

Density Fluctuations in Fluids Having an Internal Degree of Freedom*

Raymond D. Mountain

Institute for Basic Standards, National Bureau of Standards, Washington, D.C. 20234

(August 18, 1967)

The frequency spectrum of density fluctuations is calculated for a fluid whose molecules possess an internal degree of freedom which is weakly coupled to the translational degree of freedom of the fluid. Irreversible thermodynamics is used to obtain an equation of motion for the internal degree of freedom. This equation plus the linearized hydrodynamic equations are solved for the frequency spectrum of density fluctuations. The results are compared with a similar calculation involving a frequency dependent volume viscosity. The results are identical for structural relaxation but there is a difference for thermal relaxation. The origin of the difference is discussed and the magnitude of the difference is examined for CCl_4 and for CS_2 .

Key Words: Brillouin scattering, density fluctuations in liquids, Rayleigh scattering, spectral distribution of scattered light, structural relaxation, thermal relaxation, volume viscosity.

1. Introduction

The spectrum of light scattered by density fluctuations in a fluid is proportional to frequency spectrum of density fluctuations [1].¹ The development of the gas laser has made it possible to measure the spectra of long wavelength density fluctuations and thereby study fluids in the frequency region of a few gigacycles down to essentially zero cycles/sec.

For dense fluids this frequency region corresponds to slowly varying processes whose time dependence may be reasonably expected to be described by the equations of irreversible thermodynamics. When considering density fluctuations the appropriate equations are the linearized equations of hydrodynamics plus two additional relations among the variables so that a solution to the initial value (or boundary value) problem is possible.

In this paper we shall consider density fluctuations in a fluid whose molecules possess an internal degree of freedom which relaxes toward local equilibrium with the density and/or the temperature [2, 3]. This is carried out in section 2. In section 3 this calculation is compared with an earlier calculation [1] where the internal degree of freedom was assumed to result in a frequency dependent volume viscosity. The introduction of a frequency dependent volume viscosity is based on statistical mechanical arguments [4, 5].

The comparison is made in two limiting cases. In the first case it is assumed that the internal variable depends only on the local temperature (thermal relaxation). It is found that the two calculations yield similar, but not identical, results. The origin and magnitude of the difference are examined. Carbon tetrachloride and carbon disulfide are used to illustrate the discussion. In the second case it is assumed that the internal variable depends only on the local density (structural relaxation). The two calculations yield identical results.

No comparison is made when both thermal relaxation and structural relaxation are present.

2. Calculation

The thermodynamic statement relating the parameters for our system is [6]

$$dU = TdS + \frac{p}{\rho_0} d\rho + A_\xi d\xi \quad (1)$$

where U is the energy, S is the entropy, T is the temperature, ρ is the density, ρ_0 is the equilibrium value of the density, p is the pressure, ξ represents an internal degree of freedom and A_ξ is the partial derivative of the Helmholtz free energy with respect to ξ ,

$$A_\xi = (\partial A / \partial \xi)_{\rho, T}. \quad (2)$$

We shall further require that $A_\xi = 0$ when the internal degree of freedom is in local equilibrium with the

*This work was sponsored by the Advanced Research Projects Agency of the Department of Defense.

¹Figures in brackets indicate the literature references at the end of this paper.

density and the temperature (whether or not the density and temperature have reached equilibrium values). This may be expressed as

$$A_{\xi}(\rho, T, \bar{\xi}) = 0 \quad (3)$$

where

$$\bar{\xi} = \xi(\rho, T) \quad (4)$$

is the local equilibrium value of ξ .

A kinetic equation for ξ is obtained by applying the methods of irreversible thermodynamics to the system with the result

$$\partial \xi / \partial t = -LA_{\xi} \quad (5)$$

where the kinetic coefficient L is > 0 . As we are concerned with small deviations from equilibrium, A_{ξ} is expanded to obtain

$$\frac{\partial \xi}{\partial t} = -L[A_{\xi\rho}(\rho - \rho_0) + A_{\xi T}(T - T_0) + A_{\xi\xi}(\xi - \xi_0)] \quad (6)$$

where $A_{\xi\rho} = (\partial A_{\xi} / \partial \rho)_{T, \xi}$, etc. If we expand eq (3) and substitute this in eq (6) we obtain

$$\partial \xi / \partial t = -LA_{\xi\xi}(\xi - \bar{\xi}). \quad (7)$$

The equations of motion for the system are the linearized hydrodynamic equations:

$$\partial \rho / \partial t + \rho_0 \psi = 0, \quad (8)$$

$$m\rho_0 \partial \psi / \partial t = -\nabla^2 p + \left(\frac{4}{3}\eta_s + \eta_v\right) \nabla^2 \psi \quad (9)$$

and

$$\rho_0 T_0 \partial S / \partial t = \lambda \nabla^2 T. \quad (10)$$

Here $\psi = \text{div } \mathbf{v}$, η_s is the shear viscosity, η_v is the volume viscosity and λ is the thermal conductivity and m is the mass of a molecule. We relate the pressure and entropy to the density, temperature and ξ by the thermodynamic relations

$$dp = \left(\frac{\partial p}{\partial \rho}\right)_{T, \xi} d\rho + \left(\frac{\partial p}{\partial T}\right)_{\rho, \xi} dT + \left(\frac{\partial p}{\partial \xi}\right)_{\rho, T} d\xi \quad (11)$$

and

$$dS = \left(\frac{\partial S}{\partial \rho}\right) d\rho + \left(\frac{\partial S}{\partial T}\right)_{\rho, \xi} dT + \left(\frac{\partial S}{\partial \xi}\right)_{T, \rho} d\xi. \quad (12)$$

The internal variable ξ is eliminated by combining eqs (6), (11), and (12). For the pressure we find

$$dp + \tau \frac{\partial dp}{\partial t} = \left(\frac{\partial p}{\partial \rho}\right)_{T, \xi} \left[d\rho + \tau \frac{\partial d\rho}{\partial t} \right]$$

$$+ \left(\frac{\partial p}{\partial T}\right)_{\rho, \xi} \left[dT + \tau \frac{\partial dT}{\partial t} \right]$$

$$+ \left(\frac{\partial p}{\partial \xi}\right)_{\rho, T} \left[-\frac{A_{\xi\rho}}{A_{\xi\xi}} d\rho - \frac{A_{\xi T}}{A_{\xi\xi}} dT \right] \quad (13)$$

where

$$\tau = (LA_{\xi\xi})^{-1}.$$

A similar equation is obtained for the entropy.

$$dS + \tau \frac{\partial dS}{\partial t} = \left(\frac{\partial S}{\partial \rho}\right)_{T, \xi} \left[d\rho + \tau \frac{\partial d\rho}{\partial t} \right]$$

$$+ \left(\frac{\partial S}{\partial T}\right)_{\rho, \xi} \left[dT + \tau \frac{\partial dT}{\partial t} \right]$$

$$+ \left(\frac{\partial S}{\partial \xi}\right)_{\rho, T} \left[-\frac{A_{\xi\rho}}{A_{\xi\xi}} d\rho - \frac{A_{\xi T}}{A_{\xi\xi}} dT \right]. \quad (14)$$

Equations (8), (9), (10), (13), and (14) constitute a complete set of equations. The next step is to obtain the Fourier-Laplace (space-time) transform of this set of equations. The result is

$$z\rho_k(z) + \rho_0\psi_k(z) = \rho_k, \quad (15)$$

$$(z + b_0 k^2)\psi_k(z) - \left[\frac{C_0^2 k^2}{\rho_0} + \frac{\Delta k^2}{\rho_0} \cdot \frac{z\tau}{1 + z\tau} \right] \rho_k(z)$$

$$- \left[\frac{C_0^2 k^2 \beta_T}{\gamma} + \frac{\rho_0}{m} A_{\xi\xi\xi\rho\xi} \tau k^2 \cdot \frac{z\tau}{1 + z\tau} \right] T_k(z)$$

$$= \psi_k + \frac{\tau k^2}{1 + z\tau} \left[\frac{\rho_k}{m\rho_0} - \left(\frac{C_0^2}{\gamma\rho_0} + \frac{\Delta}{\rho_0} \right) \rho_k \right]$$

$$- \left(\frac{C_0^2 \beta_T}{\gamma} + \frac{\rho_0}{m} A_{\xi\xi\xi\rho\xi} \tau \right) T_k. \quad (16)$$

and

$$- \left[\frac{z(\gamma - 1)}{\rho_0 \beta_T} + \frac{z^2 \tau T_0 A_{\xi\xi\xi\rho\xi} \tau}{C_v(1 + z\tau)} \right] \rho_k(z)$$

$$+ \left[z - \frac{(C_l/C_v)z^2\tau}{1 + z\tau} + ak^2 \right] T_k(z)$$

$$= -\frac{z\tau}{1 + z\tau} \left[\frac{T_0 S_k}{C_v z\tau} + \left(\frac{\gamma - 1}{\rho_0 \beta_T} + \frac{T_0 A_{\xi\xi\xi\rho\xi} \tau}{C_v} \right) \rho_k \right]$$

$$- (1 - C_l/C_v) T_k. \quad (17)$$

Here we have made use of thermodynamic relationships which are developed in the appendix. The transformed quantities are

$$\rho_k(z) = \int_0^{\infty} dt e^{-zt} \int_v d\mathbf{r} e^{i\mathbf{k} \cdot \mathbf{r}} [\rho(\mathbf{r}, t) - \rho_0]. \quad (18)$$

$T_k(z)$ and $\psi_k(z)$ are obtained in the same way. In eq (16) $b_0 = \left(\frac{4}{3}\eta_s + \eta_v\right)/m\rho_0$, C_0 is the low-frequency sound speed, γ is the ratio of specific heats,

$$\Delta = \rho_0^2 A_{\xi\xi} \xi_{\rho}^2 / m,$$

β_T is the isothermal coefficient of thermal expansion, $\xi_{\rho} = -A_{\xi\rho}/A_{\xi\xi}$ and $\xi_T = -A_{\xi T}/A_{\xi\xi}$. In eq (17) $C_l = T_0 A_{\xi\xi} \xi_T^2$ and $a = \lambda/\rho_0 C_v$. The quantity C_l represents the contribution of the internal degree of freedom to the specific heat when the density is held constant.

The right-hand sides of eqs (16) and (17) may be simplified by noting that in equilibrium

$$\frac{1}{m\rho_0} dp = \frac{C_0^2}{\gamma\rho_0} d\rho + \frac{C_0^2 \beta_T}{\gamma} dT \quad (19)$$

and

$$\frac{T_0 dS}{C_v} = -\frac{\gamma-1}{\beta_T \rho_0} d\rho + dT. \quad (20)$$

This simplification is permissible because we are interested in computing the correlation function $\langle \rho_k \rho_{-k}(z) \rangle$ in terms of the equilibrium correlation function $\langle |\rho_k|^2 \rangle$.

To obtain $\langle \rho_k \rho_{-k}(z) \rangle$ we solve eqs (15-17) for $\rho_k(z)$ in terms of the initial values ρ_k , T_k and ψ_k . Only the terms involving ρ_k are of interest because

$$\langle \rho_k T_{-k} \rangle = \langle \rho_k \psi_{-k} \rangle = 0.$$

3. Comparison With a Calculation Using a Frequency Dependent, Single Relaxation Time, Volume Viscosity

3.1. Thermal Relaxation

We are interested in the case where the relaxing parameter is independent of the density, i.e., $\xi_{\rho} = 0$. The correlation function is found to be

$$\frac{\langle \rho_k \rho_{-k}(z) \rangle}{\langle |\rho_k|^2 \rangle} = \frac{F(z)}{G(z)} \quad (21)$$

where

$$\begin{aligned} F(z) = & z^3 \tau \left(1 - \frac{C_l}{C_v}\right) \\ & + z^2 [1 + ak^2 \tau + b_0 k^2 \tau (1 - C_l/C_v)] \\ & + z \left[ak^2 + b_0 k^2 + ab_0 k^4 \tau + C_0^2 k^2 \tau \left(1 - \frac{1}{\gamma}\right) \right] \\ & + ab_0 k^4 + C_0^2 k^2 (1 - 1/\gamma) \end{aligned} \quad (22)$$

and

$$\begin{aligned} G(z) = & z^4 \tau (1 - C_l/C_v) \\ & + z^3 [1 + ak^2 \tau + b_0 k^2 \tau (1 - C_l/C_v)] \\ & + z^2 [ak^2 + b_0 k^2 + ab_0 k^4 \tau + C_0^2 k^2 \tau (1 - C_l/C_v)] \\ & + z [ab_0 k^4 + C_0^2 k^2 (1 + ak^2 \tau/\gamma)] \\ & + ak^2 C_0^2 k^2 / \gamma. \end{aligned} \quad (23)$$

For purposes of comparison let us recall the corresponding expressions derived earlier for the case of a frequency dependent volume viscosity [1]. There

$$\begin{aligned} \tilde{F}(z) = & z^3 \tilde{\tau} + z^2 [1 + \tilde{\tau}(ak^2 + b_0 k^2)] \\ & + z [ak^2 + b_0 k^2 + b_1 k^2 + ab_0 k^4 \tilde{\tau} + C_0^2 k^2 \tilde{\tau} (1 - 1/\gamma)] \\ & + ab_0 k^4 + ab_1 k^4 + C_0^2 k^2 (1 - 1/\gamma). \end{aligned} \quad (24)$$

and

$$\begin{aligned} \tilde{G}(z) = & \tilde{\tau} z^4 + z^3 [1 + \tilde{\tau}(ak^2 + b_0 k^2)] \\ & + z^2 [ak^2 + b_0 k^2 + b_1 k^2 + \tilde{\tau}(C_0^2 k^2 + ab_0 k^4)] \\ & + z [C_0^2 k^2 + ab_0 k^4 + ab_1 k^4 + \tilde{\tau} C_0^2 k^2 ak^2 / \gamma] \\ & + C_0^2 k^2 ak^2 / \gamma. \end{aligned} \quad (25)$$

[Quantities with a tilde refer to the calculation in ref. 1.] Here b_0 is the nonrelaxing part of the kinematic viscosity, the relaxing part is $b_1/(1 + i\omega\tilde{\tau})$

$$\text{where} \quad b_1 = \frac{(C_p - C_v) C_l}{(C_v - C_l) C_p} C_0^2 \tilde{\tau}. \quad (26)$$

Direct comparison of G and \tilde{G} shows that the two expressions are not equivalent. This may be realized by noting that G contains the combination

$$z^3 b_0 k^2 \tau (1 - C_l/C_v) + z^2 C_0^2 k^2 (1 - C_l/C_v) \tau$$

while the corresponding terms in \tilde{G} are

$$z^3 b_0 k^2 \tilde{\tau} + z^2 C_0^2 k^2 \tilde{\tau}.$$

If we consider the limiting case where the internal degree of freedom provides the only loss mechanism for translational degrees of freedom it is possible to make G and \tilde{G} into equivalent expressions. In this limit where $a = b_0 = 0$

$$\begin{aligned} G(z) = & z^4 \tau (1 - C_l/C_v) + z^3 \\ & + z^2 C_0^2 k^2 \tau (1 - C_l/C_v) + z C_0^2 k^2 \end{aligned} \quad (27)$$

and

$$\begin{aligned} \tilde{G}(z) &= z^4 \tilde{\tau} + z^3 \\ &+ z^2 C_0^2 k^2 \tilde{\tau} \left(1 + \frac{C_p - C_r}{C_r - C_l} \cdot \frac{C_l}{C_p} \right) + z C_0^2 k^2. \end{aligned} \quad (28)$$

A simple comparison shows that if

$$\tilde{\tau} = \tau(1 - C_l/C_r) \quad (29)$$

then $\tilde{G} = G$ in this limit. It also can be shown that $\tilde{F} = F$ under these conditions.

In an experiment what is measured is not $F(z)/G(z)$ but the real part of F/G when $z = i\omega$:

$$\pi \frac{\langle \rho_k \rho_{-k}(\omega) \rangle}{\langle |\rho_k|^2 \rangle} = \text{Re} \frac{F(i\omega)}{G(i\omega)}. \quad (30)$$

A comparison of the complete expressions requires that we compare

$$\text{Re} \frac{F(i\omega)}{G(i\omega)} \quad \text{with} \quad \text{Re} \frac{\tilde{F}(i\omega)}{\tilde{G}(i\omega)}.$$

To do this we write

$$\text{Re} \frac{F(i\omega)}{G(i\omega)} = \text{Re} \frac{N_1 + iN_2}{D_1 + iD_2} = \frac{N_1 D_1 + N_2 D_2}{D_1^2 + D_2^2} \quad (31)$$

and

$$\text{Re} \frac{\tilde{F}(i\omega)}{\tilde{G}(i\omega)} = \frac{\tilde{N}_1 \tilde{D}_1 + \tilde{N}_2 \tilde{D}_2}{\tilde{D}_1^2 + \tilde{D}_2^2}. \quad (32)$$

From eqs (22) and (23) it follows that

$$\begin{aligned} N_1 &= -\omega^2 [1 + ak^2 \tau + b_0 k^2 \tilde{\tau}] + ab_0 k^4 + C_0^2 k^2 (1 - 1/\gamma) \\ N_2 &= -\omega^3 \tilde{\tau} + \omega [ak^2 + b_0 k^2 + ab_0 k^4 \tau + C_0^2 k^2 \tau (1 - 1/\gamma)] \\ D_1 &= \omega^4 \tilde{\tau} - \omega^2 [ak^2 + b_0 k^2 + ab_0 k^4 \tau + C_0^2 k^2 \tau (1 - C_l/C_p)] \\ &+ ak^2 C_0^2 k^2 / \gamma \end{aligned} \quad (33)$$

and

$$\begin{aligned} D_2 &= -\omega^3 [1 + ak^2 \tau + b_0 k^2 \tilde{\tau}] \\ &+ \omega \left[ab_0 k^4 + C_0^2 k^2 \left(1 + \frac{ak^2 \tau}{\gamma} \right) \right]. \end{aligned}$$

Here use has been made of eq (29).

The corresponding expressions for \tilde{N}_1 , etc., are

$$\begin{aligned} \tilde{N}_1 &= -\omega^2 [1 + ak^2 \tilde{\tau} + b_0 k^2 \tilde{\tau}] + ab_0 k^4 \\ &+ C_0^2 k^2 (1 - 1/\gamma) + C_0^2 k^2 ak^2 \tau \frac{C_l}{C_r} (1 - 1/\gamma) \end{aligned}$$

$$\begin{aligned} \tilde{N}_2 &= -\omega^3 \tilde{\tau} + \omega [ak^2 + b_0 k^2 + ab_0 k^4 \tilde{\tau} + C_0^2 k^2 \tau (1 - 1/\gamma)] \\ \tilde{D}_1 &= \omega^4 \tilde{\tau} - \omega^2 [ak^2 + b_0 k^2 + ab_0 k^4 \tilde{\tau} + C_0^2 k^2 \tau (1 - C_l/C_p)] \\ &+ C_0^2 k^2 ak^2 / \gamma \end{aligned} \quad (34)$$

and

$$\begin{aligned} \tilde{D}_2 &= -\omega^3 [1 + ak^2 \tilde{\tau} + b_0 k^2 \tilde{\tau}] \\ &+ \omega \left[C_0^2 k^2 \left(1 + ak^2 \frac{\tilde{\tau}}{\gamma} \right) + ab_0 k^4 \right. \\ &\left. + ak^2 \tau C_0^2 k^2 \frac{C_l}{C_r} \left(1 - \frac{1}{\gamma} \right) \right]. \end{aligned}$$

Examination of these expressions reveals: (a) they are not identical term for term, (b) there will be no significant difference in their values if

$$\alpha = ak^2 \tau C_l / C_r \quad (35)$$

is small compared to 1.

Using the parameters listed in ref. 1, we find that α is 6.4×10^{-4} for CCl_4 at 20°C and is 2.0×10^{-2} for CS_2 at 20°C . The wavevector was taken to be 10^5 cm^{-1} . This could be increased to $\alpha = 0.2$ for CS_2 if we consider scattering angles on the order of 180° using the He-Ne laser as the light source.

The spectra predicted by eqs (31) and (32) have been evaluated for CCl_4 and CS_2 using the parameters listed in ref. 1. For CCl_4 there is no difference between the two curves. This is not surprising considering the small value of α .

The two curves are not identical for

$$\text{CS}_2 (k = 3 \times 10^5 \text{ cm}^{-1}).$$

The central components are shown in figure 1. The

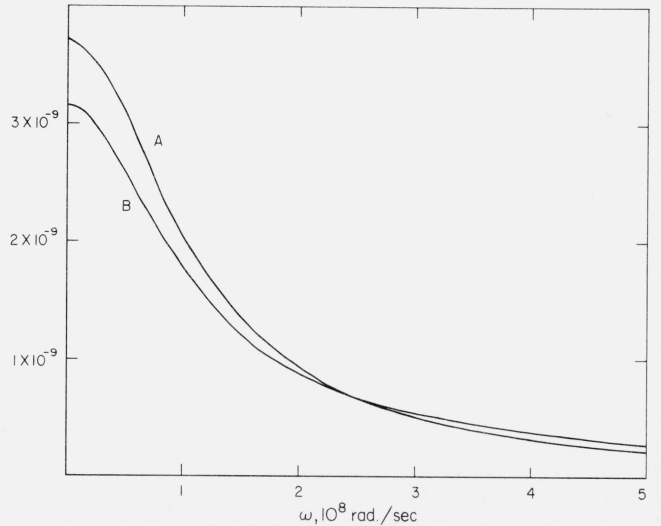


FIGURE 1. The central component of light scattered from CS_2 as predicted by eq (32), curve A and as predicted by eq (31) curve B. The parameters are taken from table of ref. 1. The wave vector $k = 3 \times 10^5 \text{ cm}^{-1}$.

curve labeled *A* was obtained using a frequency dependent volume viscosity (eq 32). The curve labeled *B* was obtained using the results of this calculation (eq 31). The difference in the amplitude at $\omega=0$ is due entirely to the term

$$C_0^2 k^2 a k^2 \tau \frac{C_I}{C_v} (1 - 1/\gamma)$$

in \bar{N}_1 . Such a quantity is missing in N_1 . It occurs as a result of multiplying the thermal diffusivity and the frequency dependent volume viscosity. We note for $\omega=0$, the present calculation yields the same amplitude as the theory which does not include internal relaxation processes.

The Brillouin components for CS_2 are shown in figure 2. The differences are due to the relatively large value of α and to the different values of $\omega_B \tau$ where ω_B is the Brillouin frequency. For curve *A*, $\omega_B \tau = 78$ while for curve *B*, $\omega_B \tau = 113$. The large value of α is the dominant feature as ω_B depends most strongly on k when $\omega_B \tau \gg 1$.

The possibility of finding a situation where α is appreciably greater than 0.2 appears to be remote. Longer relaxation times exist for rotational isomers [3], however, C_I/C_v is very small so α is still much less than unity.

3.2. Structural Relaxation

Next let us examine briefly the other limiting case which involves a structural relaxation rather than a thermal relaxation. A purely structural relaxation occurs when $\xi_T = 0$. The examination is speedily concluded by observing that if we formally identify Δ in eq (16) with $b_1/\tau = C_x^2 - C_0^2$ (see eq (22) of ref. 1) then this case and the frequency dependent volume viscosity calculation yield identical results. Also no scaling of the relaxation times is needed.

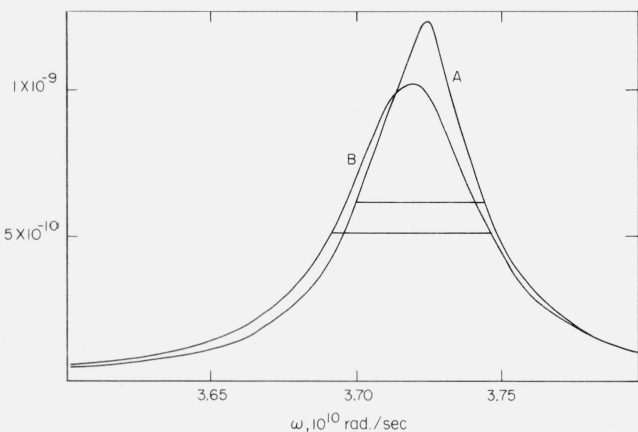


FIGURE 2. The Brillouin components of light scattered from CS_2 as predicted by eq (32), curve *A* and as predicted by eq (31) curve *B*.

The parameters taken from table of ref. 1. The wave vector $k = 3 \times 10^5 \text{ cm}^{-1}$. The horizontal lines indicate the full width at half maximum for the components.

4. Summary and Discussion

The frequency spectrum of density fluctuations in a fluid containing an internal degree of freedom has been calculated. The procedure used was to obtain an equation of motion for the internal variable ξ by the methods of irreversible thermodynamics and then to solve the resulting set of coupled equations for the spectrum of the density fluctuations.

This calculation was compared with an earlier calculation which treated the internal degree of freedom as a frequency dependent volume viscosity rather than as a separate variable with an equation of motion of its own. Two limiting cases were examined. The structural relaxation case, $\xi_T = 0$ was found to yield identical results when compared with the earlier calculation. The thermal relaxation case, $\xi_\rho = 0$ does not agree exactly with the earlier calculation. The difference results from the ways the stresses due to the internal variable are treated. In the present calculation the stresses are additive only to first order [7]. In the earlier calculation they were strictly additive.

The equation of motion approach worked out in this paper has an intuitive appeal in that one can see directly how the internal variable enters the problem and how it is related to the temperature and the density. The introduction of a frequency dependent volume viscosity in the case of thermal relaxation is required by statistical mechanical considerations [4, 5] and is therefore the preferred way to handle internal degrees of freedom which are weakly coupled to the translational degrees of freedom.

This calculation could be adapted to a chemically reacting system. This aspect of fluctuation theory and light scattering is discussed at length in recent publications [8, 9] so we shall not discuss it here.

5. Appendix

Starting with eq (1) the differential expression for the Helmholtz free energy is

$$dA = -SdT + \frac{p}{\rho_0^2} d\rho + A_\xi d\xi. \quad (36)$$

The Maxwell relations implied by eq (36) are

$$\begin{aligned} \left(\frac{\partial S}{\partial \xi}\right)_{T, \rho} &= -A_{\xi T} \\ \left(\frac{\partial S}{\partial \rho}\right)_{T, \xi} &= -\frac{1}{\rho_0^2} \left(\frac{\partial p}{\partial T}\right)_{\rho, \xi} \end{aligned} \quad (37)$$

and

$$\frac{1}{\rho_0^2} \left(\frac{\partial p}{\partial \xi}\right)_{\rho, T} = A_{\xi \rho}.$$

In equilibrium $A_\xi=0$ so that

$$dA_\xi = A_{\xi\rho}d\rho + A_{\xi T}dT + A_{\xi\xi}d\xi = 0.$$

It follows that

$$A_{\xi\rho} = -A_{\xi\xi}\xi_\rho$$

and

$$A_{\xi T} = -A_{\xi\xi}\xi_T$$

where $\xi_\rho = (\partial\xi/\partial\rho)_T$ and $\xi_T = (\partial\xi/\partial T)_\rho$.

If we combine these results with eqs (11) and (12) we obtain

$$\left(\frac{\partial\rho}{\partial\rho}\right)_{T,\xi} = \left(\frac{\partial\rho}{\partial\rho}\right)_T + \rho_0^2 A_{\xi\xi}\xi_\rho^2$$

$$\left(\frac{\partial\rho}{\partial T}\right)_{\rho,\xi} = \left(\frac{\partial\rho}{\partial T}\right)_\rho + \rho_0^2 A_{\xi\xi}\xi_\rho\xi_T$$

$$\left(\frac{\partial S}{\partial\rho}\right)_{T,\xi} = \left(\frac{\partial S}{\partial\rho}\right)_T - A_{\xi\xi}\xi_T\xi_\rho \quad (38)$$

and

$$\left(\frac{\partial S}{\partial T}\right)_{\rho,\xi} = \left(\frac{\partial S}{\partial T}\right)_\rho - A_{\xi\xi}\xi_T^2.$$

Finally we note that

$$\frac{mC_0^2}{\gamma} = \left(\frac{\partial\rho}{\partial\rho}\right)_T$$

$$\frac{m\rho_0\beta_T C_0^2}{\gamma} = \left(\frac{\partial\rho}{\partial T}\right)_\rho$$

and

$$\left(\frac{\partial S}{\partial\rho}\right)_T = -\frac{C_p - C_v}{\rho_0 T \beta_T}.$$

A most interesting discussion with G. I. A. Stegeman provided the stimulus for this work.

6. References

- [1] R. D. Mountain, J. Res. NBS **70A** (Phys. and Chem.), No. 3, 207 (1966). Section 2 of this paper contains a summary of the formalism relating light scattering and density fluctuations.
- [2] Karl F. Herzfeld and T. A. Litovitz, Absorption and Dispersion of Ultrasonic Waves (Academic Press, New York, 1959).
- [3] S. R. de Groot and P. Mazur, Non-Equilibrium Thermodynamics (North Holland Publishing Co., Amsterdam, 1962).
- [4] L. I. Komarov, Soviet Physics JETP **21**, 99 (1965).
- [5] Robert Zwanzig, J. Chem. Phys. **43**, 714 (1965).
- [6] V. T. Shmatov, Soviet Physics JETP **6**, 1044 (1958).
- [7] R. M. Mazo, J. Chem. Phys. **28**, 1223 (1958).
- [8] B. J. Berne and H. L. Frisch, J. Chem. Phys. **47**, 3675 (1967).
- [9] L. Blum and Z. W. Salsburg, J. Chem. Phys., to be published.

(Paper 72A1-486)