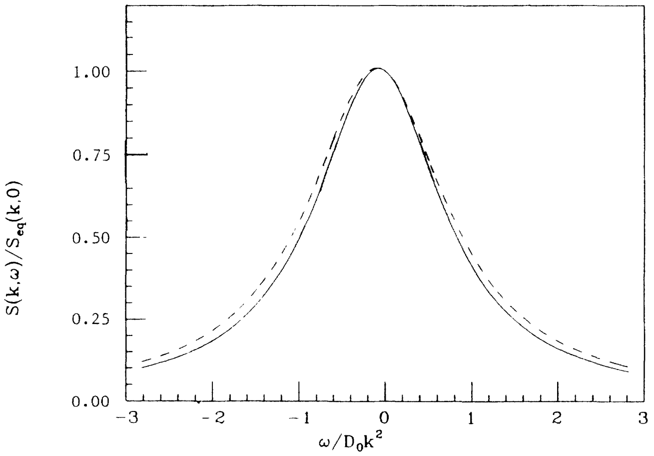

FIG. 2. Nonequilibrium structure factor for liquid salol in the presence of a density gradient [defined in (4.14)] $|\nabla v_{\parallel}|\sim10^{-1}$. The parameters are the same as in Fig. 1. The solid line corresponds to the viscoelastic case, while the dashed line refers to the Newtonian case.

C. Velocity gradient

The dynamic structure factor (3.24) reads (see Fig. 3)

$$\tilde{S}(\tilde{\omega})=\frac{1}{\tilde{\omega}^2+1}\left[1+\frac{1}{2}\tilde{\beta}^2\frac{\tilde{\omega}^4\lambda+\tilde{\omega}^2\gamma-1}{(\tilde{\omega}^2+1)^3}\right], \tag{4.21}$$

where use has been made of (4.12), (4.13), and (4.15) and

$$\begin{aligned}\lambda&=4\omega_0\tau-1 ,\\ \gamma&=6(1-\tfrac{2}{3}\omega_0\tau) .\end{aligned} \tag{4.22}$$

Notice that in this case, since the relaxation time enters the expression of the structure factor through λ and γ, (4.21) does not exhibit universality as in the preceding cases.

To proceed we will analyze the maximum of $\tilde{S}(\omega)$ as a function of the velocity gradient. Deriving $\tilde{S}(\tilde{\omega})$ with respect to $\tilde{\omega}$ and equating it to zero we find

$$\begin{aligned}&-\tilde{\omega}[(\tilde{\omega}^2+1)^3+\tfrac{1}{2}\tilde{\beta}^2(\tilde{\omega}^4\lambda+\tilde{\omega}^2\gamma-1)]\\ &\qquad+\tilde{\omega}\tfrac{1}{2}\tilde{\beta}^2[(2\lambda\tilde{\omega}^2+\gamma)(\tilde{\omega}^2+1)-3(\lambda\tilde{\omega}^4+\gamma\tilde{\omega}^2-1)]=0 .\end{aligned} \tag{4.23}$$

One solution of (4.23) is $\tilde{\omega}=0$. This solution also is present in equilibrium which means that there is no shift in the maximum of the structure factor due to the velocity gradient. However, the presence of a velocity gradient is responsible for new solutions of (4.23). This last equation gives

$$\begin{aligned}&-[(\tilde{\omega}^2+1)^3+\tfrac{1}{2}\tilde{\beta}^2(\tilde{\omega}^4\lambda+\tilde{\omega}^2\gamma-1)]\\ &\qquad+\tfrac{1}{2}\tilde{\beta}^2[(2\lambda\tilde{\omega}^2+\gamma)(\tilde{\omega}^2+1)-3(\lambda\tilde{\omega}^4+\gamma\tilde{\omega}^2-1)]=0 .\end{aligned} \tag{4.24}$$

Proceeding as in the case of the density gradient, we will find the lowest-order effect. To do that, we find the unperturbed solutions of (4.24),

$$\Omega=\pm i . \tag{4.25}$$

Substituting $\tilde{\omega}$ for Ω in all the terms proportional to the dimensionless velocity gradient, we finally obtain

$$\begin{aligned}\tilde{\omega}_{\pm}&=\pm 2^{2/3}(1-\omega_0\tau)^{1/6}\\ &\quad\times\left[\tilde{\beta}^{2/3}-\frac{1}{2^{4/3}(1-\omega_0\tau)^{1/3}}\right]^{1/2} .\end{aligned} \tag{4.26}$$

Notice that in the case in which

$$\tilde{\beta}>\frac{1}{4(1-\omega_0\tau)^{1/2}}\equiv\tilde{\beta}_c \tag{4.27}$$

the roots corresponding to (4.26) are real and the central maximum splits into two symmetric peaks creating a dip in the spectrum at $\tilde{\omega}=0$. This effect is present even for Newtonian fluids and is similar to what happens in the harmonic oscillator when computing the correlation function $\langle x(\omega)x(-\omega)\rangle$. In fact, in the overdamped case the maximum is centered at $\omega=0$, while in the oscillating case, the maximum also splits into two peaks centered at the frequency of the oscillations. From the preceding analysis we may conclude that the system exhibits a transition from one characteristic frequency ($\tilde{\omega}=0$) to three characteristic frequencies ($\tilde{\omega}=0$ and $\tilde{\omega}=\tilde{\omega}_{\pm}$). According to (4.26) and (4.27) the critical value of $\tilde{\beta}$ is $\tilde{\beta}_c=\frac{1}{4}$ for Newtonian fluids. The effect of the viscoelastic time scale is, on the one hand, to modify the positions of the maxima with respect to the Newtonian case, due to the lowering of the relaxation frequency of the diffusion modes. On the other hand, in view of (4.27), the effect is to modify the critical value of $\tilde{\beta}$, which tends to increase $\tilde{\beta}_c$ (see Fig. 4).

To conclude let us say some words about physical systems that could be used for testing our results. As far as we know, there are no experimental data available in the literature to check our results. However, according to our preceding analysis, experiments should be made using fluids with large relaxation times and low viscosities. A good candidate would be a suspension of spherical parti-

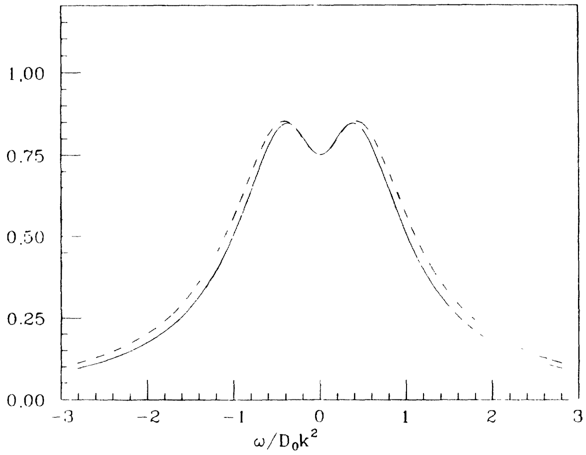

FIG. 3. Nonequilibrium structure factor for liquid salol in the presence of a velocity gradient [defined in (4.15)] $\tilde{\beta}=0.750$. Again, the parameters are those of Fig. 1. The solid line corresponds to the viscoelastic case, while the dashed line refers to the Newtonian case.

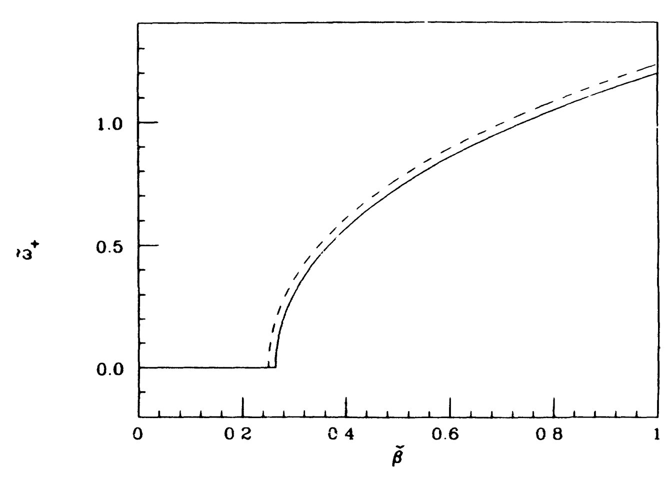

FIG. 4. Value of ω_+ is plotted as a function of $\tilde{\beta}$. The solid line corresponds to the viscoelastic fluid (salol), whereas the dashed line refers to the Newtonian case.

cles in liquid salol (the relevant parameters are those of Fig. 1). In the nonequilibrium situations, possible values for the external gradients belonging to the range of validity of our theory, have been proposed in Figs. 2 and 3.

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[1] P. N Pusey and R. J. A. Tough, in *Dynamic Light Scattering: Applications of Photon Spectroscopy,* edited by R. Pecora (Plenum, New York, 1985).

[2] W. van Megen and I. Snook, Adv. Colloid Interface Sci. **21**, 119 (1984).

[3] G. D. Patterson and A. Muñoz-Rojas, Ann. Rev. Phys. Chem. **38**, 191 (1987).

[4] L. Landau and G. Placzek, Phys. Z. Sowjetunion **5**, 172 (1934).

[5] B. J. Berne and R. Pecora, *Dynamic Light Scattering* (Wiley, New York, 1976).

[6] C. H. Wang, *Spectroscopy of Condensed Media* (Academic, New York, 1985).

[7] H. Mori, Prog. Theor. Phys. **33**, 423 (1965); R. Zwanzig, in *Lectures in Theoretical Physics,* edited by W. Brittin (Wiley-Interscience, New York, 1961), Vol. 3.

[8] H. A. Anderson and R. Pecora, J. Chem. Phys. **54**, 2584 (1971); Y. H. Lin and C. H. Wang, *ibid.* **70**, 681 (1979); R. A. MacPhail and D. Kivelson, *ibid.* **80**, 2102 (1984).

[9] S. M. Ritov, Zh. Eksp. Teor. Fiz. **33**, 166 (1957) [Sov. Phys.—JETP **32**, 1153 (1971)].

[10] R. F. Rodriguez, O. Manero, and M. Aguado, Phys. Rev. B **38**, 4827 (1988).

[11] A. Pérez-Madrid and J. M. Rubí, Physica A **147**, 152 (1987).

[12] B. Quéntrec and P. Bezot, Mol. Phys. **39**, 427 (1980).

[13] B. Quéntrec, Phys. Rev. A **15**, 1304 (1977).

[14] R. F. Fox, J. Phys. Chem. **86**, 2812 (1982); J. M. Rubí, in *Recent Developments in Nonequilibrium Thermodynamics: Fluids and Related Topics,* Vol. 253 of *Lecture Notes in Physics,* edited by J. Casas Vazquez, D. Jou and J. M. Rubí (Springer, Berlin, 1986).

[15] A. M. S. Tremblay in *Recent Developments in Nonequilibrium Thermodynamics,* Vol. 199 of *Lecture Notes in Physics,* edited by J. Casas-Vázquez, D. Jou, and G. Lebon (Springer, Berlin, 1984), and references therein.

[16] A. M. S. Tremblay, M. Arai and E. D. Siggia, Phys. Rev. A **23**, 1451 (1981).

[17] D. Ronis, Phys. Rev. A **29**, 1453 (1984).

[18] J. Machta, I. Oppenheim, and I. Procaccia, Phys. Rev. A **22**, 2809 (1980).

[19] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon, London, 1959).

[20] A. Díaz-Guilera, J. M. Rubí, and D. Bedeaux, Physica A **154**, 257 (1989).

[21] D. Bedeaux and P. Mazur, Physica A **73**, 431 (1974).

[22] *Lectures in Theoretical Physics,* Ref. 7, Chap. 17; A Pérez-Madrid and J. M. Rubí, Phys. Rev. A **33**, 2716 (1986).

[23] P. Mazur and D. Bedeaux, Physica A **76**, 235 (1974).

[24] R. B. Bird, C. F. Curtiss, R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids,* Vol. 1 of *Fluid Mechanics* (Wiley, New York, 1987).