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Light Scattering in Rarefied Polyatomic Gases Based on Extended Thermodynamics

拡張された熱力学に基づく多原子分子希薄気体における光散乱の解析

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1. Introduction

Light scattering caused by the fluctuations in the dielectric constant ε associated with the fluctuations in the mass density ρ has been widely studied in fluids. In a light scattering experiment, the intensity of the scattered light is directly related to the so-called dynamic structure factor [1]:

$$S(\mathbf{q},\omega)=\frac{1}{\pi}\left(\frac{\partial\varepsilon}{\partial\rho}\right)^2 \mathrm{Re}\left\langle \delta\rho^*(\mathbf{q},0)\delta\hat{\rho}(\mathbf{q},s)\right\rangle_{s=i\omega}, \qquad (1)$$

where $\mathbf{q}$ is the scattering vector, the magnitude of which is given by $|\mathbf{q}|=(4\pi/\lambda)\sin(\theta/2)$ with λ and θ being the wavelength of the incident light and the scattering angle, ω is the shift in angular frequency, and $\langle\delta\rho^*(\mathbf{q},0)\delta\hat{\rho}(\mathbf{q},s)\rangle$ is the Laplace transformation of the autocorrelation of the density fluctuations $\langle\delta\rho^*(\mathbf{q},0)\delta\rho(\mathbf{q},t)\rangle$. The dynamic structure factor $S(\mathbf{q},\omega)$ has been studied by means of two approaches: the hydrodynamic approach based on the Navier-Stokes-Fourier (NSF) theory [2] which assumes the local thermodynamic equilibrium (LTE), and the kinetic theory based on a special model.

In recent decades, Extended Thermodynamics (ET) [1] has been proposed as a phenomenological theory which can describe a nonequilibrium phenomena in which steep gradients and rapid changes of the physical quantities occur beyond the assumption of the LTE. In particular, lately, the ET theory for rarefied polyatomic gases and also for dense gases has been established [3].

The purpose of the present paper is to make clear the validity of the ET theory through studying the light scattering. The dynamic structure factor is derived by this theory, and compared with experimental data and that by the NSF theory.

2. Basic equations

We study rarefied polyatomic gases with the equations of state for the pressure $p=a\rho T$ and the specific internal energy $e=e(T)$, where T is the temperature and $a=k_B/m$ with k_B and m being the Boltzmann constant and the mass of a molecule.

We assume that a nonequilibrium state can be characterized by 14 independent fields $\mathbf{u}=(\rho, v_i, T, S_{<ij>}, \Pi(=S_{ii}/3), q_i)$ $(i,j=1,2,3)$, where $v_i, S_{<ij>}, \Pi$ and q_i are the velocity, symmetric traceless part of viscous stress, dynamic pressure and heat flux, respectively. Here the summation convention is adopted. Let us consider the linearized system in the neighborhood of an equilibrium state $\mathbf{u}_0=(\rho_0, 0, T_0, 0, 0, 0)$. The system of equations for perturbed fields $\mathbf{u}$ are expressed as follows [3]:

$$\frac{\partial\rho}{\partial t}+\rho_0\frac{\partial v_k}{\partial x_k}=0,$$

$$\rho_0\frac{\partial v_i}{\partial t}+aT_0\frac{\partial\rho}{\partial x_i}+a\rho_0\frac{\partial T}{\partial x_i}-\frac{\partial S_{<ij>}}{\partial x_j}+\frac{\partial\Pi}{\partial x_i}=0,$$

$$a\rho_0 c_v^*\frac{\partial T}{\partial t}+a\rho_0 T_0\frac{\partial v_k}{\partial x_k}+\frac{\partial q_k}{\partial x_k}=0,$$

$$\frac{\partial S_{<ij>}}{\partial t}-2a\rho_0 T_0\frac{\partial v_{<i}}{\partial x_{j>}}-\frac{2}{1+c_v^*}\frac{\partial q_{<i}}{\partial x_{j>}}=-\frac{1}{\tau_S}S_{<ij>},$$

$$\frac{\partial\Pi}{\partial t}+\left(\frac{2}{3}-\frac{1}{c_v^*}\right)a\rho_0 T_0\frac{\partial v_k}{\partial x_k}+\frac{2c_v^*-3}{3c_v^*(1+c_v^*)}\frac{\partial q_k}{\partial x_k}=-\frac{1}{\tau_\Pi}\Pi,$$

$$\frac{\partial q_i}{\partial t}+(1+c_v^*)a^2\rho_0 T_0\frac{\partial T}{\partial x_i}-aT_0\frac{\partial S_{<ik>}}{\partial x_k}+aT_0\frac{\partial\Pi}{\partial x_i}=-\frac{1}{\tau_q}q_i,$$

where c_v^* is the dimensionless specific heat defined by $(\mathrm{d}e/\mathrm{d}T)_{T=T_0}/a$. The value of c_v^* can be estimated by experimental data or statistical-mechanical study. The relaxation times τ_S, τ_Π and τ_q are related to the shear viscosity μ, bulk viscosity ν and heat conductivity κ as follows [3]:

$$\mu=p_0\tau_S,\ \nu=\left(\frac{2}{3}-\frac{1}{c_v^*}\right)p_0\tau_\Pi,\ \kappa=(1+c_v^*)ap_0\tau_q. \qquad (2)$$

3. Dynamic structure factor based on ET

The system can be decomposed into two uncoupled systems:

$$\mathbf{u}_L=\left(\rho, \frac{\partial v_i}{\partial x_i}, T, \frac{\partial^2 S_{<ij>}}{\partial x_i\partial x_j}, \Pi, \frac{\partial q_i}{\partial x_i}\right) \quad \text{and}$$
$$\mathbf{u}_T=\left(\varepsilon_{ijk}\frac{\partial v_k}{\partial x_j}, \varepsilon_{ijk}\frac{\partial^2 S_{<jn>}}{\partial x_k\partial x_n}, \varepsilon_{ijk}\frac{\partial q_k}{\partial x_j}\right),$$

where ε_{ijk} is the Levi-Civita symbol. For the present purpose we adopt the system $\mathbf{u}_L$ because only this system affects the density fluctuations. The Fourier (space) and Laplace (time) transformed basic equations for $\mathbf{u}_L$ can be summarized in the following matrix form

$$\mathbf{A}\ \hat{\mathbf{u}}_L(\mathbf{q},s)=\mathbf{u}_L(\mathbf{q},0), \qquad (3)$$

where $\hat{\mathbf{u}}_L(\mathbf{q},s)$ denotes the Fourier and Laplace transformation of $\mathbf{u}_L(\mathbf{x},t)$, $\mathbf{u}_L(\mathbf{q},0)$ denotes the initial value of the spatial Fourier transformation of $\mathbf{u}_L(\mathbf{x},t)$, and the coefficient matrix $\mathbf{A}$ is given by

$$\mathbf{A}=\begin{pmatrix} s & \rho_0 & 0 & 0 & 0 & 0 \\ -q^2\dfrac{p_0}{{\rho_0}^2} & s & -q^2 & -\dfrac{1}{\rho_0} & -\dfrac{q^2}{\rho_0} & 0 \\ 0 & \dfrac{T_0}{c_v^*} & s & 0 & 0 & \dfrac{1}{a\,c_v^*\rho_0} \\ 0 & \dfrac{4}{3}q^2\,p_0 & 0 & s+\dfrac{1}{\tau_S} & 0 & \dfrac{4q^2}{3(1+c_v^*)} \\ 0 & \left(\dfrac{2}{3}-\dfrac{1}{c_v^*}\right)p_0 & 0 & 0 & s+\dfrac{1}{\tau_\Pi} & \dfrac{2c_v^*-3}{3c_v^*(1+c_v^*)} \\ 0 & & -q^2\left(1+c_v^*\right)a\,p_0 & -\dfrac{p_0}{\rho_0} & -q^2\dfrac{p_0}{\rho_0} & s+\dfrac{1}{\tau_q} \end{pmatrix}.$$

From (1), (3) and the Onsager's regression hypothesis, the dynamic structure factor $S(\mathbf{q},\omega)$ can be calculated. It is useful to introduce the dimensionless frequency x and the dimensionless wavelength y defined by

$$x=\frac{\omega}{v_0\,q} \quad \text{and} \quad y=\frac{p_0}{\mu\;v_0\,q}=\frac{1}{\tau_S\,v_0\,q},$$

and then the relative intensity of $S(\mathbf{q},\omega)$ can be expressed as a function of x, y, c_v^*, τ_q/τ_S and τ_Π/τ_S .

4. Comparison with experimental data

The dynamic structure factor by ET is compared with the laser scattering experiments of Greytak and Benedek [4] and with that by NSF for the carbon dioxide gas at temperature 300 K. At this temperature c_v^* is estimated as 3.45. We can, in principle, estimate τ_S, τ_Π and τ_q from (2) with the help of the experimental data on μ, ν and κ . However, at present, as we have the reliable data only on μ and κ ($\tau_q/\tau_S = 1.33$), we adopt τ_Π/τ_S as an adjustable parameter. In the present analysis, τ_Π/τ_S is estimated to be 2.3.

In the comparison, the instrumental function is approximated by a Lorentzian with a full-width at half-maximum of about 28 MHz, and is convolved with the theoretical predictions.

The figures show the light scattering spectra for the values of parameter y=11.1 and 1.01 . A good agreement with the ET theory and experiments is observed from these figures.

5. Summary and concluding remarks

We have seen clearly that the recent ET theory at least for rarefied polyatomic gases, is consistent with the experimental data even in the small y (kinetic regime) where NSF is no more valid. We have also evaluated the bulk viscosity, and the value has a good agreement with the result from the kinetic theoretical approach [5].

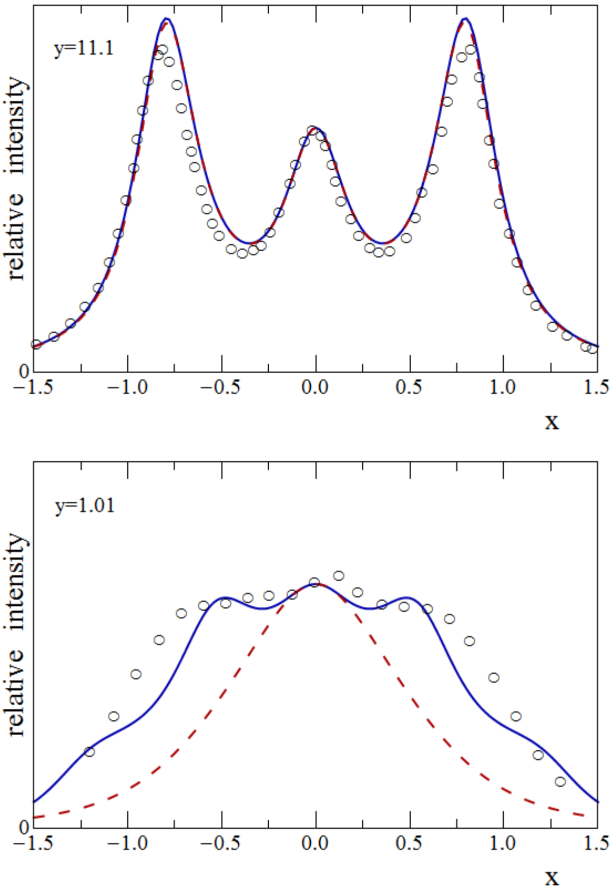

Fig. The relative intensity of the dynamic structure factor $S(\mathbf{q},\omega)$ for CO_2 at 300K with y=11.1(upper) and y=1.01(lower). The solid and dashed lines denote, respectively, the predictions by the ET and NSF theories in the case that τ_Π/τ_S is selected as 2.3. The circles in the figures are the experimental data by Greytak and Benedek [4].

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