

Rayleigh peak in a molecular fluid in the presence of a temperature gradient

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The study of fluctuations around nonequilibrium steady states has shown a very interesting behavior when we calculate the density-density correlation function. In particular, the intensity of the Rayleigh peak is enhanced as a consequence of a resonant coupling between the heat mode induced on the system by external means and the transversal velocity modes. Here we consider a kinetic model for a molecular fluid, obtain the equations of motion, and calculate such an effect. Our results reproduce the calculated and measured characteristics of the spectra and show in an explicit way how the internal degrees of freedom in the molecule modify the structure factor.

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I. INTRODUCTION

The coupling between hydrodynamical modes in a simple fluid has been extensively studied in the literature, when the system is near the equilibrium state. The influence of such couplings manifests itself through different aspects, such as the behavior of the density-density correlation function, the dispersion and absorption of sound, and some others [1–3]. In contrast, the behavior of such modes around a nonequilibrium steady state is a subject which is not completely understood, although some recent results have given some insight about the problems involved. It is a known result that hydrodynamic fluctuations around a nonequilibrium steady state (NESS) have an anomalous behavior measured by the wave vector dependence in the density-density correlation function [4–7]. In fact the steady state obtained by means of a fixed temperature gradient applied to the system has shown an asymmetry in the Brillouin peaks when the linear terms in the temperature gradient are considered. This effect, which has been corroborated in the experiment, is absent when the wave vector and the temperature gradient are perpendicular to each other [8]. This geometry offers us the opportunity to study the Rayleigh-Brillouin spectra beyond the linear regime. It has been shown that there exists an enhancement of the Rayleigh line because of a coupling between the transversal part of the velocity fluctuations and the temperature gradient applied to the system to maintain it in such a steady state [9]. This kind of behavior has been studied recently through several approaches, kinetic theory [10], mode-mode coupling theories [11], and fluctuating hydrodynamics [5,7,9,12]. This last approach has given a way to calculate a resonant coupling which in a simple fluid behaves as $|\langle \nabla T \rangle_0|^2/k^4$ in the Rayleigh peak. Besides, the intensity has been measured in an accurate way [13,14] and those measurements show how the calculations agree with qualitative behavior. On the other hand it seems that the quantitative comparison needs some correction factors taking into account the temperature dependence of transport coefficients as well as the inhomogeneities in the temperature field, to have a good

agreement [14].

Here we are interested in the calculation of the enhancement of the Rayleigh peak in the presence of an external temperature gradient by means of fluctuating hydrodynamics in a molecular fluid, in such a way that the internal degrees of freedom in the molecule will be taken into account in an explicit way.

Notice should be made that the behavior of a molecular fluid has been studied in the past when the fluctuations occur around the equilibrium state, and as a result there are some modifications in the light scattering spectra [15]. Also there has been some work concerning the nonequilibrium steady state for molecules having orientational fluctuations, which shows several interesting phenomena [16].

In contrast with earlier work we have introduced a kinetic model for a polyatomic molecule, based on the Wang-Chang-Uhlenbeck-De Boer equation (WCUB) and Grad's moments method of solution. The details of this model will be discussed in Sec. II. The model allows the construction of constitutive equations which contain in an explicit way the contribution of the internal degrees of freedom, as well as the introduction of the corresponding fluctuating hydrodynamic treatment. Section III is devoted to such a calculation. In Sec. IV we calculate the resonant Rayleigh peak produced by our model and, finally, in Sec. V we specify the results for the rough sphere model in a polyatomic gas.

II. KINETIC MODEL

The simplest generalization of the Boltzmann equation to take into account the internal degrees of freedom in a molecular fluid is the so called WCUB equation which considers in a semiclassical way the contribution to the inelastic binary collision taking place between molecules [17]. The description is then made through a one particle distribution function $f(\mathbf{c}, \alpha, \mathbf{x}, t)$ where \mathbf{c} is the molecular velocity and α is the set of quantum numbers or internal coordinates needed to describe the energy associated to the internal degrees of freedom. The WCUB equation in the absence of external forces is then given by

$$\frac{\partial f}{\partial t} + \mathbf{c} \cdot \nabla f = \sum_{\alpha_1, \alpha', \alpha'_1} \int (f' f'_1 - f f_1) |\mathbf{c}_1 - \mathbf{c}| I(|\mathbf{c}_1 - \mathbf{c}|, \alpha, \alpha_1; |\mathbf{c}'_1 - \mathbf{c}'|, \alpha', \alpha'_1) d\Omega d\mathbf{c}_1, \quad (1)$$

where $I(|\mathbf{c}_1 - \mathbf{c}|, \alpha, \alpha_1; |\mathbf{c}'_1 - \mathbf{c}'|, \alpha', \alpha'_1)$ is the cross section and $d\Omega$ the solid angle. The primes on the distribution function and the molecular velocity indicate that they are evaluated after the collision. Equation (1) takes into account the change in the internal degrees of freedom caused by collision through the distribution function and the value of the cross section.

This equation is solved by Grad's method taking an expansion around the local equilibrium distribution function of the system

$$f^{(0)}(\mathbf{c}, \alpha, \mathbf{x}, t) = \frac{n}{Z} \left[\frac{m}{2\pi k_B T} \right]^{3/2} \exp \left[-\frac{m\mathbf{C}^2}{2k_B T} - \frac{E_\alpha}{k_B T} \right], \quad (2)$$

where

$$Z = \sum_{\alpha} \exp \left[-\frac{E_\alpha}{k_B T} \right] \quad (3)$$

is the corresponding partition function associated with the internal degrees of freedom in local equilibrium [18,19]. Here

$$n = \sum_{\alpha} \int f(\mathbf{c}, \alpha, \mathbf{x}, t) d\mathbf{c} \quad (4)$$

is the number density, $\mathbf{C} = \mathbf{c} - \mathbf{u}$ is the chaotic velocity, and

$$n\mathbf{u} = \sum_{\alpha} \int \mathbf{c} f(\mathbf{c}, \alpha, \mathbf{x}, t) d\mathbf{c} \quad (5)$$

is the hydrodynamic velocity. The temperature T is defined through the total energy

$$nC_v T = \sum_{\alpha} \int \left[\frac{m\mathbf{C}^2}{2} + E_\alpha \right] f d\mathbf{c}, \quad (6)$$

where C_v is the total specific heat, which has contributions coming from the translational as well as from the internal degrees of freedom.

Notice should be made that the inelastic collision between particles implies that the mean kinetic energy as well as the mean energy associated to the internal degrees of freedom are nonconserved quantities, but they balance each other. In fact this comment drives us to the definition of the relevant variable we want to study,

$$n\xi(\mathbf{x}, t) = \sum_{\alpha} \int E_\alpha f(\mathbf{c}, \alpha, \mathbf{x}, t) d\mathbf{c}. \quad (7)$$

The pressure tensor is now defined as

$$P_{ij} = \sum_{\alpha} \int m C_i C_j f d\mathbf{c} \quad (8)$$

and its trace becomes essentially the mean kinetic energy which can be split into the hydrostatic pressure and the trace of the viscous tensor p_v in such a way that

$$P_{ij} = p\delta_{ij} + \frac{p_v}{3}\delta_{ij} + P_{ij}^0. \quad (9)$$

The quantities $\xi(\mathbf{x}, t)$ and $p_v(\mathbf{x}, t)$ are not independent because the total energy is a summational invariant. On the other hand, two heat fluxes are associated with this problem. One of them corresponds to the translational energy and the other to the internal energy flux. Those are defined as follows:

$$\mathbf{q}^{\text{tra}} = \sum_{\alpha} \int \frac{1}{2} m \mathbf{C}^2 \mathbf{C} f d\mathbf{c} \quad (10)$$

and

$$\mathbf{q}^{\text{int}} = \sum_{\alpha} \int E_\alpha \mathbf{C} f d\mathbf{c}. \quad (11)$$

Next we will introduce Grad's expansion by means of writing the one particle distribution function in terms of Hermite polynomials and the Wang-Chang-Uhlenbeck polynomials [20],

$$f(\mathbf{c}, \alpha, \mathbf{x}, t) = f^{(0)} \sum_{r,s} \frac{1}{r!s!} a^{(r,s)}(\mathbf{x}, t) H^{(r)}(\mathbf{c}) h^{(s)}(\alpha) \quad (12)$$

and consider only a six-moment calculation. The relevant moments in the description will be the five conserved variables available in Eq. (2) and the internal variable ξ describing the internal degrees of freedom. It means that the closure assumption in the expansion (12) considers only the $a^{(2,0)}$ and $a^{(0,1)}$ moments of the distribution function which, in fact, are directly related to p_v and ξ . As we noticed before, those moments are not independent and we will write all expressions only in terms of ξ . The distribution function in this six-moment approximation is then given as

$$f = f^{(0)} \left[1 + \phi(\mathbf{C}, \alpha) \left[\frac{\xi - \bar{E}}{k_B T} \right] \right], \quad (13)$$

where the function $\phi(\mathbf{C}, \alpha)$ contains the velocity and the E_α dependence beyond the local equilibrium [21,22] and can be written as

$$\phi(\mathbf{C}, \alpha) = \frac{1}{3} \left[3 - \frac{m\mathbf{C}^2}{k_B T} \right] + \frac{[E_\alpha - \bar{E}]}{k_B T (\delta\epsilon)^2}, \quad (14)$$

where $\bar{E} = Z^{-1} \sum_{\alpha} E_\alpha \exp[-E_\alpha/k_B T]$ is the mean energy associated with the internal degrees of freedom and

$$k_B (\delta\epsilon)^2 = Z^{-1} \sum_{\alpha} \left[\frac{E_\alpha - \bar{E}}{k_B T} \right]^2 \exp \left[-\frac{E_\alpha}{k_B T} \right] = C_v^{\text{int}}.$$

Such a distribution function is consistent with the usual conservation laws, namely,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{u} = 0 \quad (15)$$

where $\rho = nm$ is the mass density,

$$\frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \cdot \rho \mathbf{u} \mathbf{u} = -\nabla p - \nabla \cdot \sigma, \quad (16)$$

where σ is the viscous tensor, and p is the hydrostatic pressure,

$$\rho \frac{\partial s}{\partial t} + \rho \mathbf{u} \cdot \nabla s = -\nabla \cdot \mathbf{q}^{\text{total}} + \frac{1}{T} \sigma : (\nabla \mathbf{u})^0. \quad (17)$$

Here, s is the entropy density, $\mathbf{q}^{\text{total}}$ is the total heat flux, and $(\)^0$ means the symmetric traceless tensor.

The equation of motion corresponding to the internal variable ξ is obtained in a direct way from the WCUB equation when we multiply by $\phi(\mathbf{C}, \alpha)$, sum over the internal degrees of freedom, and integrate in the velocity space. In fact, the resulting equation is nonlinear, but we will consider the linearized version around the nonequilibrium steady state. This is not a restriction since we are only interested in the study of fluctuations. Notice that we keep the hydrodynamical derivative because it will give a very important contribution in the steady state, as we will discuss later on. Then we obtain the following expression:

$$\frac{D(\xi - \bar{E})}{Dt} = -\frac{2pC_v^{\text{int}}(\xi - \bar{E})}{3\xi C_v} - \frac{3C_v^{\text{int}}}{2nC_v} \nabla \cdot \left[-\frac{2}{3} \mathbf{q}^{\text{tra}} + \frac{k_B}{C_v^{\text{int}}} \mathbf{q}^{\text{int}} \right]. \quad (18)$$

We notice that this equation contains the heat fluxes defined in Eqs. (10) and (11), and it means that we will need their corresponding constitutive equations, which can be obtained also from the WCUB equation by assuming a steady state in those fluxes [19]. In fact, the Navier-Newton equation is taken as

$$\sigma = -2\eta(\nabla \mathbf{u})^0 - \zeta(\nabla \cdot \mathbf{u}) \underline{I}, \quad (19)$$

where η , ζ are the shear and bulk viscosities, respectively, and \underline{I} is the unit tensor. The total heat flux is given by

$$\mathbf{q}^{\text{total}} = \mathbf{q}^{\text{tra}} + \mathbf{q}^{\text{int}}, \quad (20)$$

where the internal and translational heat fluxes are expressed in terms of the translational and internal parts of the thermal conductivity

$$\mathbf{q}^{\text{tra}} = -\lambda^{\text{tra}}(\nabla T) - \lambda^{\text{tra}}(\nabla \xi), \quad (21)$$

$$\mathbf{q}^{\text{int}} = -\lambda^{\text{int}}(\nabla T) - \lambda^{\text{int}}(\nabla \xi), \quad (22)$$

the λ coefficients are all given in terms of the well known collision integrals introduced by Mason and Monchick [17,18],

$$\lambda^{\text{tra}} = \frac{75}{8} \frac{k_B^2 T}{m(XZ - Y^2)} Z, \quad (23)$$

$$\lambda^{\text{int}} = \frac{3}{2} \frac{TC_v^{\text{int}}}{m(XZ - Y^2)} X, \quad (24)$$

$$\lambda^{\text{int}} = \frac{15}{4} \frac{k_B TC_v^{\text{int}}}{m(XZ - Y^2)} Y, \quad (25)$$

and $\lambda^{\text{tra}} = \lambda^{\text{tra}}/C_v^{\text{int}}$, which can be calculated for some intermolecular potentials.

III. FLUCTUATING HYDRODYNAMICS

The set of equations we have constructed in Sec. II can be linearized around a nonequilibrium steady state (NESS) caused by a fixed temperature gradient. The resulting set describes the behavior of fluctuations in the relevant variables and in fact are the averaged equations corresponding to a set of stochastic ones. Now we are interested in the stochastic equations and we will write the fluctuating parts of them in order to establish the correlation between the fluctuating fluxes. According to the usual treatments [12,23,24], we add a fluctuating part to the constitutive equations representing the fluxes.

$$\sigma_{ij}(\mathbf{x}, t) = -2\eta[\nabla \mathbf{u}(\mathbf{x}, t)]_{ij}^0 - \zeta[\nabla \cdot \mathbf{u}(\mathbf{x}, t)]\delta_{ij} + \Pi_{ij}(\mathbf{x}, t), \quad (26)$$

$$\mathbf{q}^{\text{tra}}(\mathbf{x}, t) = -\lambda^{\text{tra}}[\nabla T(\mathbf{x}, t)] - \lambda^{\text{tra}}[\nabla \xi(\mathbf{x}, t)] + \mathbf{Q}^{\text{tra}}(\mathbf{x}, t), \quad (27)$$

$$\mathbf{q}^{\text{int}}(\mathbf{x}, t) = -\lambda^{\text{int}}[\nabla T(\mathbf{x}, t)] - \lambda^{\text{int}}[\nabla \xi(\mathbf{x}, t)] + \mathbf{Q}^{\text{int}}(\mathbf{x}, t). \quad (28)$$

Notice should be made that the fluctuating parts Π_{ij} , \mathbf{Q}^{tra} , and \mathbf{Q}^{int} are functions of both spatial coordinates and time. They will be given by Gaussian, stationary, and Markovian noises, with zero average and δ correlated in the two spaces, namely,

$$\begin{aligned} \langle \Pi_{ij}(\mathbf{x}, t) \Pi_{lm}(\mathbf{x}', t') \rangle &= 2k_B T [\eta(\delta_{il}\delta_{jm} + \delta_{im}\delta_{jl}) \\ &\quad + (\xi - \frac{2}{3}\eta)\delta_{ij}\delta_{lm}] \\ &\quad \times \delta(\mathbf{x} - \mathbf{x}')\delta(t - t'), \end{aligned} \quad (29)$$

$$\begin{aligned} \langle \mathbf{Q}_i^{\text{tra}}(\mathbf{x}, t) \mathbf{Q}_j^{\text{tra}}(\mathbf{x}', t') \rangle &= 2k_B T^2 [\lambda^{\text{tra}} C_v^{\text{int}} + \lambda^{\text{tra}}] \\ &\quad \times \delta(\mathbf{x} - \mathbf{x}')\delta(t - t')\delta_{ij}, \end{aligned} \quad (30)$$

$$\begin{aligned} \langle \mathbf{Q}_i^{\text{int}}(\mathbf{x}, t) \mathbf{Q}_j^{\text{int}}(\mathbf{x}', t') \rangle &= 2k_B T^2 [\lambda^{\text{int}} C_v^{\text{int}} + \lambda^{\text{int}}] \\ &\quad \times \delta(\mathbf{x} - \mathbf{x}')\delta(t - t')\delta_{ij}, \end{aligned} \quad (31)$$

$$\begin{aligned} \langle \mathbf{Q}_i^{\text{int}}(\mathbf{x}, t) \mathbf{Q}_j^{\text{tra}}(\mathbf{x}', t') \rangle &= 2k_B T^2 [(\lambda^{\text{tra}} + \lambda^{\text{int}})C_v^{\text{int}} + \lambda^{\text{tra}} + \lambda^{\text{int}}] \\ &\quad \times \delta(\mathbf{x} - \mathbf{x}')\delta(t - t')\delta_{ij}. \end{aligned} \quad (32)$$

The coefficients λ^{tra} , λ^{tra} , λ^{int} , and λ^{int} contribute in a somewhat independent way. However, they correspond to the translational and internal parts of thermal conductivity, in fact $\lambda^{\text{tra}} = \lambda^{\text{tra}} C_v^{\text{int}} + \lambda^{\text{tra}}$ is the translational part and $\lambda^{\text{int}} = \lambda^{\text{int}} C_v^{\text{int}} + \lambda^{\text{int}}$ the internal part [17,21].

As a next step we solve the set of equations in the NESS; it means that we take all time derivatives equal to zero. Also, the flux in the equation associated to the internal degrees must be equal to zero, in order to assure a balance between the interchange in kinetic energy and the internal contribution,

$$\mathbf{q}^{\text{tra}} = \frac{C_v^{\text{tra}}}{C_v^{\text{int}}} \mathbf{q}^{\text{int}}. \quad (33)$$

This last condition means that the transport between kinetic energy and the energy involved in the internal degrees of freedom is not arbitrary but depends on the quo-

tient of specific heats. It also implies the existence of a fixed gradient in the energy corresponding to the internal degrees of freedom, which in fact appears as a consequence of the temperature gradient fixed externally to maintain the NESS,

$$(\nabla\xi)_0 = \begin{pmatrix} \lambda^{ii} - \lambda^{ii} \frac{C_v^{\text{tra}}}{C_v^{\text{int}}} \\ \lambda^{ii} \frac{C_v^{\text{tra}}}{C_v^{\text{int}}} - \lambda^{ii} \end{pmatrix} (\nabla T)_0. \quad (34)$$

Now we linearize around the steady state and take the Fourier transform of all quantities, the resulting set of

equations can be written in matrix form as follows:

$$\mathcal{H}(\mathbf{k}, \omega) \times \mathcal{A}(\mathbf{k}, \omega) = \mathcal{F}(\mathbf{k}, \omega) \quad (35)$$

where $\mathcal{H}(\mathbf{k}, \omega)$ is the hydrodynamic matrix, $\mathcal{A}(\mathbf{k}, \omega)$ is a column matrix representing the Fourier transforms of the fluctuating variables, and $\mathcal{F}(\mathbf{k}, \omega)$ is the corresponding fluctuating fluxes, all these quantities are given as follows:

$$\mathcal{A}(\mathbf{k}, \omega) = \begin{pmatrix} p(\mathbf{k}, \omega) \\ T(\mathbf{k}, \omega) \\ \xi(\mathbf{k}, \omega) \\ u_l(\mathbf{k}, \omega) \\ \mathbf{u}_t(\mathbf{k}, \omega) \end{pmatrix}, \quad (36)$$

$$\mathcal{F}(\mathbf{k}, \omega) = \begin{pmatrix} 0 \\ \frac{i\mathbf{k}}{\rho_0 C_p} \cdot \mathbf{Q}^{\text{total}}(\mathbf{k}, \omega) \\ -\frac{3C_v^{\text{int}}}{2nC_v} i\mathbf{k} \cdot \left[-\frac{2}{3} \mathbf{Q}^{\text{tra}}(\mathbf{k}, \omega) + \frac{k_B}{C_v^{\text{int}}} \mathbf{Q}^{\text{int}}(\mathbf{k}, \omega) \right] \\ \frac{i\mathbf{k}}{\rho_0} \hat{\mathbf{k}} \hat{\mathbf{k}} \cdot \Pi(\mathbf{k}, \omega) \\ \frac{1}{\rho_0} [i\mathbf{k} \cdot \Pi(\mathbf{k}, \omega)] \cdot (\underline{I} - \hat{\mathbf{k}} \hat{\mathbf{k}}) \end{pmatrix}, \quad (37)$$

$$\mathcal{H}(\mathbf{k}, \omega) = \begin{pmatrix} -i\omega\gamma_p & -i\omega\gamma_T & i\omega\gamma_\xi & -ik & A(\nabla T)_0 \\ -\frac{T\gamma_T}{\rho_0 C_p} i\omega & (i\omega + \chi_1 k^2) & \left[\frac{\chi_\xi}{C_p} i\omega + \chi_2 k^2 \right] & 0 & \frac{T}{C_p} C(\nabla T)_0 \\ 0 & -C_1 k^2 & \left[i\omega + \frac{1}{\tau} - a_1 k^2 \right] & 0 & B(\nabla T)_0 \\ -\frac{ik}{\rho_0} & 0 & 0 & (i\omega + \nu_l k^2) & 0 \\ 0 & 0 & 0 & 0 & (i\omega + \nu_t k^2) \end{pmatrix}, \quad (38)$$

where several quantities appearing in the hydrodynamic matrix are defined in the Appendix.

We notice that the transversal part of the velocity $\mathbf{u}_t(\mathbf{k}, \omega)$ can be obtained only in terms of the fluctuating part of the viscous tensor and, in fact, it can be completely eliminated from the set of equations. Its coupling with the external temperature gradient influences the equations of motion and it gives the main effect in this calculation. This effect represents the coupling between a hydrodynamical mode typical of viscous terms with a heat mode imposed on the system by external means.

Now we solve the equation for $\mathbf{u}_t(\mathbf{k}, \omega)$ and obtain

$$\mathbf{u}_t(\mathbf{k}, \omega) = \frac{i\mathbf{k} \cdot \Pi(\mathbf{k}, \omega) \cdot (\underline{I} - \hat{\mathbf{k}} \hat{\mathbf{k}})}{\rho_0 (i\omega + \nu_t k^2)} \quad (39)$$

and its direct substitution in the set of hydrodynamic equations allows us to obtain a resonant coupling.

The next step in this procedure is the solution of the hydrodynamical set to obtain an expression for the longitudinal part of the velocity $u_l(\mathbf{k}, \omega)$, and such an expression can be used to construct the density fluctuations

$$i\omega\rho(\mathbf{k}, \omega) = ik u_l(\mathbf{k}, \omega) - A(\nabla T)_0 \cdot \mathbf{u}_t(\mathbf{k}, \omega). \quad (40)$$

Equation (40) shows in a clear way that the density fluctuations contain the contribution of the resonant effect and they will give us an enhancement in the spectra. In fact, after substitution of $u_l(\mathbf{k}, \omega)$ and $\mathbf{u}_l(\mathbf{k}, \omega)$ we obtain the following expression:

$$\rho_1(\mathbf{k}, \omega) - \rho_{\text{eq}}(\mathbf{k}, \omega) = A \frac{[i\mathbf{k} \cdot \Pi(\mathbf{k}, \omega)] \cdot (\underline{I} - \hat{\mathbf{k}}\hat{\mathbf{k}}) \cdot (\nabla T)_0}{\rho_0(i\omega + \nu_l k^2)} \left[1 - \frac{ik\rho_0}{\Delta_1(\mathbf{k}, \omega)} [D_1(\mathbf{k}, \omega) - D_2(\mathbf{k}, \omega) + D_3(\mathbf{k}, \omega)] \right], \quad (41)$$

where $\Delta_1(\mathbf{k}, \omega)$, $D_1(\mathbf{k}, \omega)$, $D_2(\mathbf{k}, \omega)$, and $D_3(\mathbf{k}, \omega)$ come from the solution of the set of equations. All these functions are explicitly written out in the Appendix. In Eq. (41), $\rho_1(\mathbf{k}, \omega)$ represents the fluctuations in density when the wave vector and the external gradient are perpendicular. Also, $\rho_{\text{eq}}(\mathbf{k}, \omega)$ corresponds to the fluctuations around the equilibrium state described by our set of equations of motion and it is written as follows:

$$\rho_{\text{eq}}(\mathbf{k}, \omega) = \frac{k\rho_0}{\omega\Delta_{\text{eq}}} \left[\frac{ik}{\rho_0} \hat{\mathbf{k}}\hat{\mathbf{k}} : \Pi(\mathbf{k}, \omega) D_2(\mathbf{k}, \omega) - \left[\frac{i\mathbf{k} \cdot \mathbf{Q}^{\text{int}}}{\rho_0 C_p} + \frac{i\mathbf{k} \cdot \mathbf{Q}^{\text{tra}}}{\rho_0 C_p} \right] D_4(\mathbf{k}, \omega) + \left[i \frac{k_B}{C_v^{\text{int}}} \mathbf{k} \cdot \mathbf{Q}^{\text{int}} + i \frac{2}{3} \mathbf{k} \cdot \mathbf{Q}^{\text{tra}} \right] D_3(\mathbf{k}, \omega) \right]. \quad (42)$$

The direct comparison between Eqs. (41) and (42) shows how the NESS influences the behavior of density fluctuations giving us a way to study some nonlinear couplings between hydrodynamic modes.

IV. RAYLEIGH PEAK

In order to calculate the contribution to the Rayleigh peak coming from density fluctuations we need the hydrodynamic modes. The proposal of a kinetic model to study this problem has introduced a new independent variable related to the energy of internal degrees of freedom, and this means that we must also have a new mode in the system. To determine the properties of this new set of hydrodynamical modes we can construct the dispersion relation associated to the set of equations, write it in terms of the complex frequency $z = i\omega$, and solve it in powers of the wave vector [3]. This procedure will give us four roots for the dispersion relation which represent an approximation to the hydrodynamical modes, namely,

$$z_1 = -\frac{1}{\tau_{\text{eff}}}, \quad (43)$$

$$z_2 = -iC_0 k - (\Gamma_1 + \mathcal{G})k^2, \quad (44)$$

$$z_3 = iC_0 k - (\Gamma_1 + \mathcal{G})k^2, \quad (45)$$

$$z_4 = -\chi_1 k^2. \quad (46)$$

Here C_0 is the Laplace sound velocity, τ_{eff} denotes the effective relaxation time, and χ_1 plays the role of thermal diffusivity. We notice that these modes reduce to the usual ones when the internal degrees of freedom are not taken into account. Two of them are propagating modes

as it should be, but the absorption coefficient, which contains the usual viscous terms through ν_l , is modified mainly by the term expressed as \mathcal{G} , containing in an explicit way the contribution of the thermal conductivities as expressed in the kinetic model

$$\Gamma_1 = \frac{1}{2}[\nu_l + \chi_1(\gamma - 1)] \quad (47)$$

and

$$\mathcal{G} = \frac{3C_v^{\text{int}}}{2nC_v} \left[\frac{2}{3}\lambda'' - \frac{k_B}{C_v^{\text{int}}}\lambda'' \right] \times \left[\frac{C_0^2 T}{C_p} (\gamma_p + \gamma_T) \gamma_\xi - \frac{\lambda'' - \lambda'' \frac{C_v^{\text{tra}}}{C_v^{\text{int}}}}{\lambda'' \frac{C_v^{\text{tra}}}{C_v^{\text{int}}} - \lambda''} \right]. \quad (48)$$

The mode expressed as z_1 describes the relaxation of the internal degrees of freedom with an effective relaxation time which has a contribution measuring the inhomogeneities in the system, through a quantity with a k^2 dependence,

$$\tau_{\text{eff}} = \frac{\tau}{(1 + \tau D_{\text{int}} k^2)}, \quad (49)$$

where D_{int} depends on the thermal conductivities and the specific heats. Its explicit value is given in the Appendix. The presence of an effective relaxation time has been considered in the literature [25], and here it becomes important through the kinetic model and all values can be calculated from it.

The calculation of the Rayleigh line is now a direct one and we just take Eq. (41) and calculate the leading contributions in the density-density correlation function,

$$(S_{\perp} - S_{\text{eq}})_{\text{Ra}} = \frac{2k_B T v_t}{\rho_0 \chi_1 (\omega^2 + v_t^2 k^4)} (\nabla T)_0^2 \left[\frac{A}{\rho_0} \right]^2 \left[\frac{\chi_1 k^2}{\omega^2 + \chi_1^2 k^4} \left[\frac{\tau^{-1} - \chi_1 k^2}{\tau_{\text{eff}}^{-1} - \chi_1 k^2} \right]^2 + \frac{\tau_{\text{eff}}}{1 + \omega^2 \tau_{\text{eff}}^2} \left[\frac{\tau_{\text{eff}}^{-1} - \tau^{-1}}{\tau_{\text{eff}}^{-1} - \chi_1 k^2} \right]^2 \right]. \quad (50)$$

This result shows in a clear way the enhancement of the Rayleigh line coming from the coupling between the transversal modes in the velocity and the external temperature gradient. The effect has the same qualitative characteristics as in a simple fluid, and it means that the spectra depend in a quadratic way on the temperature gradient and we have a k^{-4} wave vector dependence. Equation (50) also shows the influence of the relaxation time coming from the internal degrees of freedom, these terms are functions of frequency and wave vector, but the k dependence in the effective relaxation time makes them of order unity.

The intensity of the Rayleigh peak is obtained by the frequency integration of the structure factor, namely,

$$[\Delta I(\mathbf{k})]_{\text{Ra}} = \frac{1}{2\pi} \int (S_{\perp} - S_{\text{eq}})_{\text{Ra}} d\omega, \quad (51)$$

the result being the following one:

$$[\Delta I(\mathbf{k})]_{\text{Ra}} = k_B T v_t (\nabla T)_0^2 \left[\frac{A}{\rho_0} \right]^2 \times \left[\frac{\mathcal{J}(\mathbf{k})}{2k^4 (v_t + \chi_1) \chi_1 v_t} + \frac{\mathcal{J}'(\mathbf{k})}{2(v_t k^2 + \tau^{-1}) \tau^{-1} v_t} \right], \quad (52)$$

where the relative intensities in these terms are given as follows:

$$\mathcal{J}(\mathbf{k}) = \left[\frac{\tau^{-1} - \chi_1 k^2}{\tau_{\text{eff}}^{-1} - \chi_1 k^2} \right]^2 \quad (53)$$

and

$$\mathcal{J}'(\mathbf{k}) = \left[\frac{\tau^{-1} - \tau_{\text{eff}}^{-1}}{\tau_{\text{eff}}^{-1} - \chi_1 k^2} \right]^2. \quad (54)$$

Notice should be made that these intensities are functions of the wave vector, in contrast with the case of a simple fluid in which the result is recovered only by the first term in Eq. (52) with $\mathcal{J}(\mathbf{k})=1$, $\gamma_{\xi}=0$ and taking χ_1 as the usual thermal diffusivity.

To compare these expressions with the experimental results in the literature [13] we consider the regime when the internal degrees of freedom behave in a diffusive way, which means that $D_{\text{int}} k^2 \gg \tau^{-1}$. This condition corresponds to a relaxation of the internal degrees of freedom less important than the transport of their energy by translational motion. Then we take the Fourier-transform of the spectra and write the density correlation function in the wave vector space as follows:

$$C_{\text{Ra}}(k, t) \sim \mathcal{A}_{\chi} \exp(-\chi_1 k^2 t) + \mathcal{A}_{D_{\text{int}}} \exp(-D_{\text{int}} k^2 t) - (\mathcal{A}_{\nu} + \mathcal{A}'_{\nu}) \exp(-\nu_t k^2 t), \quad (55)$$

where the amplitudes in each term are given by

$$\mathcal{A}_{\chi} = \frac{\mathcal{J}(\mathbf{k})}{v_t^2 - \chi_1^2} \left[\frac{v_t}{\chi_1} \right] \frac{(\nabla T)_0^2}{k^4}, \quad (56)$$

$$\mathcal{A}_{D_{\text{int}}} = \frac{\mathcal{J}'(\mathbf{k})}{v_t^2 - \chi_1^2} \left[\frac{v_t}{\chi_1} \right] \frac{(\nabla T)_0^2}{k^4}, \quad (57)$$

$$\mathcal{A}_{\nu} + \mathcal{A}'_{\nu} = \left[\frac{\mathcal{J}(\mathbf{k})}{v_t^2 - \chi_1^2} + \frac{\mathcal{J}'(\mathbf{k})}{v_t^2 - D_{\text{int}}^2} \left[\frac{D_{\text{int}}}{\chi_1} \right] \right] \frac{(\nabla T)_0^2}{k^4}, \quad (58)$$

which reduce to the usual ones when we neglect the influence of the internal degrees of freedom. The most important point in this result is the wave vector dependencies in the amplitudes. In fact they do not change the qualitative behavior of the spectra but certainly manifest some inhomogeneities in the system, which otherwise have been attached to the transport coefficients themselves [14]. In principle, our kinetic model has provided us with an alternative way to interpret the small differences in the experimental results when compared with fluctuating hydrodynamics for a simple fluid.

V. CONCLUDING REMARKS

The kinetic model we have introduced to study the viscoheat effect in a fluid with internal degrees of freedom has allowed us to find a modification of the Rayleigh line and its intensity.

The modification comes from the fact that in the NESS all fluxes in the system are zero except for the heat flux which is encharged to maintain the steady state. In this particular case such a condition means that the external temperature gradient induces a fixed gradient in the energy associated to the internal degrees of freedom. This characteristic also appears in the treatment of binary mixtures where the temperature gradient induces a concentration gradient, proportional to the thermal diffusion ratio [26,27]. Here we have another example where this phenomenon appears as a consequence of the external conditions imposed on the system.

The characteristics of this NESS imply also the resonant coupling of the external gradient and the viscous modes in the system, which has essentially the same qualitative behavior as the simple fluid. It is not the case when we compare the results in a quantitative way. First of all the fluctuating hydrodynamics must be developed according to the introduction of a new variable, with their corresponding fluctuating fluxes. Also, the hydrodynamical modes are somewhat different in their specific values, besides the new one associated with the internal variable. The new modes introduce a different behavior in the density-density correlation function, with the corresponding modification in the Rayleigh line.

In order to gain an insight about the meaning of such a modification we have taken the rough sphere model to evaluate all collision integrals and obtained a value for

the modification in the effect [28,29]. First of all let us recall that the rough sphere model characterizes the molecule by a dimensionless parameter $\kappa = 4I/m\sigma^2$, measuring the moment of inertia I with respect to a sphere of diameter σ . Interesting values for this parameter are $(0, \frac{2}{3}, \frac{2}{5})$ and they correspond to different configurations in the mass distribution.

The quantity B giving the gradient in the internal degrees of freedom is

$$B = \frac{75}{4} k_B \left[\frac{1 + \kappa + 2\kappa^2}{6 + 13\kappa} \right] \quad (59)$$

which is of the same order of magnitude as the external temperature gradient.

Concerning the effective relaxation time we have two contributions, the bare relaxation time τ which depends on the kind of internal degrees of freedom we consider and their diffusive behavior. Here we will only take the rotational ones to be consistent with the rough sphere model, but we are allowed to also take vibrational degrees of freedom or both, as it is sometimes done in the literature [30]. This contribution can be obtained in a direct way through the bulk viscosity ζ as follows:

$$\tau = \frac{3\zeta C_v}{2pC_v^{\text{int}}} = \frac{C_v^{\text{int}}}{4nC_v} \left[\frac{\pi m}{k_B T} \right]^{1/2} \left[\frac{4}{3} \kappa \frac{\pi \sigma^2}{(\kappa + 1)^2} \right]^{-1}, \quad (60)$$

where the first part of this equality is valid in general and the second one corresponds to its value for the rough sphere model.

The diffusive part of this relaxation time D_{int} is a complicated function of κ , the dimensionless inertia moment.

Here we will only give some special values, $D_{\text{int}}(\kappa=0)=0.4 \text{ cm}^2/\text{s}$, $D_{\text{int}}(\kappa=\frac{2}{3})=0.304 \text{ cm}^2/\text{s}$, $D_{\text{int}}(\kappa=\frac{2}{5})=0.311 \text{ cm}^2/\text{s}$ for molecular nitrogen at $T=500 \text{ K}$, $p=1 \text{ atm}$, $\sigma=3.75 \times 10^{-8} \text{ cm}$, and $n=1.468 \times 10^{19} \text{ molecules/cm}^3$, which in fact coincide in order of magnitude with some others calculated in the literature [30].

All these values help us to estimate the amplitudes in the viscoheat effect and see if they go in the right way. For example, if we take $k \sim 10^4 \text{ cm}^{-1}$ the amplitude is $\mathcal{J}(\mathbf{k}) \sim 0.6$, which seems to be of adequate order to explain the small discrepancy between the calculated spectra and the measured one [9]. On the other hand, we estimated $\mathcal{J}'(\mathbf{k}) \sim 1$ for toluene taking $\chi_1 \sim 10^{-3} \text{ cm}^2/\text{s}$ and $D_{\text{int}} \sim 0.35 \text{ cm}^2/\text{s}$.

Notice that the values of the amplitudes come from our model without making any additional assumption, but certainly they must be seen as an alternative explanation because our model is a simplified one. In fact the internal degrees of freedom that can contribute to the spectra in the case of toluene are not taken in full form, however the calculation shows how these kinds of characteristics can give an alternative account of the existing differences. A detailed comparison between the spectra calculated with this model and the experimental data will require the knowledge of the thermal conductivity coefficients in a separate way for the systems measured and the conditions of the experiment. These kind of data are not available since these coefficients consider the transport of kinetic energy and internal degrees of freedom in an independent way, and just some specific models allow for their calculation.

APPENDIX

Some useful definitions are

$$\rho_0 \gamma_T = - \left[\frac{\partial \rho}{\partial T} \right]_{p, \xi}, \quad \rho_0 \gamma_p = - \left[\frac{\partial \rho}{\partial p} \right]_{T, \xi}, \quad \rho_0 \gamma_\xi = \left[\frac{\partial \rho}{\partial \xi} \right]_{T, p},$$

$$A = \rho_0 (-\gamma_T + \gamma_\xi B), \quad B = \frac{\lambda^{\text{tr}} - \lambda^{\text{tr}} \frac{C_v^{\text{tra}}}{C_v^{\text{int}}}}{\lambda^{\text{tr}} \frac{C_v^{\text{tra}}}{C_v^{\text{int}}} - \lambda^{\text{tr}}}, \quad C = \frac{C_p}{T} + \chi_\xi B,$$

$$\chi_\xi = \left[\frac{\partial s}{\partial \xi} \right]_{p, T}, \quad \tau = \frac{3\zeta C_v}{2pC_v^{\text{int}}}, \quad \nu_l = \frac{4}{3} \eta + \zeta, \quad \nu_t = \frac{\eta}{\rho_0},$$

$$a_1 = \frac{3C_v^{\text{int}}}{2nC_v} \left[\frac{2}{3} \lambda^{\text{tr}} - \frac{k_B}{C_v^{\text{int}}} \lambda^{\text{tr}} \right], \quad C_1 = \frac{3C_v^{\text{int}}}{2nC_v} \left[\frac{2}{3} \lambda^{\text{tr}} - \frac{k_B}{C_v^{\text{int}}} \lambda^{\text{tr}} \right],$$

$$\chi_1 = \frac{\lambda^{\text{tr}} + \lambda^{\text{tr}}}{\rho_0 C_p}, \quad \chi_2 = \frac{\lambda^{\text{tr}} + \lambda^{\text{tr}}}{\rho_0 C_p},$$

$$D_{\text{int}} = \frac{\lambda^{\text{tr}} + \lambda^{\text{tr}}}{\lambda^{\text{tr}} + \lambda^{\text{tr}}} C_1 - a_1,$$

$$D_1(\mathbf{k}, \omega) = \frac{ik}{\rho_0} (i\omega + \chi_1 k^2) \left[i\omega + \frac{1}{\tau} - a_1 k^2 \right] - \frac{iC_1 k^3}{\rho_0} \left[\frac{i\omega \chi_\xi T}{C_p} + \chi_2 k^2 \right],$$

$$D_2(\mathbf{k}, \omega) = -\frac{k^3}{\rho_0} C_1 \omega \gamma_\xi + \frac{k}{\rho_0} \omega \gamma_T \left[i\omega + \frac{1}{\tau} - a_1 k^2 \right],$$

$$D_3(\mathbf{k}, \omega) = \frac{k}{\rho_0} \omega \gamma_\xi (i\omega + \chi_1 k^2) + \frac{k}{\rho_0} \left[i\omega + \frac{1}{\tau} - a_1 k^2 \right],$$

$$D_4(\mathbf{k}, \omega) = i\omega \gamma_p (i\omega + \chi_1 k^2) \left[i\omega + \frac{1}{\tau} - a_1 k^2 \right] - \omega^2 C_1 \gamma_\xi \frac{T \gamma_T}{C_p \rho_0} k^2 + i\omega \gamma_p c_1 k^2 \left[i\omega \frac{\chi_\xi T}{C_p} + \chi_2 k^2 \right] \\ + \omega^2 \frac{T \gamma_T^2}{C_p \rho_0} \left[i\omega + \frac{1}{\tau} - a_1 k^2 \right].$$

$\Delta_1(\mathbf{k}, \omega)$ corresponds to the determinant of the set of equations when the wave vector and the gradient are perpendicular, whereas $\Delta_{\text{eq}}(\mathbf{k}, \omega)$ is the determinant when the gradient is absent.

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