

Bulk viscosity in relaxing media

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Two approaches for the calculation of an acoustical property of relaxing media, namely the bulk viscosity, are analysed. One of them is the thermodynamic relaxation theory and another one is the analysis of the statistical expression for the bulk viscosity. In the frame of the statistical method the system of hydrodynamic equations is constructed for relaxing media. It is shown that the discrepancy between the thermodynamic and statistical approaches is connected with the influence of momentum on relaxational processes which is not contained in the thermodynamic method.

1. Introduction

One of the main problems of physical acoustics is the investigation of various physical processes leading to the sound velocity dispersion and sound attenuation. First of all these phenomena are the various internal relaxational processes such as vibrational relaxational in liquids and gases, chemical relaxational, systems near the critical points and so on. There are two approaches to the problem of obtaining the acoustical characteristics of the system. One of them is based on the calculation of the complex thermodynamic derivatives such as adiabatic bulk modulus and heat capacity for harmonic processes [1–5]. Another one [6–8] is the approach based on the calculation of the complex bulk viscosity coefficient starting from its statistical expression. The natural problem appears concerning the identity of both approaches. It may turn out that they lead to different results. Firstly this problem was discussed by Sarid and Cannell [9]. In this work the velocity dispersion and the sound attenuation were analysed in the vicinity of the critical point. It was shown that at high reduced frequencies the results of both approaches are quite different. Further Kawasaki and Shiwa [10] discussed this problem for the simplest system with a single internal relaxation process. They estimated that

the difference between the results of statistical and thermodynamic approaches is connected with a different definition of the relaxing part of the internal energy.

This work is devoted to the statistical calculation of the bulk viscosity coefficient for the system containing the single relaxation variable. It is shown that the discrepancy is connected with terms containing the momentum that the thermodynamical relaxation theory does not include.

The paper is organized as follows. Section 2 contains the basic equations of the thermodynamical relaxation theory. In section 3 a statistical approach is given. In section 4 and 5, the relation between both methods is discussed.

2. Thermodynamic relaxation approach

In the thermodynamic relaxation theory [1,3,5] the state of the system is described by ordinary thermodynamic parameters such as pressure p , temperature T and by an additional relaxation variable ξ . This variable is a function of the parameters p, T in equilibrium while for the nonequilibrium state it becomes an independent variable. The differential of the internal energy E containing the additional term connected with the relaxational variable has the form

$$dE = -p dV + T dS + \psi d\xi . \quad (1)$$

Here S is the entropy, V is the volume, ψ is the force conjugate to the variable ξ (in equilibrium $\psi = 0$). In the linear approximation the relaxation of ξ is described by the following equation:

$$\frac{\partial \delta\xi}{\partial t} = -b \left(\frac{\partial^2 E}{\partial \xi^2} \right) (\delta\xi - \delta\xi^e) , \quad (2)$$

where b is the kinetic coefficient, $\delta\xi^e = (\partial\xi^e/\partial V)_S \delta V + (\partial\xi^e/\partial S)_V \delta S$, and ξ^e is the equilibrium value of the variable ξ . The relaxation equation (2) is valid when ξ is an intensive variable or some value per unit of mass. When the internal relaxation variable $h = \xi\rho$ refers to the unit of volume the relaxation equation should include an additional term connected with the mass transfer,

$$\frac{\partial \delta h}{\partial t} + h^e \operatorname{div} \mathbf{v} = -b' \left(\frac{\partial^2 E}{\partial h^2} \right) (\delta h - \delta h^e) . \quad (3)$$

Usually the relaxation equation (2) is used in the thermodynamic relaxation

theory. Eq. (3) can be transformed into (2) by a suitable change of the relaxation variable.

From eqs. (1) and (2) the contribution of the relaxation process to the adiabatic bulk modulus $\Delta\tilde{K}_s(\omega)$ and consequently to the sound velocity dispersion $c^2(\omega) - c_0^2$ and the bulk viscosity coefficient $\Delta\eta_v(\omega)$ can be found,

$$\begin{aligned} c^2(\omega) - c_0^2 &= \frac{1}{\rho} \operatorname{Re} \Delta\tilde{K}_s(\omega), \\ \Delta\eta_v(\omega) &= -\frac{1}{\omega} \operatorname{Im} \Delta\tilde{K}_s(\omega), \end{aligned} \quad (4)$$

where [1,3,5]

$$\begin{aligned} \Delta\tilde{K}_s(\omega) &= \rho(c_\infty^2 - c_0^2) \frac{-i\omega\tau}{1 - i\omega\tau} = V \left(\frac{\partial \xi^\varepsilon}{\partial V} \right)_s^2 \left(\frac{\partial^2 E}{\partial \xi^2} \right) \frac{-i\omega\tau}{1 - i\omega\tau}, \\ \tau &= \frac{1}{b(\partial^2 E / \partial \xi^2)}, \quad c_\infty^2 = \left(\frac{\partial p}{\partial \rho} \right)_{s,\xi}, \quad c_0^2 = \left(\frac{\partial p}{\partial \rho} \right)_{s,\psi}. \end{aligned} \quad (5)$$

c_0, c_∞ are the sound velocities at zero and infinite frequency, respectively.

3. Statistical approach

In the statistical approach the bulk viscosity coefficient is calculated. In such a case $\Delta\tilde{\eta}_v(\omega)$ is complex and this coefficient is connected with the modulus $\Delta\tilde{K}_s(\omega)$ by a simple relation

$$\Delta\tilde{K}_s(\omega) = -i\omega \Delta\tilde{\eta}_v(\omega). \quad (6)$$

To find the contribution to the bulk viscosity due to the internal relaxation variable X we use the Fourier transform of the linear hydrodynamic equations in the form [11]

$$\frac{\partial A_{j,q}(t)}{\partial t} = \left\langle (iL\hat{A}_{j,q})\hat{A}_{m,-q} \right\rangle A'_{m,q}(t) - \int_0^\infty ds \langle \hat{f}_{j,q}\hat{f}_{m,-q}(-s) \rangle A'_{m,q}(t-s), \quad (7)$$

where $\{\hat{A}\}$ is the set of variables including the collective variable $\{\delta\hat{a}\}$ and an additional variable $\delta\hat{X}$. In the set of variables $\{\hat{A}\}$ the equilibrium values are excluded. The symbol $\hat{}$ means that this value is microscopical, i.e. dependable on the coordinates and momenta of the system's particles. The set of

thermodynamic variables $\{\delta\hat{a}\}$ includes the number density $\delta\hat{n}_q$, the energy density $\delta\hat{e}_q$ and the momentum density $p_{\alpha,q}$ for a one-component system.

As \hat{X} is the relaxation variable the equilibrium value $\langle\hat{X}\rangle$ depends on the values $a_j = \langle\hat{a}_j\rangle$ from the set $\{\hat{a}\}$. In the system of equations (7) the summing over the repeated indexes is implied, L is the Liouville operator, $\hat{f}_{j,q} = (1 - P_A)\hat{L}\hat{A}_{j,q}$ is the stochastic force, conjugated to the variable $\hat{A}_{j,q}$, P_A is the projection operator on the set of variables $\{\hat{A}\}$,

$$\begin{aligned} P_A \hat{Y}_q &= \langle \hat{Y}_q \hat{A}_{j,-q} \rangle \langle \hat{A}_q \hat{A}_{-q} \rangle_{jl}^{-1} \hat{A}_{l,q}, \\ A'_{j,q} &= \langle \hat{A}_q \hat{A}_{-q} \rangle_{jl}^{-1} A_{l,q}. \end{aligned} \quad (8)$$

The Fourier component is defined by

$$Y_q = \frac{1}{\sqrt{V}} \int d\mathbf{r} Y(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}}. \quad (9)$$

The microscopic expressions for the densities of the collective variables have the following form:

$$\begin{aligned} \hat{n}_q &= \frac{1}{\sqrt{V}} \sum_j e^{-i\mathbf{q}\cdot\mathbf{r}_j}, \\ \hat{e}_q &= \frac{1}{\sqrt{V}} \sum_j \left(\frac{p_j^2}{2m} + \frac{1}{2} \sum_{l \neq j} U_{lj} \right) e^{-i\mathbf{q}\cdot\mathbf{r}_j}, \\ \hat{p}_{\alpha,q} &= \frac{1}{\sqrt{V}} \sum_j p_{\alpha,j} e^{-i\mathbf{q}\cdot\mathbf{r}_j}, \end{aligned} \quad (10)$$

where \sum_j means summing over all particles, m and p_j are the mass and momentum of each particle, respectively, and U_{lj} is the potential of the pair interaction between the particles j and l . The conservation laws are valid if we introduce the densities

$$\begin{aligned} \dot{\hat{n}}_q &= -iq_\alpha \hat{J}_{\alpha,q}^{(n)}, \\ \dot{\hat{e}}_q &= -iq_\alpha \hat{J}_{\alpha,q}^{(e)}, \\ \dot{\hat{p}}_{\alpha,q} &= -iq_\beta \hat{\pi}_{\beta\alpha,q}, \end{aligned} \quad (11)$$

where $\hat{J}_q^{(n)}$, $\hat{J}_q^{(e)}$ are the flux densities of the particles and the energy, and $\hat{\pi}_{\alpha\beta,q}$ is the pressure tensor.

It is convenient to introduce into the hydrodynamic set $\{\delta\hat{a}\}$ the new variables $\delta\hat{S}_q$ and $\delta\hat{p}_q^{(1)}$ instead of $\delta\hat{n}_q$ and $\delta\hat{e}_q$ by the following formulae:

$$\begin{aligned} \delta\hat{S}_q &= \left(\frac{\partial S}{\partial n}\right)_e \delta\hat{n}_q + \left(\frac{\partial S}{\partial e}\right)_n \delta\hat{e}_q, \\ \delta\hat{p}_q^{(1)} &= \left(\frac{\partial p}{\partial n}\right)_e \delta\hat{n}_q + \left(\frac{\partial p}{\partial e}\right)_n \delta\hat{e}_q. \end{aligned} \tag{12}$$

The new variables $\delta\hat{p}^{(1)}$ and $\delta\hat{S}$ are the thermodynamic fluctuations of the pressure and the entropy. As before the set $\{\delta\hat{a}\}$ includes also the momentum density. For this set of thermodynamic variables the following relations are valid:

$$\langle \delta\hat{a}_{i,q=0} \delta\hat{a}_{j,q=0} \rangle \sim \delta_{ij}, \tag{13}$$

which means that the set $\{\delta\hat{a}\}$ consists of independent variables. The formula (13) is a consequence of the thermodynamic theory of fluctuations [12].

For the variables $\delta\hat{S}_q$ and $\delta\hat{p}_q^{(1)}$ analogous conservation laws are valid,

$$\begin{aligned} \delta\dot{\hat{S}}_q &= -iq_\alpha \hat{J}_{\alpha,q}^{(S)}, \\ \delta\dot{\hat{p}}_q^{(1)} &= -iq_\alpha \hat{J}_{\alpha,q}^{(p)}, \end{aligned}$$

where $\hat{J}_q^{(S)}$ and $\hat{J}_q^{(p)}$ are the densities of the flux conjugates to the variables $\delta\hat{S}_q, \delta\hat{p}_q^{(1)}$.

The operators P_a and $P_{\tilde{x}}$ are the projection operators on the set of variables $\{\delta\hat{a}\}$ and on $\delta\tilde{X} \equiv (1 - P_a) \delta\hat{X}$, i.e. on the part of the relaxation variable which is orthogonal to $\{\delta\hat{a}\}$,

$$P_a \hat{Y}_q = \langle \hat{Y}_q \delta\hat{a}_{j,-q} \rangle \langle \delta\hat{a}_q \delta\hat{a}_{-q} \rangle_{jl}^{-1} \delta\hat{a}_{l,q}, \tag{14}$$

$$P_{\tilde{x}} \tilde{Y}_q = \frac{\langle \tilde{Y}_q \delta\hat{X}_{-q} \rangle}{\langle |\delta\hat{X}_q|^2 \rangle} \delta\hat{X}_q. \tag{15}$$

In such a case the projection operator P_A can be expressed in the form

$$P_A = P_a + P_{\tilde{x}}. \tag{16}$$

Starting from system (7) and using relation (16) we can write the equation for the momentum

$$\begin{aligned} \frac{\partial p_{\alpha,q}(t)}{\partial t} = & -iq_{\beta} \delta\pi_{\alpha\beta,q}^{(1)}(t) - iq_{\beta} \frac{\langle \hat{\pi}_{\alpha\beta,q} \delta\hat{X}_{-q} \rangle}{\langle |\delta\hat{X}_q|^2 \rangle} \delta\tilde{X}_q(t) \\ & - \frac{1}{kT} \int_0^{\infty} ds \langle \hat{f}_{p_{\alpha,q}} \hat{f}_{p_{\beta,-q}}(-s) \rangle v_{\beta,q}(t-s), \end{aligned} \quad (17)$$

where

$$\delta\pi_{\alpha\beta,q}^{(1)}(t) = \langle \hat{\pi}_{\alpha\beta,q} \delta\hat{a}_{j,-q} \rangle \langle \delta\hat{a}_q \delta\hat{a}_q \rangle_{jl}^{-1} \delta a_{l,q}(t),$$

$v_{\beta,q} = \sqrt{V} p_{\beta,q} / mn_{q=0}$ is the mass velocity. In eq. (17) we used the following relation:

$$\langle \hat{p}_{\alpha,q} \hat{p}_{\beta,-q} \rangle = \frac{kT}{\sqrt{V}} mn_{q=0} \delta_{\alpha\beta}, \quad (18)$$

where k is the Boltzmann constant. From eq. (17) one can see that the equation for the momentum includes only the part of the relaxation variable orthogonal to the collective variables set $\{\delta\hat{a}\}$.

The system (7) gives us the equation for the variable $\delta\tilde{X}_q(t)$,

$$\frac{\partial \delta\tilde{X}_q(t)}{\partial t} = \langle \delta\hat{X}_q \hat{p}_{\alpha,-q} \rangle \langle \hat{p}_{\alpha,q} \hat{p}_{\beta,-q} \rangle^{-1} p_{\beta,q}(t) - \frac{\delta\tilde{X}_q(t)}{\tau_q}, \quad (19)$$

where $\delta\hat{X}_q \equiv iL\hat{X}_q$. Eq. (19) was written under the condition of quite rapid decay of the stochastic forces temporal correlator.

Here we introduced the relaxation time

$$\tau_q = \frac{\langle |\delta\hat{X}_q|^2 \rangle}{b_k T}, \quad (20)$$

and the kinetic coefficient

$$b = \frac{1}{kT} \int_0^{\infty} \langle \hat{f}_{\tilde{X},q} \hat{f}_{\tilde{X},-q}(-s) \rangle ds. \quad (21)$$

For the variable $\delta X_q(t)$ the analogous equation may be written with the help of relation (15) in the following form:

$$\frac{\partial \delta X_q(t)}{\partial t} = \langle \delta \dot{X}_q \hat{p}_{\alpha, -q} \rangle \langle \hat{p}_{\alpha, q} \hat{p}_{\beta, -q} \rangle^{-1} p_{\beta, q}(t) - \frac{\delta X_q(t) - P_a \delta X_q(t)}{\tau_q}. \quad (22)$$

To transform the first term in the right hand side of eq. (22) we rewrite the correlator $\langle \delta \dot{X}_q \hat{p}_{\alpha, -q} \rangle$ with the help of the relation

$$\langle \delta \dot{X}_q \hat{p}_{\alpha, -q} \rangle = -\langle \delta \dot{X}_q \hat{p}_{\alpha, q} \rangle. \quad (23)$$

Here we used the well-known fact that the operator L is Hermitian. Using the conservation law (11) we find

$$\langle \delta \dot{X}_q \hat{p}_{\alpha, -q} \rangle \langle \hat{p}_{\alpha, q} \hat{p}_{\beta, -q} \rangle^{-1} p_{\beta, q}(t) = -iq_\gamma \langle \delta \dot{X}_q \hat{\pi}_{\gamma\alpha, -q} \rangle \langle \hat{p}_{\alpha, q} \hat{p}_{\beta, -q} \rangle^{-1} p_{\beta, q}(t). \quad (24)$$

After substitution (18) in (24) in the lowest approximation on q we have

$$\langle \delta \dot{X}_q \hat{p}_{\alpha, -q} \rangle \langle \hat{p}_{\alpha, q} \hat{p}_{\beta, -q} \rangle^{-1} p_{\beta, q}(t) = -\frac{\langle \delta \dot{X}_{q=0} \delta \hat{p}_{q=0} \rangle}{kT} iq_\alpha v_{\alpha, q}(t). \quad (25)$$

Here we take into account the expression for pressure

$$\hat{p}_q = \frac{1}{3} \hat{\pi}_{\alpha\alpha, q}. \quad (26)$$

Substituting expression (25) into eq. (22) and using the equation of continuity in the lowest order of q we have

$$\frac{\partial \delta X_{q=0}(t)}{\partial t} + \frac{\langle \delta \dot{X}_{q=0} \delta \hat{p}_{q=0} \rangle}{kTV} \frac{\partial \delta V_{q=0}(t)}{\partial t} = -\frac{\delta X_{q=0}(t) - P_a \delta X_{q=0}(t)}{\tau_{q=0}}. \quad (27)$$

with help of the following expressions [13]:

$$\langle \delta \hat{p}_{q=0}^{(1)} \delta \hat{Y}_{q=0} \rangle = -kTV \left(\frac{\partial \langle \hat{Y} \rangle}{\partial V} \right)_S, \quad (28)$$

$$\langle \delta \hat{S}_{q=0} \delta \hat{Y}_{q=0} \rangle = kTV \left(\frac{\partial \langle \hat{Y} \rangle}{\partial T} \right)_P, \quad (29)$$

we may rewrite the term $P_a \delta X_{q=0}(t)$ in the next form:

$$P_a \delta X_{q=0}(t) = \left(\frac{\partial X^e}{\partial V} \right)_S \delta V_{q=0}(t) + \left(\frac{\partial X^e}{\partial S} \right)_V \delta S_{q=0}(t) = \delta X_{q=0}^e(t), \quad (30)$$

where $X^e = \langle \hat{X} \rangle$.

The relation (27) is the relaxation equation for the internal variable obtained by the method of statistical mechanics. It is important to compare it with the relaxation equation (2) which is used in the thermodynamic relaxation theory.

4. Comparison of the two methods

First of all we may see that the relaxation times are equal in both methods since [13]

$$\langle |\delta \hat{X}_{q=0}|^2 \rangle = kTV / \left(\frac{\partial^2 \phi}{\partial X^2} \right) \quad (31)$$

and

$$\langle |\delta \hat{X}_{q=0}|^2 \rangle = kTV / \left(\frac{\partial^2 E}{\partial X^2} \right). \quad (32)$$

Here $\phi = \phi(p, T, X)$ is the Gibbs thermodynamic potential. The validity of the expression (32) is proved in the appendix. It should be noted that the thermodynamic potential ϕ is the function of variables p, T, X while the potential E is the function of variables V, S, X . It is necessary to have the relation between the thermodynamic derivatives $\partial^2 E / \partial X^2$ and $\partial^2 \phi / \partial X^2$. Such an expression is given by formulae (A.2), (A.6) in the appendix,

$$\left(\frac{\partial^2 E}{\partial X^2} \right)^{-1} = \left(\frac{\partial^2 \phi}{\partial X^2} \right)^{-1} + \left(\frac{\partial X}{\partial V} \right)_s^2 \left(\frac{\partial V}{\partial p} \right)_s - \left(\frac{\partial X}{\partial T} \right)_p \left(\frac{\partial T}{\partial S} \right)_p. \quad (33)$$

If we take the variable ξ instead of X then the relaxation equation (27) under the condition

$$\langle \delta \hat{\xi}_{q=0} \delta \hat{p}_{q=0} \rangle = 0 \quad (34)$$

is of the same form as eq. (2).

For the variable h the analogue takes place under the condition

$$\langle \delta \hat{h}_{q=0} \delta \hat{p}_{q=0} \rangle = kTh^e. \quad (35)$$

It is important to note that a priori there are no reasons for the validity of these relations. Furthermore the statistical mechanics calculations show that eqs. (22) and (27) for the variable X includes the term describing the dependence of \hat{X} on the momentum.

The validity of the relations (34) and (35) is supposed in the thermodynamic relaxation theory. Hence the dependence on the momentum is not considered in this approach.

Using the space-time Fourier transform and substituting the variable $\delta\hat{X}_q(\omega)$ to (17) from (19) we obtain the following equation for the momentum:

$$\begin{aligned}
 -i\omega p_{\alpha,q}(\omega) = & -iq_\beta \delta\pi_{\alpha\beta,q}^{(1)} - q^2 \left(\frac{1}{kTq^2} \int_0^\infty ds e^{i\omega s} \langle \hat{f}_{p_\alpha,q} \hat{f}_{p_\beta,-q}(-s) \rangle \right) \\
 & + \frac{1}{kT} \frac{q_\alpha q_\beta}{q^2} \langle \delta\hat{X}_{q=0} \delta\hat{p}_{q=0} \rangle^2 \langle |\delta\hat{X}_{q=0}|^2 \rangle^{-1} \frac{\tau}{1-i\omega\tau} v_{\beta,q}(\omega).
 \end{aligned}
 \tag{36}$$

So for the longitudinal component of the momentum we have

$$\begin{aligned}
 -i\omega p_{\alpha,q}^\ell(\omega) = & -iq_\alpha \frac{q_\beta q_\gamma}{q^2} \delta\pi_{\beta\gamma,q}^{(1)} - q^2 \left(\frac{1}{kTq^2} \int_0^\infty ds e^{i\omega s} \langle \hat{f}_{p_\beta,q}^\ell \hat{f}_{p_\beta,-q}^\ell(-s) \rangle \right) \\
 & + \frac{1}{kT} \frac{\langle \delta\hat{X}_{q=0} \delta\hat{p}_{q=0} \rangle^2}{\langle |\delta\hat{X}_{q=0}|^2 \rangle} \frac{\tau}{1-i\omega\tau} v_{\alpha,q}^\ell(\omega),
 \end{aligned}
 \tag{37}$$

where $Y_\alpha^\ell = q_\alpha q_\beta / q^2 Y_\beta$.

The expression in large parentheses in the right-hand side of eq. (37) is the longitudinal viscosity coefficient $\eta_q^\ell(\omega)$. The second term in brackets is connected with the relaxing variable. From eq. (36) one can see that the transverse viscosity coefficient $\eta_q^{\text{tr}}(\omega)$ has not a contribution from variable X . When $q = 0$ the coefficients η^{tr} and η^ℓ are connected with the coefficients of the bulk viscosity η_b and shear viscosity η_s by the relations

$$\eta^{\text{tr}} = \eta_s, \quad \eta^\ell = \frac{4}{3}\eta_s + \eta_v.$$

One can see that the relaxation process contributes to the coefficient of bulk viscosity only. So we have

$$\begin{aligned}
\Delta \tilde{\eta}_v(\omega) &= \frac{1}{kT} \frac{\langle \delta \hat{X}_{q=0} \delta \hat{p}_{q=0} \rangle^2}{\langle |\delta \hat{X}_{q=0}|^2 \rangle} \frac{\tau}{1 - i\omega\tau} \\
&= \frac{1}{kT} \frac{\langle \delta \hat{X}_{q=0} (\delta \hat{p}_{q=0} - \delta \hat{p}_{q=0}^{(1)}) \rangle^2}{\langle |\delta \hat{X}_{q=0}|^2 \rangle} \frac{\tau}{1 - i\omega\tau} \\
&= \frac{1}{kT} \frac{[\langle \delta \hat{X}_{q=0} \delta \hat{p}_{q=0} \rangle + kTV(\partial X^e / \partial V)_s]^2}{\langle |\delta \hat{X}_{q=0}|^2 \rangle} \frac{\tau}{1 - i\omega\tau}. \tag{38}
\end{aligned}$$

As to the thermodynamics relaxation theory, the substitution of the expression for $\Delta \tilde{K}_s$ from (5) into expression (6) gives us the formula (38) without correlator $\langle \delta \hat{X}_{q=0} \delta \hat{p}_{q=0} \rangle$.

If we use eq. (27) instead of (2) in the thermodynamics relaxation theory we get the expression (38), i.e. the same results as in statistical approach.

5. Discussion

The main difference between the two approaches is the form of the relaxation equation for the additional variable. The general system of the linear hydrodynamic equations (7) leads to the relaxation equation in the form (22). This equation has the following structure:

$$\frac{\partial \delta X}{\partial t} = P_{\text{therm}} \delta \dot{X} + P_p \delta \dot{X}, \tag{39}$$

where the first term in the right-hand side has the form $-(\delta X - \delta X^e)/\tau$ as in the thermodynamic approach. This term describes the relaxation of the additional variable in the space-homogeneous media with the thermodynamic parameters which can vary with time. As to the second term, it is the projection of $\delta \dot{X}$ on the momentum. This term describes the reaction of the additional variable caused by the space-inhomogeneous distribution of the momentum in the system. This term arises already in the linear approximation and a priori its magnitude may be of the same order as the thermodynamic one. It is necessary to have a microscopic model of the additional variable for its calculation.

It follows from the comparison of eqs. (5) and (6) with eq. (38) that the term connected with the projection on the momentum leads to a correction of the thermodynamic value for the complex coefficient of the bulk viscosity, but does not violate its frequency dependence. So in acoustical measurements the

full sound velocity dispersion as well as the total alteration of the bulk viscosity $\eta_v(0) - \eta_v(\infty)$ contains not only the thermodynamic contribution but also the kinetical contribution connected with the space-inhomogeneous distribution of the momentum.

Now it can be noted that the result of the statistical approach may be obtained directly from the statistical expression of the bulk viscosity coefficient,

$$\tilde{\eta}_v(\omega) = \frac{1}{kT} \int_0^\infty ds e^{i\omega s} \langle (\delta\hat{p}_{q=0} - \delta\hat{p}_{q=0}^{(1)}) (\delta\hat{p}_{q=0} - \delta\hat{p}_{q=0}^{(1)})(-s) \rangle ,$$

where $\delta\hat{p}_{q=0} - \delta\hat{p}_{q=0}^{(1)}$ is the fluctuation of the nonthermodynamic part of the pressure. To obtain the contribution connected with the additional variable X we may project the fluctuation $\delta\hat{p}_{q=0} - \delta\hat{p}_{q=0}^{(1)}$ on $\delta\hat{X}_{q=0}$. It can be noted that we must project the nonthermodynamic part of the pressure only on the nonthermodynamic part of the additional variable. Thus we have

$$\Delta\tilde{\eta}_v(\omega) = \frac{1}{kT} \int_0^\infty ds e^{i\omega s} \times \frac{\langle (\delta\hat{p}_{q=0} - \delta\hat{p}_{q=0}^{(1)}) \delta\hat{X}_{q=0} \rangle \langle (\delta\hat{p}_{q=0} - \delta\hat{p}_{q=0}^{(1)}) \delta\hat{X}_{q=0}^{(s)} \rangle}{\langle |\delta\hat{X}_{q=0}|^2 \rangle} .$$

Using the solution of eq. (19) for $q = 0$,

$$\delta\hat{X}_{q=0}(t) = e^{-t/\tau} \delta\hat{X}_{q=0}(0) ,$$

we obtain after a simple calculation the previous result (38).

To illustrate these results we consider the system near the second order phase transition point. To obtain the sound velocity dispersion and attenuation of sound caused by the relaxation of the order parameter average value (Landau-Khalatnikov mechanism [14]) we can write the Helmholtz free energy of the system in the following form:

$$F(X) = F_0 + \frac{1}{2}AX^2 + (1/4!)CX^4 .$$

From this relation we can obtain the expression for the pressure depending on the order parameter,

$$p(X) = p_0 - \frac{1}{2} \left(\frac{\partial A}{\partial V} \right)_T X^2,$$

$$\delta p(X) = \delta p_0 - \left(\frac{\partial A}{\partial V} \right)_T X^e \delta X,$$

where we put $(\partial C/\partial V)_T = 0$ for simplicity. In the Gaussian approximation in lowest order in X^e it can be obtained for the correlator $\langle \delta X_{q=0} \delta p_{q=0} \rangle$ that

$$\langle \delta X_{q=0} \delta p_{q=0} \rangle = - \left(\frac{\partial A}{\partial V} \right)_T X^e \langle |\delta X_{q=0}|^2 \rangle = -k_B TV \left(\frac{\partial^2 \phi}{\partial X^2} \right)^{-1} \left(\frac{\partial A}{\partial V} \right)_T X^e.$$

After substitution of this expression in eq. (38) we have

$$\begin{aligned} \Delta \tilde{\eta}_v(\omega) &= \frac{1}{(1 - i\omega\tau)b} \left[V \left(\frac{\partial X^e}{\partial V} \right)_s - \left(\frac{\partial^2 \phi}{\partial X^2} \right)^{-1} V \left(\frac{\partial A}{\partial V} \right)_T X^e \right]^2 \\ &= \frac{1}{(1 - i\omega\tau)b} \left[\rho \left(\frac{\partial X^e}{\partial \rho} \right)_s - \left(\frac{\partial^2 \phi}{\partial X^2} \right)^{-1} \rho \left(\frac{\partial A}{\partial \rho} \right)_T X^e \right]^2. \end{aligned} \quad (40)$$

To approximate the numerical values of the terms in brackets we use the parameters of the nematic liquid crystal MBBA near the phase transition point to the isotropic phase. The coefficient A has the structure $A = A_0(T - T^*(p))$ where $A_0 \sim 1.5 \times 10^{-6} \text{ erg cm}^{-3} \text{ K}^{-1}$ [15]. The thermodynamic derivative $(\partial A/\partial \rho)_T$ can be rewritten as follows:

$$\left(\frac{\partial A}{\partial \rho} \right)_T = \frac{c^2}{\gamma} \left(\frac{\partial A}{\partial p} \right)_T = - \frac{c^2 A_0}{\gamma} \frac{dT^*}{dp},$$

where $\gamma = C_{p,0}/C_{v,0} \sim 1.2$, $c \sim 1.5 \times 10^5 \text{ cm s}^{-1}$, $dT^*/dp \sim 4 \times 10^{-8} \text{ K cm}^3 \text{ erg}^{-1}$ [16]. The magnitude of the order parameter X^e is a function of the argument $T - T^*(p)$. In this case we may transform the last term in (40) as

$$\begin{aligned} \rho \left(\frac{\partial X^e}{\partial \rho} \right)_s &= c \sqrt{\frac{T(\gamma - 1)}{C_{p,0}}} \left(\frac{\partial X^e}{\partial T} \right)_s \\ &= c \sqrt{\frac{T(\gamma - 1)}{C_{p,0}}} \left(1 - \frac{dT^*}{dp} \frac{\rho C_{p,0}}{T \alpha_T} \right) \left(\frac{\partial X^e}{\partial T} \right)_p, \end{aligned}$$

where $C_{p,0}$ is the regular part of the heat capacity under the constant pressure per unit mass, $C_{p,0} \sim 2 \times 10^7 \text{ erg g}^{-1} \text{ K}^{-1}$, α_T is the coefficient of the heat expansion, $\alpha_T \sim 7.3 \times 10^{-4} \text{ K}^{-1}$ [17]. The values X^e , $(\partial X^e/\partial T)_p$, $(\partial^2 \phi/\partial X^2)$ variate with T , and for $T^* - T \sim 1 \text{ K}$ they are $X^e \sim 0.4$, $(\partial X^e/\partial T)_p \sim$

-0.04 K^{-1} , $(\partial^2\phi/\partial X^2) \sim 8 \times 10^6 \text{ erg cm}^{-3}$; for $T^* - T \sim 10 \text{ K}$ they are $X^e \sim 0.6$, $(\partial X^e/\partial T)_p \sim -0.01 \text{ K}^{-1}$, $(\partial^2\phi/\partial X^2) \sim 4 \times 10^7 \text{ erg cm}^{-3}$ [18]. So we have for $T^* - T \sim 1 \text{ K}$,

$$\rho \left(\frac{\partial X^e}{\partial \rho} \right)_s \sim 30, \quad \left(\frac{\partial^2\phi}{\partial X^2} \right)^{-1} \rho \left(\frac{\partial A}{\partial \rho} \right)_T X^e \sim -25,$$

and for $T^* - T \sim 10 \text{ K}$,

$$\rho \left(\frac{\partial X^e}{\partial \rho} \right)_s \sim 10, \quad \left(\frac{\partial^2\phi}{\partial X^2} \right)^{-1} \rho \left(\frac{\partial A}{\partial \rho} \right)_T X^e \sim -7.5.$$

As is seen from this rough estimate there is no a priori reason for neglecting the dependence on the momentum in the relaxation equation (39).

It should be noted that the phase transition between nematic and isotropic phase is the so-called “weak first order” phase transition. For the pure second order phase transition the influence of the momentum term may be somewhat smaller because of the vanishing of the order parameter X^e when $T^* - T \rightarrow 0$.

In some similar situation the correlator with momentum (23) may be accurately calculated. This calculation is provided for the gas–liquid critical point or for the binary mixture separation point. The additional variables here are the Fourier components of density or concentration fluctuations, $\delta\hat{c}_q \delta\hat{c}_{-q}$. In this case the correlator $\langle \hat{p}_{\alpha,q} \delta\hat{c}_{-k} \delta\hat{c}_{k-q} \rangle$ is calculated precisely,

$$\langle \hat{p}_{\alpha,q} \delta\hat{c}_{-k} \delta\hat{c}_{k-q} \rangle_{q \rightarrow 0} \cong \left[ik_\alpha \frac{(\mathbf{k} \cdot \mathbf{q})}{k} \left(\frac{\partial}{\partial k} \langle |\delta\hat{c}_k|^2 \rangle \right) - iq_\alpha \langle |\delta\hat{c}_k|^2 \rangle \right] \frac{k_B T \rho}{V^{1/2}}.$$

The time dependence of fluctuations is described by the diffusion equation

$$\delta c_q(t) = e^{-\mathcal{D}(q) q^2 t} \delta c_q(0) = e^{-t/\tau_{\mathcal{D}}} \delta c_q(0),$$

where $\mathcal{D}(q)$ is the diffusion coefficient. Hence for the bulk viscosity coefficient we have

$$\begin{aligned} \Delta \tilde{\eta}_v(\omega) = & \frac{k_B T}{2V} \sum_k \left[\left(\frac{\partial}{\partial \rho} \rho \langle |\hat{c}_k|^2 \rangle \right)_{s,c} \right. \\ & \left. + \frac{k_z^2}{k} \frac{\partial}{\partial k} \langle |\delta\hat{c}_k|^2 \rangle \right]^2 \langle |\delta\hat{c}_k|^2 \rangle^{-2} \frac{\tau_{\mathcal{D}}}{1 - i\omega\tau_{\mathcal{D}}}. \end{aligned}$$

By the pure thermodynamic calculations we obtain in brackets only the terms

$$\left(\frac{\partial}{\partial \rho} \rho \langle |\delta \hat{c}_k|^2 \rangle \right)_{s,c}$$

The additional contribution is quite small [19].

6. Summary

For the system with the internal relaxation process the bulk viscosity coefficient is calculated in a linear approximation in two approaches, namely thermodynamic and statistical. These approaches lead to different results due to the following reason. In the thermodynamic approach, the contribution to the bulk viscosity is taken into account, caused only by the variation of the thermodynamic variables during the relaxation process. In the statistical approach the variation of the momentum in the relaxation process is considered, along with the variation of the thermodynamic variables. This additional nonthermodynamic contribution conserves the frequency dependence but can vary the magnitude of the effect.

The numerical simulation for the system near the phase transition point with the parameters of the nematic liquid crystal MBBA shows that the thermodynamic and nonthermodynamic contributions to the bulk viscosity are of a same order.

An analogous nonthermodynamic contribution which is arisen due to relaxation of the order parameter fluctuations in a critical region, may be somewhat smaller. In particular, it follows from calculations in the vicinity of liquid–gas and liquid–liquid critical points.

In general, the problem of the correct calculation of the nonthermodynamic input into the bulk viscosity reduces to computation of the correlator $\langle \Delta \hat{p}_{q=0} \delta \hat{X}_{q=0} \rangle$ for an arbitrary relaxation variable X .

Appendix

In this appendix starting from the expression

$$\langle |\delta \hat{X}_{q=0}|^2 \rangle = kTV / \left(\frac{\partial^2 \phi}{\partial X^2} \right), \quad (\text{A.1})$$

we prove the validity of the relation

$$\langle |\delta \hat{X}_{q=0}|^2 \rangle = kTV / \left(\frac{\partial^2 E}{\partial X^2} \right). \quad (\text{A.2})$$

Here the thermodynamic potentials ϕ and E are considered as the functions of its intrinsic variables, i.e. $\phi = \phi(p, T, X)$, $E = E(V, S, X)$. We can write the expressions for the thermodynamic potential differentials similar to eq. (1),

$$d\phi = -S dT + V dp + \psi dx, \quad (\text{A.3})$$

$$dE = T dS - p dV + \psi dX. \quad (\text{A.4})$$

Using the definition $\delta \hat{X}_{q=0} = (1 - P_a) \delta \hat{X}_{q=0}$, one can write

$$\begin{aligned} \langle |\hat{X}_{q=0}|^2 \rangle &= \langle |\delta \hat{X}_{q=0}|^2 \rangle - \langle \delta \hat{X}_{q=0} \delta \hat{p}_{q=0}^{(1)} \rangle^2 \langle |\delta \hat{p}_{q=0}^{(1)}|^2 \rangle^{-1} \\ &\quad - \langle \delta \hat{X}_{q=0} \delta \hat{S}_{q=0} \rangle^2 \langle |\delta \hat{S}_{q=0}|^2 \rangle^{-1}. \end{aligned} \quad (\text{A.5})$$

Substituting the correlation function in the right-hand side of (A.5) by the thermodynamic derivatives with the help of (A.1), (28) and (29) we get

$$\begin{aligned} \langle |\delta \hat{X}_{q=0}|^2 \rangle &= kTV / \left(\frac{\partial^2 \phi}{\partial X^2} \right) + kTV \\ &\quad \times \left[\left(\frac{\partial X}{\partial V} \right)_{s,\psi}^2 \left(\frac{\partial V}{\partial p} \right)_{s,\psi} - \left(\frac{\partial X}{\partial T} \right)_{p,\psi}^2 \left(\frac{\partial T}{\partial S} \right)_{p,\psi} \right]. \end{aligned} \quad (\text{A.6})$$

Using the relation

$$\frac{\partial^2 \phi}{\partial X^2} = \left(\frac{\partial \psi}{\partial X} \right)_{p,s} \left(\frac{\partial S}{\partial T} \right)_{p,x} / \left(\frac{\partial S}{\partial T} \right)_{p,\psi}, \quad (\text{A.7})$$

we obtain

$$\begin{aligned} \langle |\delta \hat{X}_{q=0}|^2 \rangle &= kTV \left[\left(\frac{\partial T}{\partial S} \right)_{p,x} / \left(\frac{\partial \psi}{\partial X} \right)_{p,s} \left(\frac{\partial T}{\partial S} \right)_{p,\psi} \right. \\ &\quad \left. + \left(\frac{\partial X}{\partial V} \right)_{s,\psi}^2 \left(\frac{\partial V}{\partial p} \right)_{s,\psi} - \left(\frac{\partial X}{\partial T} \right)_{p,\psi}^2 \left(\frac{\partial T}{\partial S} \right)_{p,\psi} \right]. \end{aligned} \quad (\text{A.8})$$

We express the thermodynamic derivatives in (A.8) through the partial derivatives of the internal energy $E(V, S, X)$. Using the notation $A_{xy} \equiv \partial^2 A / \partial x \partial y$ we have

$$\begin{aligned}
\left(\frac{\partial T}{\partial S}\right)_{p,X} &= E_{SS} - \frac{E_{SV}^2}{E_{VV}}, \\
\left(\frac{\partial T}{\partial S}\right)_{p,\psi} &= E_{SS} - \frac{E_{SV}^2}{E_{VV}} - \left(E_{SX} - \frac{E_{SV}E_{VX}}{E_{VV}}\right)^2 / \left(E_{XX} - \frac{E_{VX}^2}{E_{VV}}\right), \\
\left(\frac{\partial \psi}{\partial X}\right)_{p,S} &= E_{XX} - \frac{E_{VX}^2}{E_{VV}}, \quad \left(\frac{\partial X}{\partial V}\right)_{s,\psi} = -\frac{E_{VX}}{E_{XX}}, \\
\left(\frac{\partial P}{\partial V}\right)_{s,\psi} &= -E_{VV} + \frac{E_{VX}^2}{E_{XX}}, \\
\left(\frac{\partial X}{\partial T}\right)_{p,\psi} &= \frac{(E_{SX} - E_{VX}E_{VS}/E_{VV})}{(E_{SX} - E_{VX}E_{VS}/E_{VV})^2 - (E_{SS} - E_{SV}^2/E_{VV})(E_{XX} - E_{VX}^2/E_{VV})}.
\end{aligned} \tag{A.9}$$

Substitution of the expressions (A.9) in (A.8) after some simple algebraic transformations leads to the formula (A.2).

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