and the perfect gas law follows. Equation (3.27) may now be eliminated on the basis that $T^{\mu\nu\prime}$ *does not* correspond to the momentum-energy tensor for the particles (see Sec. 5) and hence the resulting equation of state can be discarded. Finally we can also discard Eq. (3.29) since the momentum and energy of the particles and of the field are *separately* conserved at equilibrium, the consequence of which is that we have to consider only $T_{\text{part.}}{}^{\mu\nu}$ and hence Eq. (3.25).

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Collective Motion in Simple Classical Fluids

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An earlier study of variational solutions of the Liouville equation for simple fluids is extended to include high-frequency thermal excitations. In the long-wavelength limit, variational eigenvalues are determined in correspondence with dispersion relations derived from linearized Navier-Stokes equations which contain frequency-dependent viscous and thermal transport coefficients. Two distinct sets of high-frequency longitudinal excitations arise. In the limit that mechanical moduli are much larger than thermal moduli, one of these excitations simplifies to a quasiphonon composed only of velocity fluctuations and associated time derivatives. On the other hand, in the case of vanishing viscosity, the excitation is seen to be composed only of energy fluctuations and time derivatives of energy fluctuations and, as such, may be the classical analog of high-frequency second sound in liquid He II. The various eigenfunctions are discussed in relation to results of recent neutron-scattering experiments.

I. INTRODUCTION AND REVIEW

A VARIATIONAL solution of the Liouville equation has recently been applied to obtain collective coordinates for simple classical fluids (monatomic liquids with pairwise interactions).[1] The variational procedure consists of choosing various functionals of the Fourier transforms of the mass, momentum, and energy density operators of the fluid, and then adjusting coefficients to provide approximate eigenvalues and eigenfunctions of the Liouville operator (see Sec. III below). In this way, we have previously determined microscopic analogs of the usual low-frequency hydrodynamic motions. Further, to the extent that rapidly varying energy fluctuations might be neglected, high-frequency collective motions have also been studied.[1] The present investigation is a continuation of the latter study, in that we now consider excitations which arise when rapidly varying energy fluctuations are included among the variational trial functions.

In Sec. II of this paper, dispersion relations are obtained from a set of linearized Navier-Stokes equations which have been modified to include the frequency dependence of all transport coefficients, including thermal conductivity. These results are then used, in Sec. III, as a guide for solution of the Liouville equation, and we obtain microscopic collective excitations which correspond to the macroscopic eigenvalues deduced from the hydrodynamic equations. A discussion of results appears in Sec. IV, where we calculate the coherent scattering function $S_c(k,\omega)$ and compare our results with dispersion relations obtained from neutron-scattering experiments. The calculation also serves as an example of the application of the variational eigenfunctions to the evaluation of transport coefficients. Finally, in Appendix A, we discuss the notion of thermal moduli and their relationship to the high-frequency thermal conductivity of an isotropic medium.

In certain cases, the eigenvalues and eigenfunctions which we present in Secs. II–IV will reduce to those arising when energy fluctuations are neglected. Thus, in the remainder of this Introduction and before discussing the new work, let us briefly summarize some results of prior application of the variational scheme. Several of these expressions are the basis for calculations discussed in Sec. IV but have not previously been presented in explicit form.

It has been shown in Ref. 1 that trial functions, when chosen only as linear combinations of the Fourier transforms of the mass, momentum, and energy density operators, provide eigenvalues and eigenfunctions corresponding to solutions of the usual low-frequency linearized Navier-Stokes equations. Thus, a trial function composed of the mass and momentum fluctuations is found to correspond to the set of hydrodynamic equations obtained when energy transport is neglected and,

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[1] R. Nossal and R. Zwanzig, Phys. Rev. **157**, 120 (1967).

when energy fluctuations are included, correspondence with the complete set of usual Navier-Stokes equations is achieved.[2] On the other hand, it has also been shown that, when time derivatives of velocity fluctuations (but not time derivatives of energy fluctuations) are included among trial functions, collective coordinates are determined analogous to solution of a *modified* set of hydrodynamic equations and appropriate to high-frequency excitations. Dispersion relations are obtained which are identical to those obtained from a set of linearized Navier-Stokes equations in which thermal conductivity has been neglected and, for viscosity coefficients, one inserts high-frequency limits as determined from time correlation function formulations.[3]

Specifically, for a single component fluid whose internal potential energy has been assumed to be the sum of symmetric pair potentials, one may show the following[1,4]: Let $\mathcal{G}_\infty(k)$ and $\mathcal{K}_\infty(k)$ represent generalized high-frequency shear and bulk moduli. With this designation, the previously derived high-frequency transverse and longitudinal eigenfrequencies may be written, respectively, as

$$\omega_{\mathrm{tr}}(k)=\pm|k|(\rho^{-1}\mathcal{G}_\infty(k))^{1/2} \tag{1.1}$$

and

$$\omega_l(k)=\pm|k|(\rho^{-1}[\tfrac{4}{3}\mathcal{G}_\infty(k)+\mathcal{K}_\infty(k)])^{1/2}, \tag{1.2}$$

where ρ is the mass density of the fluid. Molecular expressions for the moduli are as follows:

$$\begin{aligned}\mathcal{G}_\infty(k)=c\beta^{-1}+\pi c^2k^{-2}\int_0^\infty dr\, r^2g_2(r)\\ \times\left\{\left[\tfrac{4}{3}-4\left\{\frac{\sin rk}{(rk)^3}-\frac{\cos rk}{(rk)^2}\right\}\right]\frac{\partial^2\varphi}{\partial r^2}+\frac{1}{r}\left[\frac{8}{3}-4\left\{\frac{\sin rk}{rk}\right.\right.\right.\\ \left.\left.\left.\times\left(1-\frac{1}{(rk)^2}\right)+\frac{\cos rk}{(rk)^2}\right\}\right]\frac{\partial\varphi}{\partial r}\right\}\end{aligned} \tag{1.3}$$

and

$$\begin{aligned}[\tfrac{4}{3}\mathcal{G}_\infty(k)+\mathcal{K}_\infty(k)]=3c\beta^{-1}+2\pi c^2k^{-2}\int_0^\infty dr\, r^2g_2(r)\\ \times\left\{\left[\tfrac{2}{3}-\frac{4}{(rk)^2}\cos rk-\frac{2\sin rk}{rk}\left(1-\frac{2}{(rk)^2}\right)\right]\frac{\partial^2\varphi}{\partial r^2}\right.\\ \left.+\frac{1}{r}\left[\tfrac{4}{3}-4\left(\frac{\sin kr}{(rk)^3}-\frac{\cos rk}{(rk)^2}\right)\right]\frac{\partial\varphi}{\partial r}\right\},\end{aligned} \tag{1.4}$$

where, in the latter, the pair correlation function $g_2(r)$ is defined as

$$g_2(r)=\frac{V\int dR_3\cdots dR_n\exp[-\beta\varphi(R^N)]}{\int dR^N\exp(-\beta\varphi(R^N))}, \tag{1.5}$$

φ is the interparticle pair potential, $\beta=(kT)^{-1}$, and c is the number density of the fluid.

The collective excitations corresponding to the frequencies given by Eqs. (1.1) and (1.2) are as follows: The transverse phonons associated with $\omega_{\mathrm{tr}}\,(k)$are

$$\varphi_\pm{}^{\mathrm{tr}}(k)\sim\{A_{1,2}(k)\mp\omega_{\mathrm{tr}}{}^{-1}(k)LA_{1,2}(k)\}, \tag{1.6}$$

and the *single set* of longitudinal phonons associated with $\omega_l(k)$ may be expressed as

$$\varphi_\pm{}^l(k)\sim\{A_3(k)\mp\omega_l{}^{-1}(k)LA_3(k)\}. \tag{1.7}$$

In the above we have defined $A_{1,2,3}$ as

$$A_{1,2}\equiv V^{-1}\sum_{j=1}^N \mathbf{p}_j\cdot\hat{u}_{1,2}e^{-i\mathbf{k}\cdot\mathbf{R}_j} \tag{1.8}$$

and

$$A_3\equiv V^{-1}\sum_{j=1}^N \mathbf{p}_j\cdot\hat{u}_3e^{-i\mathbf{k}\cdot\mathbf{R}_j}, \tag{1.9}$$

where, in turn, $\hat{u}_3$ is defined as $\hat{u}_3\equiv\mathbf{k}/|k|$, and $\hat{u}_1$ and $\hat{u}_2$ ($\hat{u}_1\perp\hat{u}_3$, $\hat{u}_2\perp\hat{u}_3$) are two arbitrary mutually perpendicular unit vectors. $\mathbf{R}_j$ and $\mathbf{p}_j$ are, respectively, the position and momentum of the jth particle, V is the volume of the assembly, and N the number of particles. L is the Liouville operator, having the property that, if A is an arbitrary dynamic variable, $LA=idA/dt$.

Note, once again, that the results presented in Eqs. (1.1)–(1.7) arise when trial functions are constructed of velocity fluctuations and their time derivatives. If, in addition, density and energy fluctuations are added to the trial functions, identical eigenvalues and eigenfunctions are obtained.[5] On the other hand, including time derivatives of energy fluctuations leads to quite different results. In particular, we obtain *two* sets of high-frequency longitudinal excitations.

II. RESULTS FROM HYDRODYNAMIC CONSIDERATIONS

When the high-frequency limits of the viscosity and thermal conductivity coefficients are inserted in the Fourier-Laplace transforms of the linearized Navier-Stokes equations, the latter may be written as

$$-i\omega\tilde{\rho}_k+i\rho_0k\tilde{v}_{k3}=0, \tag{2.1}$$

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[2] In the first case one finds the usual isothermal sound velocity as dispersion relation (eigenvalue) whereas, in the latter, the adiabatic sound velocity is obtained. Also, there is demonstrable correspondence between the variational eigenfunctions and the eigensolutions of the hydrodynamic equations.

[3] R. Zwanzig and R. D. Mountain, J. Chem. Phys. **43**, 4464 (1965).

[4] R. Zwanzig, Phys. Rev. **156**, 190 (1967).

[5] These dispersion relations may be derived directly from Hamilton's principle [R. Nossal (to be published)]. Similar results have also been obtained by application of various sum rules; see R. D. Puff, Phys. Rev. **137**, A406 (1965).

$$-i\rho_0\omega\tilde{v}_{k3}+\left(\frac{\partial P}{\partial\rho}\right)_U ik\tilde{\rho}_k+\left(\frac{\partial P}{\partial U}\right)_\rho ik\tilde{U}_k$$
$$=(i\omega)^{-1}[\tfrac{4}{3}G_\infty+K_\infty-K_0]k^2\tilde{v}_{k3}\,, \quad (2.2)$$

$$-i\omega\rho_0\tilde{U}_k+P_0ik\tilde{v}_{k3}=\frac{\Xi_\infty}{i\omega}\left[\left(\frac{\partial T}{\partial\rho}\right)_U\tilde{\rho}_k+\left(\frac{\partial T}{\partial U}\right)_\rho\tilde{U}_k\right], \quad (2.3)$$

$$-i\omega\tilde{v}_{k1,2}=k^2G_\infty(i\omega\rho_0)^{-1}\tilde{v}_{k1,2}\,, \quad (2.4)$$

where ρ is the mass per unit value, U is the internal energy per unit mass, and $v_{1,2}$ and v_3 are, respectively, the transverse and longitudinal fluid velocities. Equations (2.1)–(2.3) pertain to longitudinal disturbances, whereas Eq. (2.4) describes the propagation of transverse phonons.[6] In the above, we have written the viscosity coefficients in their familiar form

$$\lim_{\omega\to\infty} i\omega\tilde{\eta}_S=-G_\infty\,, \quad (2.5)$$

$$\lim_{\omega\to\infty} i\omega\tilde{\eta}_V=-(K_\infty-K_0)\,, \quad (2.6)$$

where K_0 is given by

$$K_0=-V(\partial P/\partial V)_S\,, \quad (2.7)$$

and G_∞ and K_∞ are the long-wavelength limits of $\mathcal{G}_\infty$ and $\mathcal{K}_\infty$ [see Eqs. (1.3) and (1.4).]

At this point we have chosen, simply, to write the thermal conductivity as

$$\lim_{\omega\to\infty} i\omega\tilde{\lambda}(\omega)=-\Xi_\infty\,, \quad (2.8)$$

although in the next section (see, also, Appendix A) we see that there is good reason to represent the high-frequency limits of the conductivity by a function having structural form similar to that of the viscosities, viz.,

$$-\lim_{\omega\to\infty} i\omega\lambda=\Theta_\infty-\Theta_0\,. \quad (2.9)$$

From Eqs. (2.1)–(2.4), dispersion relations are found to be the following: The (transverse) eigenvalue obtained from Eq. (2.4) is clearly not affected by changing the form of the thermal conductivity, and is still given by the long-wavelength limit of Eqs. (1.1) and (1.3). On the other hand, in contrast to Eqs. (1.2) and (1.4), the longitudinal eigenvalues are now given as

$$\omega_\pm{}^2=\frac{k^2}{2\rho_0}\Bigg[\left[\tfrac{4}{3}G_\infty+K_\infty+\Xi_\infty\left(\frac{\partial T}{\partial U}\right)_\rho\right]$$
$$\pm\left[\left(\tfrac{4}{3}G_\infty+K_\infty+\Xi_\infty\left(\frac{\partial T}{\partial U}\right)_\rho\right)^2$$
$$-4(\tfrac{4}{3}G_\infty+K_\infty-K_0)\Xi_\infty\left(\frac{\partial T}{\partial U}\right)_\rho\right]^{1/2}\Bigg]. \quad (2.10)$$

Note that Eq. (2.10) is an expression for the square of the frequency and, in effect, there are four eigenvalues. We shall find a similar result from the variational procedure, corresponding to four distinct eigenfunctions (i.e., two distinct sets of excitations).

III. VARIATIONAL SOLUTION

The variational solution is performed as follows. Suppose we start with the trial function of the form

$$\Psi=\sum_{i=1}^{9}\alpha_iB_i\,, \quad (3.1)$$

where the α_i are to be determined by the variational procedure, the B_i are given as

$$\begin{aligned}&B_1=A_1, \quad B_2=LA_1, \quad B_3=A_2\,,\\ &B_4=LA_2, \quad B_5=A_3, \quad B_6=LA_3\,,\\ &B_7=A_4, \quad B_8=A_5, \quad B_9=LA_5\,,\end{aligned} \quad (3.2)$$

and L is, once again, the Liouville operator. The dynamical functions $A_1\cdots A_5$ are the following: $A_{1,2,3}$ are defined as above in Eqs. (1.8) and (1.9); A_4 and A_5 are, respectively, the density and energy fluctuations, viz.,

$$A_4=V^{-1}\sum_{j=1}^{N} me^{-i\mathbf{k}\cdot\mathbf{R}_j}\,, \quad (3.3)$$

and

$$A_5=V^{-1}\sum_{j=1}^{N}(p_j{}^2/2m+\tfrac{1}{2}\sum_{l\neq j}\varphi_{jl})e^{-i\mathbf{k}\cdot\mathbf{R}_j}. \quad (3.4)$$

Eigenfunctions are obtained from solution of the following characteristic equation

$$|\boldsymbol{\Theta}-\omega\mathbf{N}|=0\,, \quad (3.5)$$

where $\boldsymbol{\Theta}$ and $\mathbf{N}$ are matrices defined as[1]

$$\boldsymbol{\Theta}_{ij}\equiv\langle B_j{}^*LB_i\rangle_T \quad (3.6)$$

and

$$\mathbf{N}_{ij}\equiv\langle B_j{}^*B_i\rangle_T\,. \quad (3.7)$$

Although $\boldsymbol{\Theta}$ and $\mathbf{N}$ are 9×9 matrices, the first four (transverse) elements of the characteristic determinant do not couple to the remaining (longitudinal) excitation components, so that we need only solve a somewhat simpler equation involving a symmetric 5×5 determinant.

However, before attempting a solution, let us make

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[6] Note that damping terms have been neglected in Eqs. (2.1)–(2.4). The high-frequency expressions used for the transport coefficients are but first approximations which, strictly speaking, pertain only to infinite frequency excitation. Equations (2.1)–(2.4) are the long-wavelength limits of more general nonlocal hydrodynamic equations. For a derivation of the latter see, e.g., B. Robertson, Phys. Rev. **160**, 175 (1967).

the following observations. Define, as before,[1]

$$A\equiv\langle A_4{}^*A_4\rangle;\quad B\equiv\langle A_5{}^*A_5\rangle;\quad C\equiv\langle A_4{}^*A_5\rangle;$$
$$\tilde{U}\equiv\langle A_3{}^*LA_5\rangle;\ W\equiv\langle A_3{}^*A_3\rangle;\quad \tilde{W}\equiv|k|W;\qquad(3.8)$$
$$\bar{X}\equiv\langle A_3{}^*L^2A_3\rangle;\ Z\equiv\langle A_5{}^*L^2A_5\rangle$$

and, furthermore,

$$Y\equiv\langle A_5{}^*L^3A_3\rangle.\qquad(3.8')$$

From previous work,[7] one can now identify K_0 as

$$k^2\rho_0{}^{-1}K_0=[\tilde{U}^2A+B\tilde{W}^2+2C\tilde{U}\tilde{W}]/W(AB-C^2)\qquad(3.9)$$

and, also, the infinite frequency mechanical moduli according to

$$k^2\rho_0{}^{-1}[\tfrac{4}{3}\mathcal{G}_\infty+\mathcal{K}_\infty]=\bar{X}/W.\qquad(3.10)$$

Further, as shown in Appendix A, the thermal conductivity coefficient may be written as in Eq. (2.9), with Θ_∞ and Θ_0 defined as

$$k^2\rho^{-1}\Theta_\infty\left(\frac{\partial T}{\partial U}\right)_\rho=ZA/(AB-C^2)\qquad(3.11)$$

and

$$k^2\rho^{-1}\Theta_0\left(\frac{\partial T}{\partial U}\right)_\rho=\tilde{U}^2A/W(AB-C^2).\qquad(3.12)$$

Thus, the dispersion relation obtained from hydrodynamics (Eq. (2.10) may be expressed as

$$\begin{aligned}2\omega_\pm{}^2=&[\bar{X}/W+A(AB-C^2)^{-1}(Z-\tilde{U}^2/W)]\\&\pm\Bigg\{[\bar{X}/W+A(AB-C^2)^{-1}(Z-{}^2\tilde{U}/W)]^2\\&-4\left(\frac{\bar{X}}{W}-\frac{\tilde{U}^2A+B\tilde{W}^2+2C\tilde{U}\tilde{W}}{W(AB-C^2)}\right)\\&\times(Z-\tilde{U}^2/W)A(AB-C^2)^{-1}\Bigg\}^{1/2}.\qquad(3.13)\end{aligned}$$

Furthermore, we note that if density fluctuations are negligible,[8] the above expression has yet a simpler form, viz.,

$$\begin{aligned}2\omega_\pm{}^2=&[\bar{X}/W-\tilde{U}^2/WB+Z/B]\\&\pm\{[\bar{X}/W-\tilde{U}^2/WB+Z/B]^2-4(\bar{X}/W-\tilde{U}^2/WB)\\&\times(Z/B-\tilde{U}^2/WB)\}^{1/2}.\qquad(3.14)\end{aligned}$$

Let us now return to the solution of the characteristic equation. In terms of the quantities given by Eqs. (3.8) and (3.8′), the nonzero matrix elements of $\mathbf{\Theta}$ and $\mathbf{N}$ are given as

$$\mathbf{\Theta}_{56}=\bar{X},\quad \mathbf{\Theta}_{57}=-\tilde{W},\quad \mathbf{\Theta}_{58}=\tilde{U},\quad \mathbf{\Theta}_{69}=Y,\qquad(3.15)$$
$$\mathbf{\Theta}_{79}=-|k|\tilde{U},\quad \mathbf{\Theta}_{89}=Z,\quad \mathbf{\Theta}_{ij}=\mathbf{\Theta}_{ji}$$

and

$$\mathbf{N}_{55}=W,\quad \mathbf{N}_{59}=\tilde{U},\quad \mathbf{N}_{66}=\bar{X},\quad \mathbf{N}_{67}=-\tilde{W},$$
$$\mathbf{N}_{68}=\tilde{U},\quad \mathbf{N}_{77}=A,\quad \mathbf{N}_{78}=C,\qquad(3.16)$$
$$\mathbf{N}_{88}=B,\quad \mathbf{N}_{99}=Z,\quad \mathbf{N}_{ij}=\mathbf{N}_{ji}.$$

Since it appears in Eq. (3.15) and, therefore, in Eq. (3.5), we must now identify the matrix element Y. This has proved a difficult problem and its resolution has required application of two important results which arose in our previous work: (1) When trial functions are formed of linear combinations of A_4, A_3, and LA_3 (or, even, A_4, A_3, LA_3, and A_5), the density fluctuation term A_4 does not appear in the eigenfunctions associated with nonzero eigenfrequencies; (2) in all previous work we have found identifiable correspondence between variational solutions and hydrodynamic dispersion relations. Consequently, as a first approximation, we consider the density fluctuations to be a negligible component of the eigenfunctions currently under consideration. In this case the characteristic equation may be written as

$$D\equiv\begin{vmatrix}-\omega W & \bar{X} & \tilde{U} & -\omega\tilde{U}\\ \bar{X} & -\omega\bar{X} & -\omega\tilde{U} & Y\\ \tilde{U} & -\omega\tilde{U} & -\omega B & Z\\ -\omega\tilde{U} & Y & Z & -\omega Z\end{vmatrix}=0.\qquad(3.17)$$

Further, the second of the above results suggests that we identify Y as

$$Y=\left(\frac{\bar{X}}{W}-\frac{\tilde{U}^2}{WB}+\frac{Z}{B}\right)\tilde{U}\qquad(3.18)$$

in which case Eq. (3.17) is satisfied by the eigenvalues given by Eq. (3.14).

It follows that associated eigenfunctions are given as

$$\begin{aligned}\Psi_\omega\sim\Bigg\{&\left[A_3+\frac{\tilde{U}((\tilde{U}^2/WB)-(Z/B))}{\omega(-\omega^2\tilde{U}+Y)}LA_3\right]\\&-\frac{((\tilde{U}^2/WB)-(Z/B))(\bar{X}-\omega^2W)}{\omega(-\omega^2\tilde{U}+Y)}\\&\times\left[A_5+\frac{\omega}{(\tilde{U}^2/WB)-(Z/B)}LA_5\right]\Bigg\}.\qquad(3.19)\end{aligned}$$

However, from Eqs. (3.14) and (3.18) one sees that

$$-\omega_\pm{}^2\tilde{U}+Y=\omega_\mp{}^2\tilde{U}\qquad(3.20)$$

so that

$$\omega_\pm(Y-\omega_\pm{}^2\tilde{U})=\omega_\mp\left[\left(\frac{\tilde{U}^2}{WB}-\frac{Z}{B}\right)\left(\frac{\tilde{U}^2}{WB}-\frac{\bar{X}}{W}\right)\right]^{1/2}\tilde{U}.\qquad(3.21)$$

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[7] See Ref. 1, especially Eqs. (2.4) and (A3) and Appendix B.

[8] It is known from prior work (see Ref. 1) that, for an "almost incompressible fluid," $k^2\rho^{-1}(\partial P/\partial\rho)_S\approx\tilde{U}^2/WB$. This result arises, for example, when trial functions are formed only of A_3 and A_5. [See, also, Appendix A, below and especially, Eq. (A12).]

Thus, $\Psi_{\omega\pm}$ may also be written as

$$\Psi_{\omega\pm}\sim\left[\left\{A_3+\frac{1}{\omega_\mp}\left[\frac{\tilde{U}^2-WZ}{\tilde{U}^2-B\bar{X}}\right]^{1/2}LA_3\right\}-\frac{(\bar{X}-\omega_\pm{}^2W)}{\omega_\mp\tilde{U}}\right.$$
$$\left.\times\left\{\frac{\tilde{U}^2-WZ}{\tilde{U}^2-B\bar{X}}\right\}^{1/2}\left\{A_5+\left[\frac{\omega_\pm WB}{(\tilde{U}^2-WZ)}\right]LA_5\right\}\right],\quad(3.22)$$

where $\omega_\pm$ is either the positive or negative square root of $\omega^2(\pm)$, the polarity of the root being consistently applied. In other words, the sign of $\omega_\pm$ must be the same as that of $\omega_\mp$ [see Eqs. (3.20), (3.21)]. Upon replacing $\tilde{U}$, W, B, etc. by their thermodynamic definitions, Eq. (3.22) may be written in more familiar terms as

$$\Psi_{\omega\pm}\sim\left[\left\{A_3+\frac{1}{\omega_\mp}\left[(\Theta_\infty-\Theta_0)\left(\frac{\partial T}{\partial U}\right)_\rho\Big/(\tfrac{4}{3}\mathcal{G}_\infty+\mathcal{K}_\infty-K_0)\right]^{1/2}LA_3\right\}-\frac{\langle A_3{}^*A_3\rangle}{\langle A_3{}^*LA_5\rangle}(k^2\rho^{-1}[\tfrac{4}{3}\mathcal{G}_\infty+K_\infty]-\omega_\pm{}^2)\right.$$
$$\left.\times\left\{(\Theta_\infty-\Theta_0)\left(\frac{\partial T}{\partial U}\right)_\rho\Big/(\tfrac{4}{3}\mathcal{G}_\infty+\mathcal{K}_\infty-K_0)\right\}^{1/2}\left\{A_5+\frac{\omega_\pm}{\rho^{-1}k^2(\Theta_\infty-\Theta_0)}\left(\frac{\partial T}{\partial U}\right)_\rho^{-1}LA_5\right\}\right].\quad(3.23)$$

IV. DISCUSSION

Direct verification of these high-frequency excitations depends upon experiments involving scattering of low-energy neutrons. Thus, let us now calculate the coherent cross section for scattering of neutrons from simple fluids. The coherent scattering cross section[9] is proportional to the scattering function $S_c(k,\omega)$ which, in the classical limit, is simply the Fourier time transform of the density-density correlation function, viz.,

$$S_c(k,\omega)=\int_{-\infty}^{\infty}dt\; e^{-i\omega t}\chi_c(k,t)\,,\quad(4.1)$$

where $\chi_c(k,t)$ is defined as

$$\chi_c(k,t)=N^{-1}\sum_{i,j=1}^{N}\sum^{N}\langle e^{-i\mathbf{k}\cdot\mathbf{R}_i(0)}e^{+i\mathbf{k}\cdot\mathbf{R}_j(t)}\rangle$$
$$=N^{-1}\langle\rho_k{}^*e^{itL}\rho_k\rangle.\quad(4.2)$$

If we integrate Eq. (4.1) by parts, an alternate expression is obtained which relates the scattering function to the current-current correlation function

$$S_c(k,\omega)=2k^2V^2(m^2\omega^2N)^{-1}\int_0^\infty dt\;\cos\omega t$$
$$\times\langle A_3{}^*(k)e^{itL}A_3(k)\rangle.\quad(4.3)$$

In the above, the current-current correlation function has been expressed in terms of the velocity fluctuation functions A_3 as defined by Eq. (1.9).

A useful approximation to the current-current correlation is obtained as follows. First solve for A_3 in terms of the four excitation functions given by Eq. (3.22). Thus

$$A_3=\tfrac{1}{2}\left[\left\{(\Psi_{+(\omega+)}+\Psi_{-\omega(+)})\Big/\left[1-\frac{\omega_+{}^2}{\omega_-{}^2}(\bar{X}-\omega_+{}^2W)/(\bar{X}-\omega_-{}^2W)\right]\right\}\right.$$
$$\left.+\left\{(\Psi_{+\omega(-)}+\Psi_{-\omega(-)})\Big/\left[1-\frac{\omega_-{}^2}{\omega_+{}^2}(\bar{X}-\omega_-{}^2W)/(\bar{X}-\omega_+{}^2W)\right]\right\}\right],\quad(4.4)$$

and the current-current correlation function may be expressed in terms of the ψ's as the sum of sixteen terms of the form $\langle\Psi_i{}^*e^{itL}\Psi_j\rangle$. Then, for example, consider $\langle\Psi_{+\omega(+)}{}^*e^{itL}\Psi_{+\omega(+)}\rangle$ and make the following approximation:

$$\langle\Psi_{+\omega(+)}{}^*e^{itL}\Psi_{+\omega(+)}\rangle\approx\langle\Psi_{\omega(+)}{}^*\Psi_{\omega(+)}\rangle e^{i\omega(+)t}.\quad(4.5)$$

[Note that the exponential appearing on the right-hand side of the above equation is obtained when one neglects coupling between $\Psi_{+\omega(+)}(k)$ and other excitation states.] If the other of the sixteen terms are evaluated to the same approximation, one obtains an expression of the form

$$\langle A_3{}^*e^{itL}A_3\rangle=a_+\cos\omega_+t+a_-\omega s\omega_-t\,,\quad(4.6)$$

where a_+ and a_- are time-independent functionals of thermodynamic variables and kinetic moduli. Thus, it is seen that to a first approximation, the coherent peaks of the scattering function are identifiable with dispersion relations given by Eqs. (2.10) and (3.13).[10]

In recent neutron-scattering experiments, only a *single* phonon branch has been discerned for each of various liquified rare gases.[11] These data may be recon-

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[9] L. Van Hove, Phys. Rev. **95**, 249 (1954).

[10] There is also a peak at zero frequency, arising in the variational solution when density fluctuations are taken into account. An explicit expression for the eigenfunction is given in Appendix B, below.

[11] S. H. Chen *et al.*, Phys. Letters **19**, 269 (1965); K. Sköld and K. E. Larsson, Phys. Rev. **161**, 102 (1967). However, Larsson (private communication) expresses the view that a second excitation also exists in liquid argon, but at frequencies somewhat below those examined in his experiments.

ciled with our results, which predict two branches, if high-frequency thermal disturbances propagate much more slowly in such fluids than do mechanical disturbances. In this case there would be two types of excitations: one group composed primarily of velocity fluctuations (and time derivatives thereof) with propagation frequencies of the order of $10^{12}-10^{13}$ cps; and a second, more slowly propagating, being a relatively complicated function of all the fluctuation variables. The former would give rise to the measurable "wings" of the coherent neutron-scattering cross sections, whereas the latter would not be discernible due to their being masked by the zero-frequency "quasi-elastic peak."

Specifically, one would have

$$-k^2 \lim_{\omega\to\infty} i\omega\hat{\lambda}(k,\omega)\left(\frac{\partial T}{\partial U}\right)_\rho \ll [\tfrac{4}{3}k^2\mathcal{G}_\infty(k)+k^2\mathcal{K}_\infty(k)] \tag{4.7}$$

or, alternatively,

$$[(Z/B)-(\tilde{U}^2/WB)] \ll \bar{X}/W. \tag{4.8}$$

Thus, the eigenvalues [see Eq. (3.14)] would be written as

$$\begin{aligned}\omega_+{}^2 &\approx [(\bar{X}/W)-(\tilde{U}/WB)+(Z/B)] \approx \bar{X}/W\\ &= k^2\rho^{-1}[\tfrac{4}{3}\mathcal{G}_\infty(k)+\mathcal{K}_\infty(k)]\end{aligned} \tag{4.9}$$

and

$$\omega_-{}^2 \approx \frac{[(\tilde{U}^2/WB)-(\bar{X}/W)][(\tilde{U}^2/WB)-(Z/B)]}{[(\bar{X}/W)-(\tilde{U}^2/WB)+(Z/B)]} \tag{4.10}$$

$$\begin{aligned}&\approx [(Z/B)-(\tilde{U}/WB)] = -k^2\rho^{-1}(\partial T/\partial U)_\rho\\ &\qquad \times \lim_{\omega\to\infty} i\omega\hat{\lambda}(k,\omega).\end{aligned} \tag{4.11}$$

The excitation associated with the higher frequency would reduce to

$$\begin{aligned}\Psi_{\pm\omega+} \sim [A_3 \pm \{k^2\rho^{-1}[\tfrac{4}{3}\mathcal{G}_\infty(k)\\ +\mathcal{K}_\infty(k)-\mathcal{K}_0]\}^{-1/2}LA_3],\end{aligned} \tag{4.12}$$

although no such simple form would ensue for the lower frequency excitation.

Note that the eigenvalues and eigenfunctions given by Eqs. (4.9) and (4.12) are similar to those which arose in our earlier work[1] in which energy terms were not considered [see Eqs. (1.2) and (1.7) above]. The only difference between these and earlier results is the spurious appearance of the adiabatic bulk modulus K_0 in the coupling term of the eigenfunction as given by Eq. (4.12). (The latter probably arises due to neglect of density fluctuations in the present calculation.)

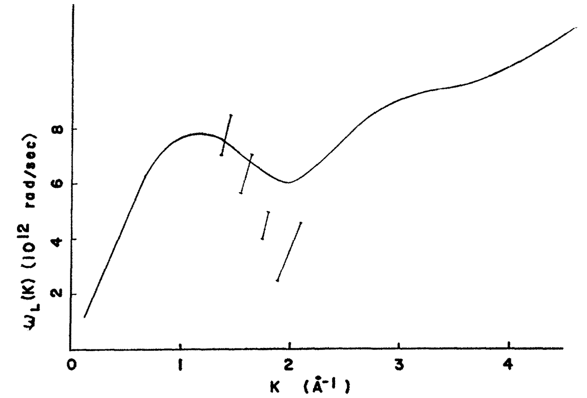

FIG. 1. Dispersion relation for liquid argon at 85°K as determined from Eq. (4.9). Data are from Chen *et al.* (Ref. 11). Note that the analytic curve has not yet been corrected for lifetime or quantum effects.

It is difficult to determine *a priori* whether Eq. (4.7) is indeed satisfied for simple classical fluids at normal temperatures and densities. Because data are not available for the high-frequency moduli, it is necessary to extrapolate from low-frequency values of transport coefficients.[12] For liquid argon, the low-frequency values of the thermal conductivity, heat capacity, and viscosity are, respectively,[13] $\lambda \approx 18\times10^{-5}$ cal/sec cm°K, $C_V{}^{(m)} \approx 0.15$ cal/g°K, and $\eta \approx 2.5\times10^{-3}$ poise. With these values we find $\lambda C_V{}^{-1} = 1.2\times10^{-3}$ g/sec cm, which is to be compared with $2\eta_s \approx 5\times10^{-3}$ g/sec cm.[12] Thus, from these considerations alone, it is hard to conclude that thermal modes totally decouple from the higher-frequency eigenfunction.

To demonstrate the feasibility of these considerations, we have calculated a dispersion relation for liquid argon, as given by Eq. (4.9) [see also, Eq. (1.21)]. A 12-6 potential has been assumed with $\epsilon/K = 118$°K, $\sigma = 3.4\times10^{-8}$ cm, $T = 85$°K, and $\rho = 1.37$ gm/cm³. Results are presented in Fig. 1. In order to simplify our calculation, we have used an analytic approximation to the pair correlation function (see Fig. 2.) It is interesting that this calculation, which does not include corrections for either lifetime or quantum effects, yields a dispersion relation in fairly good agreement with available data.[11] A more extensive computational study is currently in progress.

It is also tempting to interpret observations of "phonon excitations" in liquid metals in terms of our results. For liquid metals, a number of investigators[14,15] have recently reported neutron-scattering data from which two phonon branches are deduced. In each case one of these excitations is ascribed to "transverse modes."[14,15] However, if we assume that high-frequency

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[12] At low frequencies, Eq. (4.7) is equivalent to $\lambda C_v{}^{-1} \ll \frac{4}{3}\eta_s + \eta_v \approx 2\eta_s$, where η_s is the shear viscosity. Another way of making this estimate is to assume that $\hat{\lambda} \sim [\Xi_\infty \tau_T]/(1+i\omega\tau_T)$, $\hat{\eta}_S \sim [G_\infty \tau_S]/(1+i\omega\tau_S)$ and, also, the Euken relation $\lim_{\omega\to0}\hat{\lambda}(\omega)C_v{}^{-1} \simeq 2 \times \lim_{\omega\to0}\hat{\eta}_s(\omega)$. It then follows that $\Xi_\infty C_v{}^{-1} \simeq 2G_\infty \tau_S/\tau_T \lesssim 2G_\infty$ which is to be compared with $\frac{4}{3}G_\infty + K_\infty \sim 3G_\infty$.

[13] S. A. Rice, J. P. Boon, and H. T. Davis, in *Simple Dense Fluids*, edited by H. L. Frisch and Z. Salzberg (Academic Press Inc., New York, to be published); J. P. Boon, J. C. Legros, and G. Thomaes, Physica **33**, 547 (1967).

[14] P. D. Randolph and W. R. Myers, Bull. Am. Phys. Soc. **12**, 556 (1967); S. J. Cocking and P. A. Egelstaff, Phys. Letters **16**, 130 (1965).

[15] U. Dahlborg and K. E. Larsson, Arkiv Fysik **33**, 271 (1966).

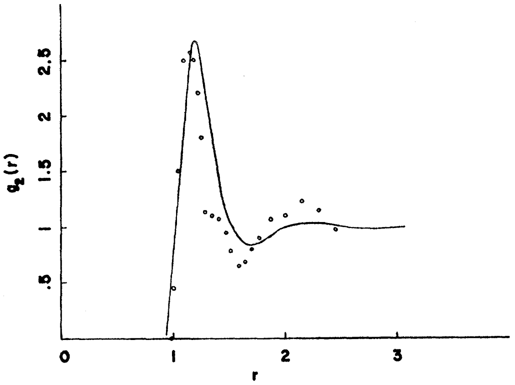

FIG. 2. The pair correlation function used in calculations of the curve given in Fig. 1. The latter was chosen primarily to simplify calculations, with the proviso that $\max(g_2^{\text{approx.}}) \approx \max(g_2^{\text{measured}})$ and, also, that oscillation about the axis $g_2=1$ be similar to that actually observed. The solid line is the approximate $g_2(r)$, whereas the data points (note: $T=91.8°\text{K}$) are from A. Eisenstein and N. S. Gringrich, Phys. Rev. **62**, 261 (1942).

fluid motion may be described by constitutive relations similar to the usual hydrodynamic equations [e.g., Eqs. (2.1)–(2.4), above] then, for isotropic fluids, density fluctuations can couple only to longitudinal disturbances. Transverse excitations will not be seen as a first-order effect in the scattering process (similar conclusions arise from a study of the matrix elements of the Liouville operator). Thus, the experiments must be probing *two longitudinal* excitations, similar to those which we are currently proposing.[16]

Finally, let us briefly consider what happens if the converse of the inequality Eq. (4.7) were to hold, i.e., if

$$-k^2 \lim_{\omega\to\infty} i\omega\hat{\lambda}(k,\omega)\left(\frac{\partial T}{\partial U}\right)_\rho \gg \left[\tfrac{4}{3}k^2\mathcal{G}_\infty(k)+k^2\mathcal{K}_\infty(k)\right]. \quad (4.13)$$

In this case the higher-frequency eigenvalues would be given by Eq. (4.11) and, according to the present analysis, the associated eigenfunctions would be the following:

$$\Psi\sim\left[A_5\pm\left\{k^2\rho^{-1}\left(\frac{\partial T}{\partial U}\right)_\rho \times\lim_{\omega\to\infty} -i\omega\hat{\lambda}(k,\omega)\right\}^{1/2} LA_5\right], \quad (4.14)$$

i.e., would be composed primarily of energy fluctuations and related time derivatives.

It may be that quantum analogs of such excitations constitute high-frequency second sound in liquid He II. In this regard, our suggestions are similar to those of Kawasaki and Mori,[17] the latter authors having postulated that second sound waves in He II are formed of energy fluctuations and their time derivatives. Also, Griffin[18] has obtained similar dispersion relations for the propagation of second sound in crystals.

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The author wishes to thank Professor R. Zwanzig for numerous helpful discussions and the continued interest which he has shown in this problem.

APPENDIX A: CALCULATION OF HIGH-FREQUENCY THERMAL MODULI

We should now like to show that Eq. (2.9) seems to be a natural form in which to express the high-frequency thermal conductivity. Also, it shall be demonstrated that Θ_∞ and Θ_0 are given by Eqs. (3.11) and (3.12) These relationships shall be proven in the long-wavelength limit, although they undoubtedly have general validity.

The time-correlation function definition of the thermal conductivity is the following[19]

$$\lambda=\beta(3VT)^{-1}\int_0^\infty dt\, \exp(i\omega t)\langle \mathbf{S}(0)\cdot\mathbf{S}(t)\rangle$$
$$\approx -\beta(3VT)^{-1}[(i\omega)^{-1}\langle \mathbf{S}(0)\cdot\mathbf{S}(0)\rangle+\cdots], \quad (\text{A1})$$

where S is a heat current defined as

$$\mathbf{S}(0)\equiv\frac{d}{dt}\sum_i (H_i-\langle h_i\rangle)\mathbf{R}_i. \quad (\text{A2})$$

$\langle h_i\rangle$ designates the enthalpy per particle, $\beta=(k_BT)^{-1}$, T is the temperature, and k_B is Boltzmann's constant. V is the volume of the assembly, $\mathbf{R}_i$ the position and H_i the energy of the ith particle [see Eq. (3.4)].

Term by term evaluation of $\langle \mathbf{S}(0)\cdot\mathbf{S}(0)\rangle$ according to Eq. (A2) is straightforward and may be shown to yield

$$\hat{\lambda}(\omega)\approx-\frac{1}{i\omega}\left[\frac{\beta}{3VT}\left\langle\frac{d}{dt}\sum_i H_j\mathbf{R}_j\cdot \frac{d}{dt}\sum_l H_l\mathbf{R}_l\right\rangle-\frac{c\langle h\rangle^2}{mT}\right]+O\left(\frac{1}{\omega^2}\right), \quad (\text{A3})$$

where $c\equiv N/V$ is the number density and m is the particle mass. Notice that the first term on the r.h.s. of the above equation may be identified as

$$\left\langle\frac{d}{dt}\sum_j H_j\mathbf{R}_j\cdot\frac{d}{dt}\sum H_l\mathbf{R}_l\right\rangle = V^2k^{-2}\lim_{k\to0}\langle(LA_5)^*(LA_5)\rangle$$
$$=V^2k^{-2}\lim_{k\to0} Z(k) \quad (\text{A4})$$

[see Eq. (3.10)].

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[16] To describe the microscopic kinetics of liquid metals it is probably necessary to consider the movement of two mutually interacting charged fluids (the electrons and ionized metal atoms). The details of our analysis would have to be modified before quantitative results could be proposed.

[17] K. Kawasaki and H. Mori, Progr. Theoret. Phys. (Kyoto) **28**, 784 (1962); see, also, H. Mori, *ibid.* **33**, 423 (1965), especially footnote p. 441.

[18] A. Griffin, Phys. Letters **17**, 208 (1965). See, also, J. B. Brown, D. Y. Chung, and P. W. Matthews, *ibid.* **21**, 241 (1966).

[19] See, e.g., R. Zwanzig, Ann. Rev. Phys. Chem. **16**, 67 (1965).

Thus, in analogy with our prior definition of G_∞ in terms of molecular quantities, we may associate Z with Θ_∞ according to

$$k^2\Theta_\infty = V\beta T^{-1}Z. \tag{A5}$$

Consequently, in order to derive Eq. (3.11) we must show

$$B - C^2/A = \rho_0 T(\beta V)^{-1}(\partial U/\partial T)_\rho. \tag{A6}$$

In this regard, let us consider the evaluation of $B \equiv \langle \mathcal{E}_k{}^* \mathcal{E}_k \rangle$, where, in terms of previous notation, $\mathcal{E}_k \equiv A_5$. Note that $\mathcal{E}_k$, which is the fluctuation in energy per unit volume, may be expressed in terms of fluctuations per unit mass according to

$$\mathcal{E}_k = -\rho_0{}^2\mathcal{E}^{(m)}\Delta V^{(m)} + \rho_0 \Delta\mathcal{E}^{(m)}. \tag{A7}$$

In the above, $\mathcal{E}^{(m)}$ is the energy per unit mass, $\Delta V^{(m)}$ is the fluctuation in volume per unit mass, etc.

Also, express the energy fluctuation in terms of temperature and volume fluctuations by

$$\Delta\mathcal{E}^{(m)} = (\partial\mathcal{E}^{(m)}/\partial V^{(m)})_T \Delta V^{(m)} + (\partial \mathcal{E}^{(m)}/\partial T)_V \Delta T. \tag{A8}$$

Thus, because $\langle (\Delta T)(\Delta V^{(m)})\rangle = 0$, we have, using (A7),

$$B = [\rho_0{}^2\mathcal{E}^{(m)} - \rho_0(\partial\mathcal{E}^{(m)}/\partial V^{(m)})_T]^2 \langle (\Delta V^{(m)})^2 \rangle + \rho_0{}^2[(\partial\mathcal{E}^{(m)}/\partial T)_V]^2 \langle (\Delta T)^2 \rangle. \tag{A9}$$

Suppose one were to neglect density fluctuations. Then, because $\langle (\Delta T)^2 \rangle$ may be given as[20]

$$\langle (\Delta T)^2 \rangle = \beta^{-1} TM/(\partial\mathcal{E}^{(m)}/\partial T)_V, \tag{A10}$$

we would have

$$B \sim \rho_0{}^2 \beta^{-1} TM(\partial\mathcal{E}^{(m)}/\partial T)_V. \tag{A11}$$

In this case, Eq. (A5) would be identical with [see, also, discussion following Eq. (3.13)]

$$k^2 \rho_0{}^{-1} \Theta_\infty (\partial T/\partial U)_V = Z/B. \tag{A12}$$

However, using similar arguments, one may show that the terms which have been neglected on the r.h.s. of (A9) are identifiable as

$$[\rho_0{}^2\mathcal{E}^{(m)} - \rho_0(\partial\mathcal{E}^{(m)}/\partial V^{(m)})_T]^2 \langle (\Delta V^{(m)})^2 \rangle = C^2/A. \tag{A13}$$

Including these terms indeed yields (A6), from which Eq. (3.21) then follows.

Referring again to Eqs. (2.9), (A3) and (A5), we see that it is proper to identify Θ_0 as

$$\Theta_0 = c(mT)^{-1}\langle h \rangle^2 = \rho T^{-1}[H^{(m)}]^2, \tag{A14}$$

where the enthalpy per unit mass $H^{(m)}$ is related to $\langle h_i \rangle$ as $\langle h_i \rangle = mH^{(m)}$. But, as pointed out in Ref. 1 [Eq. (A7)], $H^{(m)}$ is related to $\tilde{U} \equiv \langle A_3{}^* L A_5 \rangle$ by

$$\tilde{U} = -|k|\rho(\beta V)^{-1} H^{(m)}. \tag{A15}$$

From Eqs. (A14), (A15), and the arguments encompassed in Eqs. (A7)–(A13), one may now also easily prove the identity Eq. (3.14).

The key point in the above discussion has been the identification made in Eq. (A4), which has been argued by analogy with identifications arising for G_∞ and K_∞. A more direct demonstration of Eq. (2.9) may be accomplished by adaptation of arguments used by Meixner[21] and De Groot and Mazur[22] in their discussions of the mechanical moduli $K(\omega)$ and $G(\omega)$. The essence of this derivation is to start with the linearized energy conservation equation of hydrodynamics

$$\omega\rho_0 \hat{H} = -i\lambda(\mathbf{k}\cdot\mathbf{k})\hat{T} + \omega\hat{p} \tag{A16}$$

and define a thermal susceptibility $\hat{X}(\omega)$ by $\hat{X} = \hat{H}/\hat{T}$. Then, identify Θ_0 with the high-frequency limit of $\rho_0 C^2 \hat{X}_0(\omega)$, where C is the sound velocity and $X_0(\omega)$ the part of $X(\omega)$ which does not vanish as $\omega \to 0$. The derivation is rather involved and not really germane to the present investigation, so we shall not discuss this point any further at the present time.

APPENDIX B: EIGENFUNCTIONS OF THE 5×5 MATRIX

The characteristic equation arising when density fluctuations are considered [see Eqs. (3.5), (3.8), and (3.17)] is

$$\begin{vmatrix} -\omega W & \bar{X} & -|k|W & \tilde{U} & -\omega\tilde{U} \\ \bar{X} & -\omega\bar{X} & \omega|k|W & -\omega\tilde{U} & Y \\ -|k|W & \omega|k|W & -\omega A & -\omega C & -|k|\tilde{U} \\ \tilde{U} & -\omega\tilde{U} & -\omega C & -\omega B & Z \\ -\omega\tilde{U} & Y & -|k|\tilde{U} & Z & -\omega Z \end{vmatrix} = 0. \tag{B1}$$

It is easy to see that $\omega = 0$ is a solution, with associated eigenvector

$$\Psi \sim [LA_3 + \{|k|(\tilde{U}^2 - WZ)\}^{-1} \times \{(\tilde{U}Y - Z\bar{X})A_4 + (WY - \bar{X}\tilde{U})A_5\}]. \tag{B2}$$

In other words, density fluctuations are a constituent of the zero frequency excitation.

A similar zero frequency eigenfunction, formed of a combination of A_4 and LA_3, was found in the previous study[1] when energy fluctuations were not considered.

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[20] See, e.g., L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley Publishing Co., Reading, Mass., 1958), p. 352.

[21] J. Meixner, Z. Naturforsh. **4a**, 594 (1949); **9a**, 654 (1954).

[22] S. R. DeGroot and P. Mazur, *Non-Equilibrium Thermodynamics* (North-Holland Publishing Co., Amsterdam, 1963).