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Kinetic effects and coupling with internal degrees of freedom in SF_6-He mixtures at moderate pressure

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We report measurements of Rayleigh-Brillouin spectra of SF_6-He mixtures at moderate pressures. Kapral and Desai's translational hydrodynamic theory [Chem. Phys. **3**, 141 (1974)] describes the data in the hydrodynamic regime. We found a transition regime in which the He partial pressure is small.

I. INTRODUCTION

Molecular-gas dynamics depend on the coupling between collective modes (thermal modes and sound mode) and internal modes (rotational and vibrational degrees of freedom). Rayleigh-Brillouin studies have been performed for pure molecular gases by several authors: May *et al.*,[1] Clark *et al.*,[2] Cazabat *et al.*,[3] and Lao *et al.*[4] Theoretical interpretations have been carried out with the models of Mountain,[5] Tenti *et al.*,[6] and Desai and Kapral.[7] Those works describe the modifications on the hydrodynamic as well as the kinetic[8] regimes due to the internal degrees of freedom.

In the kinetic regime the collisions between particles must be taken into account. The wave length q^{-1} selected by the experimental geometry is in this case equivalent or smaller than the mean free path l. In the hydrodynamic regime, collisions can be ignored, the wavelength q^{-1} is then bigger than l, and the medium can be considered as a continuum.

Gornall *et al.*,[9] Bloembergen *et al.*,[10,11] and Lowdermilk *et al.*[12] studied polyatomic-monatomic disparate-mass mixtures of gases. They gave an interpretation of their experimental Rayleigh-Brillouin results in the light of Mountain's theory of molecular relaxation of transport and thermodynamic coefficients. In their studies of SF_6-He mixtures, the authors started from SF_6 in the hydrodynamic regime, to which they added helium; they never found a kinetic regime. In our studies of Xe-He disparate gas mixtures[13] we found a transition regime when small amounts of He were added to hydrodynamic Xe; the hydrodynamic regime was recovered when more He was added.

This paper presents a study of SF_6-He mixtures with better experimental conditions than previous works. Contrary to one previous work, we find a kineticlike regime similar to that found in Xe-He mixtures. Experimental conditions (higher resolution and stray-light-free spectra) made possible an improvement in the knowledge of the dynamics of polyatomic-monatomic disparate-mass gas mixtures.

Numerical simulations show a discrepancy with Mountain's theory[5] whereas experimental results agree with Kapral and Desai's translational hydrodynamic theory which is described in Sec. II. Assumptions for numerical simulations and experimental descriptions are given in Sec. III. Section IV is devoted to discussion and conclusion.

II. THE TH THEORY

Kapral and Desai[14] extended their translational hydrodynamic (TH) theory to binary relaxing mixtures. The TH theory applies to thermal as well as structural relaxation processes. The system is described as a ternary mixture, in which nonexcited and excited molecules of the relaxing component are taken as two distinct species. We applied the TH theory to moderate-pressure gaseous mixtures with one thermal relaxation process. The following set of orthonormal dimensionless variables was used:

$$X_1(\mathbf{r},t)=dc \ ,$$

$$X_2(\mathbf{r},t)=\frac{d\xi}{\rho_0} \ ,$$

$$X_3(\mathbf{r},t)=\frac{dT}{T} \ ,$$

$$X_4(\mathbf{r},t)=\frac{d\theta}{T} \ ,$$

$$X_5(\mathbf{r},t)=W=-\frac{\nabla\cdot\mathbf{V}_0}{qV_T} \ ,$$

where dc is the concentration fluctuation of the heavier component A, $d\xi$ is the part of the density fluctuation $d\rho$ independent of dc, dT is the whole temperature fluctuation, $d\theta$ is the difference between whole and internal temperature fluctuations, $\mathbf{V}_0$ is the barycentric velocity, V_T is the thermal velocity defined as $V_T=(\rho\chi_T)^{-1/2}$, and χ_T is the isothermal compressibility. After Fourier-Laplace transforms, the hydrodynamic equations take the matrix form:

$$\underline{M}\cdot\mathcal{V}=\mathcal{V}^0 \ ,$$

where the vectors $\mathcal{V}$ and $\mathcal{V}^0$ are built up with the transforms of the X_i at variable and initial conditions, respectively. The M_{ij} matrix elements are

$$M_{11}=D_{AB}q^2,\quad M_{12}=\frac{Mx(1-x)(m_B-m_A)}{\overline{m}}\frac{\Delta_1}{\Delta_3\Delta_4}M_{11}\ ,$$

$$M_{13}=Mx(1-x)FM_{11},\quad M_{14}=\frac{C_I}{C_V^*}M_{13},\quad M_{15}=M_{51}=0\ ,$$

$$M_{2i}=\frac{m_B-m_A}{M\overline{m}}\Delta_1 M_{1i}\quad (i=1,4),\quad M_{25}=qV_T\ ,$$

$$M_{31}=\frac{F}{G}M_{11},\quad M_{32}=\frac{F}{G}M_{12},\quad M_{33}=\frac{F}{G}M_{13}+\frac{\lambda}{\rho C_p}q^2\ ,$$

$$M_{34}=\frac{C_I}{C_V^*}(M_{33}-D'q^2),\quad M_{35}=\frac{\gamma-1}{\Delta_2}qV_T\ ,$$

$$M_{41}=M_{31},\quad M_{42}=M_{32},\quad M_{43}=M_{33}-D'q^2\ ,$$

$$M_{44}=M_{34}+D'q^2+\frac{C_V}{C_V^*\tau_R}\ ,$$

$$M_{54}=\frac{C_I}{C_V^*}M_{53},\quad M_{55}=\frac{b}{\rho}q^2\ .$$

m_A and m_B are the molecular masses of the relaxing and nonrelaxing constituents, respectively (referred to as A and B), x is the molar fraction of the A constituent,

$$\overline{m}=m_A x+m_B(1-x),\quad M=\frac{m_A m_B}{(\overline{m})^2}\ ,$$

C_V^*, C_I are the nonrelaxing and relaxing parts of the total specific heat at constant volume C_V, and

$$F=\alpha_{AB}+\frac{(m_B-m_A)}{\overline{m}}\frac{\Delta_1\Delta_2}{\Delta_3\Delta_4},\quad G=\frac{MC_V}{\Delta_4}\ .$$

The expressions of the nonideality corrections Δ_i ($i=1,5$) are given in the Appendix ($\Delta_i=1$ for an ideal-gas mixture). $\gamma=C_p/C_V$; D_{AB},λ,b are, respectively, the mutual diffusion coefficient, the thermal conductivity, and the total longitudinal viscosity ($b=\frac{4}{3}\eta_S+\eta_V$) of the mixture. α_{AB} is the thermal diffusion coefficient, τ_R the thermal relaxation time:

$$D'=D_S D_{AB}/(xD_{AB}+(1-x)D_S)\ ,$$

where D_S is the self-diffusion coefficient of the polyatomic gas.

III. NUMERICAL SIMULATION AND EXPERIMENT

The Rayleigh-Brillouin spectrum $I(\mathbf{q},\omega)$ is proportional to the space-time Fourier transform of the autocorrelation function of the fluctuations in the local dielectric constant:

$$I(\mathbf{q},\omega)\alpha\mathrm{Re}\langle\epsilon(\mathbf{q},\omega)\epsilon(-\mathbf{q})\rangle\ .$$

Taking $(\partial\epsilon/\partial T)_{c,\xi}=0$ (Ref. 14), the only two variables which couple with the dielectric-constant fluctuations are $d\xi$ and dc. The coupling coefficients are derived from the Clausius-Mossotti formula:

$$\epsilon(\mathbf{q},\omega)=Ed\xi(\mathbf{q},\omega)+\rho\left[E'-\frac{\overline{m}(m_B-m_A)}{m_A m_B}\Delta_1\right]dc(\mathbf{q},\omega)\ ,$$

with

$$E=\frac{\alpha_A x+\alpha_B(1-x)}{\overline{m}}\ ,$$

$$E'=\frac{\alpha_A}{m_A}-\frac{\alpha_B}{m_B}\ .$$

The polarizabilities α_A and α_B are reported in Table I.

TABLE I. Parameters for SF_6-He mixture calculations.[a]

$\left[\frac{\epsilon}{k_B}\right]_{SF_6}=200.9$ K	$\left[\frac{\epsilon}{k_B}\right]_{He}=10.22$ K
$\sigma_{SF_6}=5.51$ Å	$\sigma_{He}=2.576$ Å
$\alpha_{SF_6}=4.537\times10^{-24}$ cm^3/mole	$\alpha_{He}=0.204\times10^{-24}$ cm^3/mole

[a] Values from Ref. 12.

A numerical simulation of the Rayleigh-Brillouin spectra requires knowledge of the transport and thermodynamic coefficients. The Chapman-Enskog procedure was used to compute transport coefficients and nonideality corrections with Lennard-Jones 6-12 potentials.[15] The potential parameters given in Table II were taken from Ref. 12. The shear viscosity and mutual diffusion coefficient of the mixture were found to be in agreement with experimental values given by Kestin *et al.*[16] (Table II).

The conductivity coefficient of the mixture was calculated using the following formula taken from Kapral and Desai:[14]

$$\lambda=\lambda_{\mathrm{mix}}^*+\rho\frac{\Delta\lambda_A}{x+(1-x)^{D_S/D_{AB}}}\ .$$

The translational contribution λ_{mix}^* was computed with the Chapman-Enskog procedure. The translational conductivity of pure SF_6 is derived from the usual relation

$$\lambda_A^*=\frac{15}{4}\frac{k_B}{m_A}\eta_A\ .$$

The value of the self-diffusion coefficient D_S is unknown. Using Kestin's universal corresponding state functions[16] we obtained

$$\frac{D_S}{D_{AB}}=0.083\quad\text{at }T=293\text{ K}\ .$$

TABLE II. Values of SF_6-He molecular coefficients.

$C_v=10.61\overset{\mathrm{R}}{\underset{\mathrm{m}}{=}}(x)^{a}$	
$\tau_R^{\mathrm{rot}}=4\times10^{-10}$ s^{a}	$\tau_R^{\mathrm{vib}}=7.410^{-7}$ s^{a}
$\left[\frac{Z_{AA}}{Z_{AB}}\right]_{\mathrm{rot}}=2.00^{b}$	$\left[\frac{Z_{AA}\eta_{AA}}{Z_{AB}\eta_{AB}}\right]_{\mathrm{vib}}=1.83^{c}$
$(x)R$ is the gas constant	$D_{AB}P=0.386$ cm^2 s^{-1} atm^{d}

[a] From Ref. 3.
[b] Estimated.
[c] From Ref. 20.
[d] Extrapolated from Ref. 16.

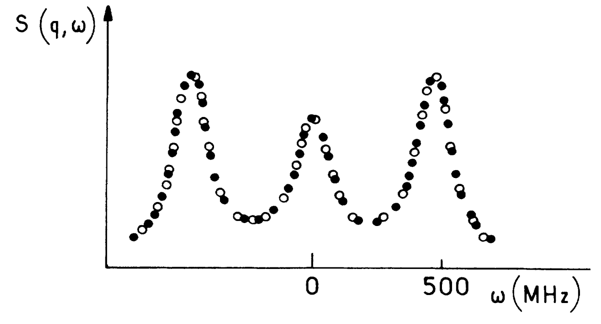

FIG. 1. Rayleigh-Brillouin spectra of SF$_6$: $P_{\rm SF_6}=2.81$ atm; Knudsen number, $Y=2.34$; wave vector, $q=2.03\times10^5$ cm^{-1}. ○, translational hydrodynamic calculation; ●, experimental. (Same symbols for the other figures.)

The increment $\Delta\lambda_A$ was adjusted in order to be found in agreement with the value of the conductivity of pure SF$_6$ ($\lambda_A=13.23$ mW m^{-1} K^{-1}) compiled by Cazabat.[17]

The relaxation time of an ideal-gas mixture is given by[18]

$$\frac{1}{\tau_R}=\frac{1}{\tau_R^A}\left[x+(1-x)\frac{\eta_A}{\eta_{AB}}\frac{Z_{AA}}{Z_{AB}}\right],$$

where τ_R^A is the relaxation time of the pure gas A at the same pressure, η_{AB} is the mutual shear viscosity, Z_{AA}/Z_{AB} is the ratio of direct to cross-collision numbers. The experimental values of the vibrational and rotational relaxation times for pure SF$_6$ have been compiled in Ref. 17. We assumed a vibrational relaxation of SF$_6$ with rotational and translational degrees always in thermal equilibrium.

A residual volume viscosity η_V occurs in the TH theory[14] (low-frequency limit of the rotational relaxation):

$$\frac{\eta_V}{\rho}q^2=\frac{RC_I^{\rm rot}}{(C_V^*)^2}\tau_R^{\rm rot}q^2,$$

where $C_I^{\rm rot}$ is the rotational heat capacity and C_V^* the translational-rotational heat capacity.

Theoretical Rayleigh-Brillouin spectra were convolved by an experimental-apparatus function before comparison with experimental results.

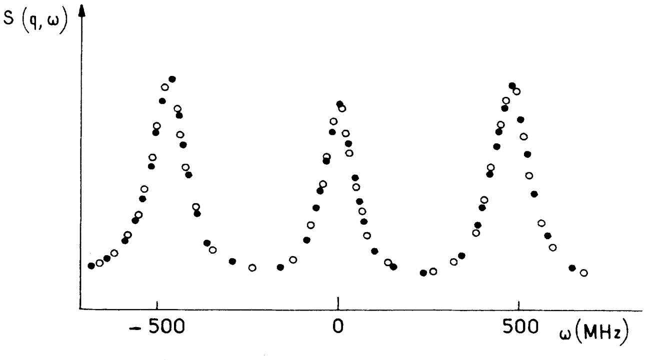

FIG. 2. Rayleigh-Brillouin spectra of SF$_6$: $P_{\rm SF_6}=5.08$ atm, $Y=6.1$, $q=2.03\times10^5$ cm^{-1}. See Fig. 1 for additional details.

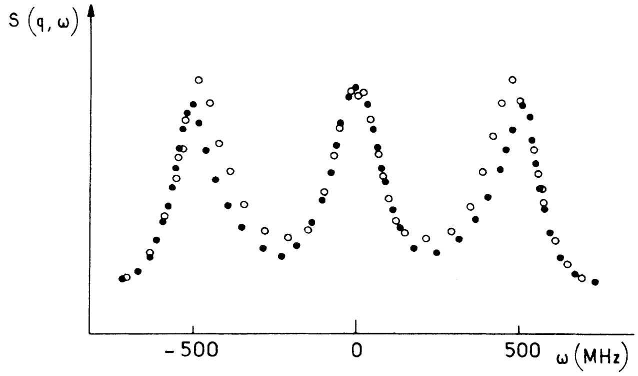

FIG. 3. Rayleigh-Brillouin spectra of SF$_6$-He mixture: $P_{\rm SF_6}=5.08$ atm; $P_{\rm He}=1.02$ atm, $Y_{\rm SF_6}=6.1$, $Y_{\rm He}=0.154$, $q=2.03\times10^5$ cm^{-1}. See Fig. 1 for additional details.

A complete description of the experimental setup is given elsewhere.[9] The main aspects are the following: a stabilized Ar$^+$ 171 Spectra Physics laser giving a monomode radiation with a width smaller than 30 MHz; a long-arm scattering cell which contributes to stray-light-free spectra, a filling system with cryogenic pumping allowing a concentration precision better than 1%; a spherical Fabry-Perot analyzer with a free spectra range of 1386 MHz and a typical finesse of 40. The q values were 2.03×10^5 cm^{-1} and 1.35×10^5 cm^{-1}.

IV. RESULTS AND DISCUSSION

The dynamic regime of a binary mixture is characterized by the Knudsen numbers $Y_i=(ql_i)^{-1}$ ($i=A,B$) expressed in terms of dynamical coefficients:[13]

$$Y_i=\frac{0.471P_i}{qv_0^i\eta_i}, \qquad (1)$$

where P_i, η_i, and v_0^i are, respectively, the partial pressure, viscosity, and thermal velocity $(k_BT/m_i)^{1/2}$ of the component i. In Figs. 1 and 2 (pure SF$_6$ at 2.81 and 5.08 atm), a good agreement is found between the experiments

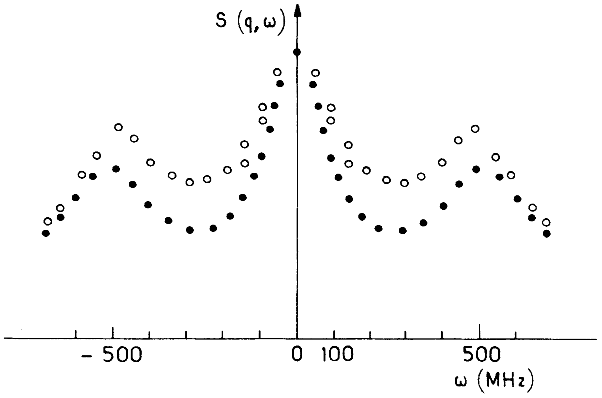

FIG. 4. Rayleigh-Brillouin spectra of SF$_6$-He mixture: $P_{\rm SF_6}=5.08$ atm, $P_{\rm He}=2.92$ atm, $Y_{\rm SF}=6.1$, $Y_{\rm He}=0.45$, $q=2.03\times10^5$ cm^{-1}. See Fig. 1 for additional details.

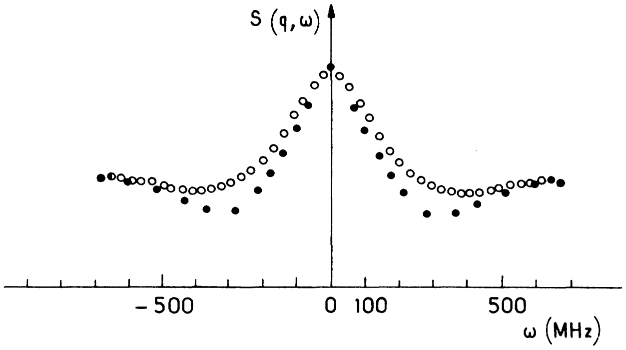

FIG. 5. Rayleigh-Brillouin spectra of SF$_6$-He mixture: $P_{SF_6}=5.08$ atm, $P_{He}=5.72$ atm, $Y_{SF_6}=6.1$, $Y_{He}=0.86$, $q=2.03\times10^5$ cm^{-1}. See Fig. 1 for additional details.

and the TH calculation. In both cases Y_{SF_6} values are bigger than one and a hydrodynamic regime is found as expected.

Starting from $P_{SF_6}=5.08$ atm, He is added with Knudsen number Y_{He} smaller than one. The experimental spectra exhibit strong discrepancies with TH simulations (Figs. 3, 4, and 5). The disagreement with TH theory disappears when Y_{He} becomes bigger than one. Figure 6 shows spectra with the same conditions as in Fig. 5, except the wave vector q which is changed from 2.03×10^5 cm^{-1} to 1.35×10^5 cm^{-1}. The good agreement with TH theory is an additional proof of occurrence of a kinetic regime when Y_{He} is smaller than one; here Y_{He} has been made bigger than one by a change in the wave vector instead of in the mean free path.

We discuss now some aspects of previous works of Gornall *et al.*[9] The authors never find any kinetic regime with, respectively, 20%, 40%, and 70% in molar fraction of He added to SF$_6$ at the initial pressure of 5 atm. From formula (1) the corresponding Knudsen numbers are the following: $Y_{SF_6}=6.14$, Y_{He} (20%)=0.19, Y_{He} (40%) =0.525, and Y_{He} (70%)=1.84. According to our criteria only the last experimental situation should be in the hydrodynamic regime. (The Knudsen number definition used by Gornall gives numerical values roughly twice than ours. Their hydrodynamic criterium is $Y>3$.) It seems that kinetic effects on the spectra are probably hidden by insufficient experimental resolution and some amount of stray light. The assumption that "... one can expect that if one component is in the hydrodynamic regime with its partial pressure, the mixture should be in the hydrodynamic regime..." of Bloembergen *et al.* (Ref. 12 in Ref. 11) is clearly unverified: kinetic contributions appear when one component is in the kinetic regime at its partial pressure.

In their papers devoted to the study of SF$_6$-He mixtures by spontaneous and stimulated light scattering, Gornall *et al.*,[9] Lowdermilk *et al.*,[12] and Bloembergen *et al.*[10,11] describe the coupling between internal degrees of freedom and collective modes on the basis of Mountain's theory. We performed numerical simulations with the values given in Appendixes A and B (Ref. 12). Agreement with experiments is found only if D_{AB} is taken at the value 0.33 cm^{2}s^{-1} at $p=1$ atm, far from the experimental value $D_{AB}P=0.386$ cm^2s^{-1}atm (Ref. 16) used in our TH calculations.

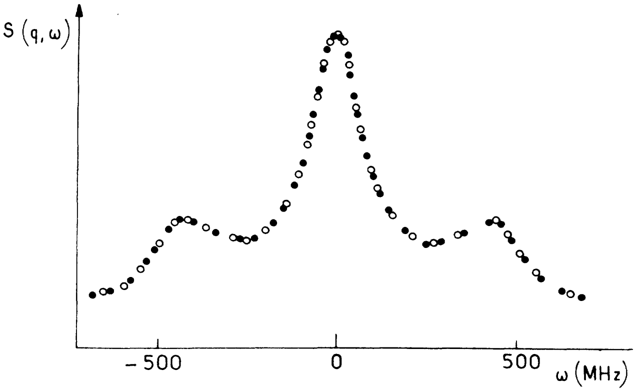

FIG. 6. Rayleigh-Brillouin spectra of SF$_6$-He mixture: $P_{SF_6}=5.08$ atm, $P_{He}=5.72$ atm, $Y_{SF_6}=9.19$, $Y_{He}=1.3$, $q=1.35\times10^5$ cm^{-1}. See Fig. 1 for additional details.

The discrepancy in D_{AB} values occurs from coupling between vibrational degrees and collective modes. This coupling is not properly described by Mountain's theory for the case of gaseous mixtures.

The two important aspects of this work are the following. (a) Evidence of a kinetic regime in SF$_6$-He mixtures with SF$_6$ in the hydrodynamic regime and He in the kinetic regime at their partial pressures was presented. (b) Kapral and Desai TH theory was shown to provide an accurate description of the hydrodynamic regime.

For a theoretical description of the kinetic regime it should be interesting to combine the theory of Boley *et al.*[8] for pure molecular gases with the model of monatomic disparate-mass mixtures developed by Letamendia *et al.*[19]

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APPENDIX

Expressions for nonideality correction terms defined in Sec. II:

$$\Delta_1=1+\bar{m}ndB/dX\ ,$$

$$\Delta_2=\frac{1+n(B+B')}{1+2nB}\ ,$$

$$\Delta_3=(1+2nB)^{-1}\ ,$$

$$\Delta_4=1+\frac{2nx(1-x)}{m}[m_B(\sigma_{AA}^3B_{AA}-\sigma_{AB}^3B_{AB})+m_B(\sigma_{BB}^3B_{BB}-\sigma_{AB}^3B_{AB})]\ ,$$

$$\Delta_5=1-\frac{2n}{3}(2B'+B'')\ .$$

B is the second virial coefficient obtained from Ref. 15. B' and B'' are temperature derivatives and n is the density number.

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