which greatly adds to the credibility of the present findings.

CONCLUSION

It appears that metastable states of Ar, H_2, and N_2 were indeed formed in the source. The Ar caused both surface self-ionization and secondary emission with some reflection of metastables. The H_2 most prominently displayed a strong emission of Lyman-α radiation on hitting the target. The nitrogen displayed a strong sensitivity to any traces of carbon (whether as an oxide or a hydrocarbon not being established), leading to the formation of CN^- on impact.

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Approximate Eigenfunctions of the Liouville Operator in Classical Many-Body Systems. II. Hydrodynamic Variables

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A variational solution of the Liouville equation is used to obtain collective coordinates for simple classical fluids. Comparison is made with macroscopic analogs determined from relevant hydrodynamic equations. Approximate eigenfunctions of the Liouville operator, when constructed from linear combinations of the spatial Fourier transforms (fluctuations) of the mass, momentum, and energy-density operators for the fluid, are found appropriate to low-frequency disturbances. When time derivatives of fluctuations are included among trial functions, the variational procedure provides fluid-state counterparts of usual solid-state phonons.

INTRODUCTION

THE states of a many-body system are characterized by the eigenfunctions of the Liouville operator L of the system. The exact eigenfunctions of the Liouville operator are not known for dense fluids, nor is it likely that their discovery is imminent. However, by selecting a functional form for the eigenfunctions (designated for example as $\{\psi\}$), and adjusting parameters such that the chosen $\{\psi\}$ satisfy a variational equation, it may be possible to determine *approximate* eigenfunctions which manifest important aspects of the collective behavior of the system. In such spirit, the present investigation is directed towards determination of collective coordinates describing excitations of simple classical fluids.

Discussion of the variational Liouville equation and the results of our calculations appear in the following sections of this paper. The calculations, themselves, are rather lengthy and are summarized in appendices. Although the analysis is complete as it stands, the reader may wish to refer to a previous article by one of the authors[1] in which certain aspects of the variational approach are discussed.

I. VARIATIONAL EQUATION

Suppose that trial functions of the form $\psi(\{\alpha\}) = \sum_i \alpha_i A_i$ are chosen, where the $\{A_i\}$ are known functions of position and momentum and the $\{\alpha_i\}$ are numerical coefficients which are to be varied. Let the "eigenfunctions" be determined according to the variational criterion that the "eigenvalues" $\{\omega\}$, defined by

$$\omega(\{\alpha\}) \equiv \frac{\langle \psi^*(\{\alpha\}) L \psi(\{\alpha\}) \rangle_T}{\langle \psi^*(\{\alpha\}) \psi(\{\alpha\}) \rangle_T} \tag{1.1}$$

approximate the actual eigenvalues $\{\omega^L\}$ as closely as possible. The subscript T signifies an average over a canonical distribution, e.g.,

$$\langle AB \rangle_T = \int dp_1 \cdots dq_n e^{-\beta H(p_1,\cdots,q_n)} A(p_1,\cdots,q_n) \times B(p_1,\cdots,q_n) \bigg/ \int dp_1 \cdots dq_n e^{-\beta H(p_1,\cdots,q_n)}. \tag{1.2}$$

When coefficients are adjusted to minimize the difference between $\{\omega\}$ and $\{\omega^L\}$ the following set of

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[1] R. Zwanzig, Phys. Rev. 144, 170 (1966).

equations for the $\{\alpha^i\}$ are obtained:

$$\sum_{i=1}^{N} \alpha_i \langle A_j^* L A_i \rangle_T = \omega \sum_{i=1}^{N} \alpha_i \langle A_j^* A_i \rangle_T , \qquad j=1,2,\cdots,N. \quad (1.3)$$

These have a nontrivial solution if, and only if, the determinant of the coefficients of the $\{\alpha_i\}$ vanishes:

$$|\mathbf{\Theta} - \omega \mathbf{N}| = 0, \quad (1.4)$$

where

$$\mathbf{\Theta}_{ij} = \langle A_j^* L A_i \rangle_T \quad (1.5)$$

and

$$\mathbf{N}_{ij} = \langle A_j^* A_i \rangle_T . \quad (1.6)$$

In this manner, both the $\{\omega\}$ and associated $\{\alpha_i\}$ may be determined.

In the following section, linear combinations of the spatial Fourier transforms (i.e., fluctuations) of the mass, momentum, and energy density operators are chosen as trial functions. Various time derivatives of these quantities also are included. Because of the Hermitian character of the Liouville operator, all eigenvalues $\{\omega\}$ are real. There are as many eigenvalues as there are components $\{A_i\}$ of the trial functions. Further, as a consequence of the particular form of the chosen $\{A_i\}$ we can make the following observation: The chosen $\{A_i\}$ are either pure even or pure odd functions of momentum. Let $n(e)$ represent the number of $\{A_i\}$ having even parity in momentum and $n(0)$ represent the number of odd $\{A_i\}$; suppose P equals the number of *nonzero* eigenvalues. Thus, because the expectation of the Liouville operator between functions of similar parity is zero, it may be shown that $P \leq 2 \min [n(e), n(0)]$. Also, the nonzero eigenvalues always appear in pairs of equal magnitude but opposite sign.[2]

II. APPROXIMATE EIGENFUNCTIONS

The Fourier transform of the momentum-density (mass-current) operator may be decomposed into one logitudinal and two transverse modes,

$$A_{1,2,3} \equiv V^{-1} \sum_{j=1}^{N} \mathbf{p}_j \cdot \hat{u}_{1,2,3} e^{-i\mathbf{k}\cdot\mathbf{R}_j} , \quad (2.1)$$

where, for example, $\hat{u}_3$ is defined as $\hat{u}_3 \equiv \mathbf{k}/|\mathbf{k}|$, and $\hat{u}_1$ and $\hat{u}_2$ 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.

The mass and energy density fluctuations of wave number $\mathbf{k}$ are defined as

$$A_4 \equiv V^{-1} \sum_{j=1}^{N} m e^{-i\mathbf{k}\cdot\mathbf{R}_j} \quad (2.2)$$

and

$$A_5 \equiv V^{-1} \sum_{j=1}^{N} (p_j^2/2m + \tfrac{1}{2} \sum_{n\neq j} \varphi_{jn}) e^{-i\mathbf{k}\cdot\mathbf{R}_j} . \quad (2.3)$$

Note that all molecules are taken to be alike and symmetric pairwise additive forces are assumed; φ_{ij} is the potential energy between the ith and jth particles.

A. Low-Frequency Disturbances

First, linear combinations of the quantities Eqs. (2.1)–(2.3) are chosen as trial functions. Consequences of also including time derivatives of these fluctuations are presented in the next section.

Using $A_1,\cdots,A_5$ and calculating approximate eigenvalues according to Eqs. (1.3)–(1.6) yields two nonzero and three zero eigenvalues. In the *long-wavelength* (*small*-$\mathbf{k}$) *limit*, we find the nonzero eigenvalues to be proportional to the adiabatic sound velocity, viz.,

$$\omega = \pm |k| C_{\mathrm{adiab}} = \pm |k| [(\partial P/\partial \rho)_S]^{1/2} . \quad (2.4)$$

In obtaining the latter result, all five fluctuation components are included (see Appendix A, below). However, if the trial function is constructed from only the mass and momentum fluctuations, one obtains instead the following expression for the (long-wavelength) dispersion relationship for $\mathbf{k}$ and ω,

$$\omega = \pm |k| C_{\mathrm{isothermal}} = \pm |k| [(\partial P/\partial \rho)_T]^{1/2} . \quad (2.5)$$

Similarly, on choosing a trial function composed only of the momentum and energy fluctuations, one obtains

$$\omega = \pm |k| [p/\rho^2 (\partial p/\partial U)_\rho]^{1/2} . \quad (2.6)$$

Note that the dispersion relation given by Eq. (2.4) is identical to that obtained from solution of the linearized Navier-Stokes equations in the limit of long wavelength. Similarly, Eq. (2.5) is obtained from hydrodynamic equations when energy transport is neglected and Eq. (2.6) is obtained from the linearized hydrodynamic equations of an almost incompressible fluid. It is evident, therefore, that the variational procedure, when applied to the quantities given by Eqs. (2.1)–(2.3), generates microscopic analogs of low-frequency, long-wavelength, hydrodynamic disturbances.[3]

This close correspondence is further evident when *eigenfunctions* of the variational Liouville equation are compared with those obtained from hydrodynamics. For example (see Appendix A) the eigenvectors corresponding to the adiabatic situation, Eq. (2.4), are

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[2] A general discussion concerning eigenfunctions composed of fluctuations and their time derivatives has been presented by one of us (R. Z.) at the recent Copenhagen IUPAP Conference on Statistical Mechanics; see also preceding paper, R. Zwanzig, Phys. Rev. **156**, 190 (1967).

[3] J. Irving and J. G. Kirkwood [J. Chem. Phys. **18**, 817 (1950)], where it was first noticed that the mass, momentum, and energy density operators could be used in conjunction with the Liouville equation to generate hydrodynamic conservation equations.

found to be proportional to

$$\psi_{\pm|k|C_{\text{adiab}}} \sim \left\{ A_5(k) - \rho_0 \left(\frac{\partial U}{\partial \rho} \right)_P A_4(k) \right.$$
$$\left. \mp \rho_0 \left(\frac{\partial U}{\partial P} \right)_\rho C_{\text{adiab}} A_3(k) \right\}, \quad (2.7)$$

where ρ_0 is the mass density per unit volume, U is the energy per unit mass, and A_3, A_4, A_5 are given by Eqs. (2.1)–(2.3). The eigenvectors obtained from the Navier-Stokes equations are

$$\psi_{\pm|k|C_{\text{adiab}}}{}^{\text{hyd}} \sim \left\{ U_k - \rho_0 \left(\frac{\partial U}{\partial \rho} \right)_P \rho_k \right.$$
$$\left. \mp \rho_0 \left(\frac{\partial U}{\partial P} \right)_\rho C_{\text{adiab}} v_{k||} \right\}, \quad (2.8)$$

where U_k, ρ_k, $v_{k||}$ are, respectively, the Fourier-Laplace transforms of the energy density, mass density, and longitudinal fluid velocity. Similar correspondence exists for eigenvectors associated with both the isothermal and incompressible assemblies.

Finally, the eigenvectors associated with the zero eigenvalues are as follows: There are two eigenfunctions composed solely of transverse current density fluctuations, $\psi \sim A_1(k)$, $\psi \sim A_2(k)$; a third has the form of an enthalpy fluctuation at constant pressure. In the first instance, hydrodynamic analogs are manifest in the inability of a fluid to propagate transverse shear waves for low-frequency disturbances. The zero-frequency enthalpy fluctuation (which also arises from the hydrodynamic equations) is perhaps associated with the inability of a classical fluid to propagate low-frequency second sound.

B. High-Frequency Excitations

Due to viscous damping, low-frequency transverse oscillations do not exist in a simple fluid. On the other hand, the high-frequency response of the fluid is primarily elastic, and rapidly varying shear disturbances will be sustained and propagated. Nondissipative response of a fluid to high-frequency mechanical disturbances is clearly seen in time-correlation function expressions for frequency-dependent viscosities.[4] It may easily be shown that the high-frequency shear and bulk viscosities are given by $\eta \simeq G_\infty / i\omega$ and $\eta_V \simeq (K_\infty - K_0)/i\omega$, where G_∞ and K_∞ are, respectively, the high-frequency shear and bulk moduli[5] and K_0 is the adiabatic (zero-frequency) bulk modulus, defined as $K_0 = -V(\partial P/\partial V)_S$.

The finite time of response to a mechanical disturbance is necessarily manifest in the hydrodynamic equations for the fluid, and suitable modification of the Navier-Stokes equations is required in order to account for this phenomenon. Thus, the (linearized) momentum balance equation should have the form

$$\rho_0 \frac{\partial \mathbf{v}(t)}{\partial t} = -\left(\frac{\partial P}{\partial \rho} \right)_U \nabla \rho(t) - \left(\frac{\partial P}{\partial U} \right)_\rho \nabla U(t) + \int_0^t d\tau$$
$$\times \eta(t-\tau) \nabla^2 \mathbf{v}(t) + \frac{1}{3} \int_0^t d\tau$$
$$\times [\eta(t-\tau) + \eta_V(t-\tau)] \nabla \cdot \nabla \cdot \mathbf{v}(\tau).$$

(Note that for a time scale relevant to slow disturbances, the viscosity kernels could be replaced by Dirac delta functions, and the familiar zero-frequency equations be obtained.) If the frequency-dependent viscosity is approximated by its high-frequency limits, one can show from the Fourier-Laplace transforms of the modified Navier-Stokes equations that transverse shear waves propagate with frequency $\pm \omega_{\text{tr}}^{(\infty)}$, the latter being given by

$$\omega_{\text{tr}}^{(\infty)} = |k| [G_\infty / \rho]^{1/2}. \quad (2.9)$$

Similarly, if thermal conductivity is neglected, one can show that longitudinal sound waves propagate with frequency $\pm \omega_l^{(\infty)}$, given by

$$\omega_l^{(\infty)} = |k| [(K_\infty + \tfrac{4}{3} G_\infty)/\rho]^{1/2}. \quad (2.10)$$

(Further discussion of high-frequency sound propagation, including an analysis of the effects of thermal conductivity upon propagation velocity, may be found in a companion paper.[6])

However, the following is perhaps the most interesting point. It is apparent from the previous discussion that, for low-frequency sound propagation, a close correspondence exists between macroscopic hydrodynamic equations and the variational Liouville equation. Here, too, a correspondence is evident: *The high-frequency dispersion relations derived from hydrodynamics, Eqs. (2.9) and (2.10), are also obtained from the variational Liouville equation when, in addition to the mass and momentum density fluctuations [Eqs. (2.1)–(2.2)], the first time derivatives of the latter are included among the components of the trial functions (cf. Appendix B, below).*

The associated eigenfunctions also have been determined. There are four (normalized) eigenfunctions for transverse excitation, viz.,

$$\varphi_{1,2}(k) = (\beta V/2\rho)^{1/2} \{ A_1 \mp \omega_{\text{tr}}^{-1}(k) L A_1 \} \quad (2.11)$$

and

$$\varphi_{3,4}(k) = (\beta V/2\rho)^{1/2} \{ A_2 \mp \omega_{\text{tr}}^{-1}(k) L A_2 \}, \quad (2.12)$$

the frequency $\omega_{\text{tr}}(k)$ appearing in Eqs. (2.11) and (2.12) being identical to the expression given by Eq. (2.9) in the limit of long wavelength. (See Eq. (B9), below, for a general expression, valid for large $\mathbf{k}$ as well.)[7]

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

[5] Molecular expressions for G_∞ and K_∞ may be found in Ref. 4. Compare, also, Eq. (B5) of Appendix B, below.

[6] R. Nossal (to be published).

[7] We recall that the Liouville operator has the property $-LA = idA/dt$. Consequently, Eqs. (2.11)–(2.13) might also be written as $\varphi \sim \{ A \pm i\omega^{-1} \dot{A} \}$.

Similar collective coordinates are obtained for longitudinal excitation. One finds

$$\varphi_{5,6}(k)=(\beta V/2\rho)^{1/2}\{A_3\mp\omega_l^{-1}(k)LA_3\}\,, \qquad (2.13)$$

where, in the long-wavelength limit $\omega_l(k)$ is identical to the expression given by Eq. (2.10).[8] In addition to the two collective coordinates given by Eq. (2.13), the variational calculation provides a third, viz.,

$$\psi\sim[A_4(k)+|k|\omega_l^{-2}(k)LA_3(k)]. \qquad (2.14)$$

The collective coordinates given by Eqs. (2.11)–(2.13) seem to be fluid state analogs of phonons in solids. Indeed, as shown in Appendix C, when the molecular expressions for $\omega_{\mathrm{tr}}(k)$ and $\omega_l(k)$ are evaluated for a harmonic solid in the limit of low temperature, the eigenfunctions given by Eqs. (2.11)–(2.13) are found to be identical to the usual normal-mode variables of a harmonic lattice with one molecule per unit cell.[9]

III. DISCUSSION

The eigenfunctions provided by Eqs. (2.11)–(2.13), i.e., those relevant to high-frequency excitation, are the most important results of this study. We hope that knowledge of convenient sets of collective coordinates will facilitate calculation of transport parameters and provide deeper understanding of properties and behavior of fluid systems.

As previously indicated, the physical importance of these functions is discerned from the correspondence between their associated dispersion relations and analogs obtained from macroscopic hydrodynamic equations. Further, the fact that the eigenfunctions reduce to the usual phonons when evaluated for a harmonic solid at low enough temperature is also strongly suggestive of their relevance. Indeed, the fluid eigenfunctions have essentially the same mathematical form as do solid-state phonons, with momentum fluctuations of the former corresponding to displacement fluctuations of the latter. We recall that a similar relationship also arises in other contexts; for example, the internal stresses in a fluid are related to the strain *rate of change*, whereas the stresses in a solid are related to the strain itself.

The frequencies for which these approximate eigenfunctions are appropriate may be estimated by examining correction terms to the high-frequency limits of the viscosities; we estimate that such collective motion exists at least for frequencies of the order of 10^{12} cps and greater. On the other hand, the low-**k** limit [to which the eigenvalues Eqs. (2.9) and (2.10) are applicable] implies that the range of disturbance must be greater than atomic dimensions. Gillis and Puff[10] estimate that for a simple fluid such as liquid argon there is only a narrow range of frequency (approximately 10^{12}–10^{13} cps) for which the high-frequency, low-**k** region exists for natural disturbances. However, this limitation is not as serious as might seem, and it may be shown that eigenfunctions appropriate for natural disturbances of higher frequency have the same structure as given by Eqs. (2.11)–(2.13), the only difference being that the eigenvalues $\omega_{\mathrm{tr}}(k)$ and $\omega_l(k)$ may have somewhat more complicated wave vector dependence [see Eqs. (8) and (9) of Appendix B, below].

There is yet no conclusive evidence to substantiate the existence of hypersonic sound velocities in simple fluids. Recent Brillouin scattering experiments,[11] while demonstrating sound velocities differing from the usual ultrasonic velocities, all have been performed on liquids of complex structure for which the variation of sound velocity might be due to internal molecular relaxation processes. On the other hand, recent experiments[12,13] involving inelastic scattering of neutrons provide considerable evidence of collective motion in simple liquids. However, we are not sure whether these data are yet sufficiently extensive to allow a conclusion that the measured collective modes are, in fact, those demonstrated by Eqs. (2.11)–(2.13). An examination of this question will be presented in a subsequent paper.

APPENDIX A: APPROXIMATE EIGENFUNCTIONS FOR LOW-FREQUENCY EXCITATION

In Sec. II, results of the variational procedure were stated for trial functions composed of fluctuations of the mass, momentum, and energy density operators [cf. Eqs. (2.1)–(2.3)]. Some details of the calculations leading to these results are presented in this Appendix.

The matrices $\mathbf{\Theta}$ and $\mathbf{N}$ [cf. Eqs. (1.8) and (1.9)] have the form

$$\mathbf{\Theta}=\begin{bmatrix}0&0&0&0\\0&0&-\tilde{W}&\tilde{U}\\0&-\tilde{W}&0&0\\0&\tilde{U}&0&0\end{bmatrix} \qquad (\mathrm{A}1)$$

$$\mathbf{N}=\begin{bmatrix}W&0&0&0&0\\0&W&0&0&0\\0&0&W&0&0\\0&0&0&A&C\\0&0&0&C&B\end{bmatrix} \qquad (\mathrm{A}2)$$

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[8] However, a more complicated eigenfunction arises when energy fluctuations and associated time derivatives are included in the trial functions. Similarly, the frequency is somewhat different than that given by Eq. (2.10) (see Ref. 6).

[9] On the other hand, the eigenfunction given by Eq. (2.14) corresponds to a zero eigenvalue and has no easily discernible physical meaning; it is found that the expression vanishes, identically, for a harmonic lattice (see Appendix C).

[10] N. S. Gillis and R. D. Puff, Phys. Rev. Letters **16**, 606 (1966).

[11] R. Y. Chiao and B. P. Stoicheff, J. Opt. Soc. Am. **54**, 1286 (1964); G. B. Benedek *et al.*, *ibid.* **54**, 1284 (1964); E. S. Stewart, and J. S. Stewart, Phys. Rev. Letters **13**, 437 (1964); D. H. Rank *et al.*, J. Opt. Soc. Am. **55**, 925 (1965); H. Z. Cummins and R. W. Gammon, J. Chem. Phys. **44**, 2785 (1966).

[12] N. Kroó *et al.*, Phys. Rev. Letters **12**, 721 (1964); in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1965), Vol. II. p. 101.

[13] S. J. Cocking and P. A. Egelstaff, Phys. Letters **16**, 130 (1965); S. H. Chen *et al.*, *ibid.* **19**, 269 (1965).

from which, by Eq. (1.10), eigenvalues are determined to be

$$\omega_{1,2}=\pm\{(A\tilde{U}^2+B\tilde{W}^2+2C\tilde{U}\tilde{W})/ \\ /(W[AB-C^2])\}^{1/2}, \quad \text{(A3)}$$

$$\omega_{3,4,5}=0. \quad \text{(A4)}$$

The eigenvectors associated with $\omega_{1,2}$ are easily seen to be

$$\psi_{1,2}(k)\sim\left\{A_5(k)-\frac{[\tilde{W}B+\tilde{U}C]}{[\tilde{W}C+A\tilde{U}]}A_4(k) -\frac{\omega_{1,2}[C^2-AB]}{[\tilde{W}C+A\tilde{U}]}A_3(k)\right\}. \quad \text{(A5)}$$

One now needs to evaluate the matrix elements A, B, C, W, $\tilde{W}$, $\tilde{U}$, and the various combinations of the latter which appear in the above expressions. As an example, let us evaluate the third term appearing in Eq. (A5), which we shall designate as γ,

$$\gamma\equiv([C^2-AB]/[\tilde{W}C+A\tilde{U}])\omega_{1,2}. \quad \text{(A6)}$$

First, we remark that, in the limit $\mathbf{k}\rightarrow 0$ (long wavelength), the quantity $\tilde{U}$, which is defined as

$$\tilde{U}\equiv\langle A_3{}^*LA_S\rangle$$

may be shown to be

$$\tilde{U}=-(|k|/\beta V)\rho H^{(m)}, \quad \text{(A7)}$$

where ρ equals the mass density and $H^{(m)}$ is the enthalpy per unit mass. Also, $\tilde{W}$, defined as $\tilde{W}\equiv-\langle A_3{}^*LA_4\rangle$ is easily demonstrated to have the explicit form

$$\tilde{W}=(|k|/\beta V)\rho. \quad \text{(A8)}$$

Consequently,

$$[\tilde{W}C+A\tilde{U}]=(k\rho_0/\beta V)[\langle\mathcal{E}_k{}^*\rho_k\rangle-H^{(m)}\langle\rho_k{}^*\rho_k\rangle],$$

where $\mathcal{E}_k$ and ρ_k are the energy and mass fluctuations per unit volume [cf. Eqs. (2.2), and (2.3)]. Convert the latter to fluctuations per unit *mass*, e.g.,

$$\langle\mathcal{E}_k{}^*\rho_k\rangle=\rho_0{}^4E^{(m)}\langle(\Delta V^{(m)})^2\rangle-\rho_0{}^3\langle(\Delta V^{(m)})(\Delta E^{(m)})\rangle \\ =\rho_0{}^3[\rho_0E^{(m)}-(\partial E^{(m)}/\partial V^{(m)})_T]\langle(\Delta V^{(m)})^2\rangle,$$

and express $[\tilde{W}C+A\tilde{U}]$ as

$$[\tilde{W}C+A\tilde{U}]=-(|k|\rho_0{}^4/\beta V) \\ \times[P+(\partial E^{(m)}/\partial V^{(m)})_T]\langle(\Delta V^{(m)})^2\rangle \\ =-(|k|\rho_0{}^4/\beta V)(\partial P/\partial T)_V\langle(\Delta V^{(m)})^2\rangle. \quad \text{(A9)}$$

Similarly, it may be shown that $[C^2-AB]$ is given by

$$[C^2-AB]=-\rho_0{}^6[(\partial E^{(m)}/\partial T)_V]^2 \\ \times\langle(\Delta V^{(m)})^2\rangle\langle(\Delta T)^2\rangle, \quad \text{(A10)}$$

where ΔT is the fluctuation in temperature. Finally, making use of various thermodynamic identities, as well as the relation

$$\langle(\Delta T)^2\rangle=(kT^2/M_{\text{total}}C_V{}^{(m)}), \quad \text{(A11)}$$

where $C_V{}^{(m)}=(\partial E^m/\partial T)_V$ is the specific heat per unit mass at constant volume, one obtains

$$\gamma=|k|^{-1}\omega_{1,2}\rho_0(\partial E^{(m)}/\partial P)_V, \quad \text{(A12)}$$

which is the third term appearing in Eq. (2.7).

Other terms appearing in Eqs. (2.4) and (2.7) are obtained from Eqs. (A3) and (A5) in similar manner, although the derivations are of somewhat greater length.

APPENDIX B: COLLECTIVE COORDINATES FOR HIGH-FREQUENCY EXCITATION

Suppose we seek an eigenfunction of the form

$$\psi=\sum_{i=1}^{n}\alpha_iB_i,$$

where $B_1=A_1(\mathbf{k})$, $B_2=LA_1(\mathbf{k})$, $B_3=A_2(\mathbf{k})$, $B_4=LA_2(\mathbf{k})$, $B_5=A_3(\mathbf{k})$, $B_6=LA_3(\mathbf{k})$, and $B_7=A_4(\mathbf{k})$. From Eqs. (1.4)–(1.6), eigenvalues are determined to be

$$\omega_{1,2}(k)=\pm(\langle(LA_1)^*LA_1\rangle/\langle A_1{}^*A_1\rangle)^{1/2} \\ \equiv\pm[X(k)/W]^{1/2}, \quad \text{(B1)}$$

$$\omega_{3,4}(k)=\pm(\langle(LA_2)^*LA_2\rangle/\langle A_2{}^*A_2\rangle)^{1/2}, \quad \text{(B2)}$$

$$\omega_{5,6}(k)=\pm(\langle(LA_3)^*LA_3\rangle/\langle A_3{}^*A_3\rangle)^{1/2}, \quad \text{(B3)}$$

$$\omega_7(k)=0. \quad \text{(B4)}$$

In the long-wavelength limit, the evaluation of $X(\mathbf{k})$ appearing in Eq. (B1) is particularly easy. First, expand $\langle(LA_1)^*LA_1\rangle$ as follows:

$$\langle(LA_1)^*LA_1\rangle\equiv X=V^{-2}\langle\{\sum_l[\mathbf{F}_l+(i\mathbf{k}\cdot\mathbf{P}_l/m)\mathbf{P}_l]\cdot\hat{u}_1e^{i\mathbf{k}\cdot\mathbf{R}_l}\}\{\sum_n[\mathbf{F}_n-[i(\mathbf{k}\cdot\mathbf{P}_n)/m]\mathbf{P}_n]\cdot\hat{u}_1e^{-i\mathbf{k}\cdot\mathbf{R}_n}\}\rangle \\ =k^2V^{-2}\langle\sum_l\{(\mathbf{F}_l\cdot\hat{u}_1)(\mathbf{R}_l\cdot\hat{k})+(\mathbf{P}_l\cdot\hat{u}_1/m)(\mathbf{P}_l\cdot\hat{k})\}\sum_n[(\mathbf{F}_n\cdot\hat{u}_1)(\mathbf{R}_n\cdot\hat{k})+(\mathbf{P}_n\cdot\hat{u}_1/m)(\mathbf{P}_n\cdot\hat{k})]\rangle+0(k^4).$$

Next, notice that the molecular definition of the high-frequency shear modulus G_∞ is given by[4]

$$G_\infty=\beta V^{-1}\langle\sum_l(d/dt)(R_l{}^zP_l{}^x)\sum_u(d/dt)(R_n{}^zP_n{}^x)\rangle \\ =c/\beta+2\pi/15c^2\int_0^\infty dr\,g^{(2)}(r)(d/dr)[r^4d\varphi/dr], \quad \text{(B5)}$$

so that one finds

$$X=(k^2/\beta V)G_\infty. \quad \text{(B6)}$$

Consequently, in the long-wavelength limit, $\omega_{1,2}$ is given by

$$\omega_{1,2}=\pm|k|(G_\infty/\rho)^{1/2}. \quad \text{(B7)}$$

This expression is identical to the dispersion relation given by Eq. (2.10).

We remark that the general expression for $\omega_{1,2}$, valid as well for large $\mathbf{k}$, may be shown to be given by

$$\omega_{1,2}=\pm|k|[\mathcal{G}_\infty(k)/\rho]^{1/2}, \tag{B8}$$

where $\mathcal{G}_\infty(k)$ is defined as

$$k^2\mathcal{G}_\infty(k)=\frac{k^2c}{\beta}+c^2\int d^3\xi\, g_2(\xi)[1-\cos\mathbf{k}\cdot\xi]\frac{\partial^2\varphi}{\partial\xi_{k1}{}^2}. \tag{B9}$$

(In the above expression, ξ_{k1} is a coordinate in a direction perpendicular to $\mathbf{k}$.) Note that Eq. (B5) is a good approximation to Eq. (B9) for values of $\mathbf{k}$ such that $|k|R_M\lesssim 1$, R_M being a molecular radius beyond which $\partial^2\varphi/\partial r^2$ is not appreciably different from zero.

The longitudinal eigenvalues $\omega_l{}^{(\infty)}$ are found in a similar manner. Determination of associated eigenvectors is without difficulty.

APPENDIX C: REDUCTION TO USUAL NORMAL-MODE VARIABLES

We now prove the assertion that the liquid-state "eigenfunctions," when evaluated for a harmonic solid in the limit of sufficiently low temperature, reduce to the usual normal-mode variables for a harmonic lattice with one atom per unit cell. In order to simplify the presentation, discussion appears for a one-dimensional solid only.

The mathematical expression for a phonon of a harmonic solid is usually given as

$$\psi_k{}^{\text{solid}}\sim[p_k\mp i\omega_k q_k], \tag{C1}$$

where q_k and p_k are defined as

$$q_k=(M/N)^{1/2}\sum_j \delta R_j e^{-kR_j{}^0} \tag{C2}$$

and

$$p_k=(MN)^{-1/2}\sum_j P_j e^{-kR_j{}^0}, \tag{C3}$$

$R_j{}^0$ being the equilibrium position of the jth atom, δR_j its displacement, and P_j its momentum. The frequency ω_k is related to wave number k according to the dispersion relation

$$M\omega_k{}^2=\sum_l {}^0\Phi_{jl}e^{ik(R_l{}^0-R_j{}^0)}. \tag{C4}$$

M is the atomic mass and ${}^0\Phi_{lj}$ is the equilibrium value of the second derivative of the potential energy of interaction between the jth and lth particles.

We now note that, because q_k is related to the time derivative of p_k as

$$\dot{p}_k=-\omega_k{}^2q_k, \tag{C5}$$

the phonon is equivalently represented by

$$\psi_k{}^{\text{solid}}\sim[p_k\pm i\omega_k{}^{-1}\dot{p}_k]. \tag{C6}$$

The expression given by Eq. (C6) is similar to the approximate eigenvalues presented in Eqs. (2.11)–(2.13) For example, from Eqs. (2.13) and (B3) we have

$$\varphi_{5,6}\sim[A_3(k)\pm i\omega^{-1}(k)\dot{A}_3(k)] \tag{C7}$$

with $A_3(k)$ defined as

$$A_3(k)=V^{-1}\sum_{j=1}^{N}\mathbf{P}_j\cdot\hat{k}e^{-i\mathbf{k}\cdot\mathbf{R}_j} \tag{C8}$$

and $\omega(k)$ defined as [cf. Eq. (B3)]

$$\omega^2(k)=\langle(LA_3)^*LA_3\rangle/\langle A_3{}^*A_3\rangle. \tag{C9}$$

Indeed, for small k, $A_3(k)$ and p_k are proportional and, in order to prove that $\varphi_{5,6}$ has the form of Eq. (C6) it is necessary only to show that the frequency derived by the variational procedure $\omega(k)$ is identical to the usual phonon frequency ω_k. (We propose, i.e., showing that the dispersion relations are equal.)

The latter is accomplished as follows. The numerator in Eq. (C9), which we shall designate as $\bar{X}$, may be expressed as

$$\bar{X}=-V^{-2}\langle\sum_j(\mathbf{P}_j\cdot\hat{k})e^{i\mathbf{k}\cdot\mathbf{R}_j}(d/dt)$$
$$\times\sum_l\{[\mathbf{F}_l-(i\mathbf{k}\cdot\mathbf{P}_l/m)\mathbf{P}_l]\cdot\hat{k}e^{-i\mathbf{k}\cdot\mathbf{R}_l}\}\rangle,$$

which, for the harmonic lattice, has the form

$$\bar{X}=3k^2N/\beta^2V^2$$
$$+(V^2\beta)^{-1}\sum_j\sum_l {}^0\Phi_{lj}e^{ik(R_j{}^0-R_l{}^0)}\langle e^{ik(\delta R_j-\delta R_l)}\rangle. \tag{C10}$$

Similarly, the denominator of Eq. (C9) is evaluated as

$$W=mN/\beta V^2. \tag{C11}$$

Thus, for the harmonic lattice $\omega(k)$ is given by

$$m\omega^2(k)=3k^2/\beta+\sum_j {}^0\Phi_{ij}e^{-ik(R_i{}^0-R_j{}^0)}\langle e^{ik(\delta R_j-\delta R_i)}\rangle. \tag{C12}$$

Because the potential energy is quadratic, the quantity $\langle e^{ik(\delta\mathbf{R}_j-\delta\mathbf{R}_l)}\rangle$ may be written as

$$\langle e^{ik(\delta\mathbf{R}_j-\delta\mathbf{R}_l)}\rangle=e^{-i(k^2/2)<(\delta\mathbf{R}_j-\delta\mathbf{R}_l)^2>}. \tag{C13}$$

But, for example,

$$\langle\delta R_i\delta R_j\rangle=-\beta^{-1}\left\{\frac{\partial}{\partial^0\Phi_{ij}}+\frac{\partial}{\partial^0\Phi_{ji}}\right\}$$
$$\times\ln\left\{\int dR^N\exp-(\beta/2)\sum_n\sum_l {}^0\Phi_{nl}\xi_n\xi_l\right\}$$
$$=(2\beta)^{-1}\left\{\frac{\partial}{\partial^0\Phi_{ij}}+\frac{\partial}{\partial^0\Phi_{ji}}\right\}\ln\{\det\mathbf{\Phi}\}$$
$$=(2\beta)^{-1}\{(\Phi^{-1})_{ij}+(\Phi^{-1})_{ji}\}.$$

Consequently, the dispersion relation may be written as

$$m\omega^2(k)=3k^2\beta^{-1}+\sum_j {}^0\mathbf{\Phi}_{ij}e^{-ik(R_i^0-R_j^0)}$$
$$\times\exp-\tfrac{1}{2}k^2\beta^{-1}\{\Phi_{ii}^{-1}+\Phi_{jj}^{-1}+\Phi_{ij}^{-1}+\Phi_{ji}^{-1}\},\quad\text{(C14)}$$

where Φ_{ij}^{-1} is the ith-jth element of the inverse of the matrix ${}^0\mathbf{\Phi}$. *For sufficiently small values of β^{-1} (i.e., for low temperatures), the usual phonon dispersion relation Eq. (C4) will follow from Eq. (C14).*

The necessary limiting value of β is related to the lattice spacings and interparticle potential energies. For example, for a lattice of nearest-neighbor interactions, Eq. (C14) may be shown to be

$$m\omega^2(k)=3\beta^{-1}k^2+2m\omega_D^2$$
$$\times\{1-(\cos k\delta)e^{-k^2(2\beta\omega_D^2m)^{-1}}\},\quad\text{(C15)}$$

where, in the above expression, $m\omega_D^2$ equals the lattice force constant and δ is the lattice spacing. Thus, in this instance, in order to obtain the usual phonon dispersion relation, the inequalities $m\omega_D^2\beta\delta^2\gg1$ and $k^2/(m\beta\omega_D^2)\ll1$ must be satisfied.

Let us now prove the assertion made in Ref. 9, viz., that the eigenfunction given by Eq. (2.14) reduces to zero when evaluated for a harmonic lattice. Indeed, for small k

$$\psi_7\equiv[A_4(k)+|k|\omega^{-2}LA_3(k)]$$
$$\sim-ik(MN/V)^{1/2}[q_k+\omega^{-2}\dot{p}_k].\quad\text{(C16)}$$

Thus, in virtue of Eq. (C5), one has

$$\psi_7^{\text{lattice}}(k)\equiv0.\quad\text{Q.E.D.}$$

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Relaxation Theory of Spectral Line Broadening in Plasmas*

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In this theory of spectral line broadening in plasmas, the radiation process is treated as the relaxation of an excited atom, weakly coupled to a thermal bath, to a state of lower energy. The theory presented here emphasizes the Liouville-operator formalism, as developed by Zwanzig, and may be considered an extension of Fano's theory of pressure broadening in neutral gases. It may further be considered an illustration of a case in which an observable quantity can be expressed in terms of a well-defined correlation function, which can be evaluated without resorting to a microscopic analysis of the interactions. A comparison is made with the impact theories of Griem, Kolb, and Baranger; specifically, it is shown that the assumption of binary collisions and the impact approximation are not necessary in the relaxation theory. Of special importance are frequency-dependent "width" and "shift" operators which produce asymmetries in the intensity profile that are not predicted by the previous plasma-broadening theories. These asymmetries are illustrated in an application of the relaxation theory to the Lyman-α line. The line shape is calculated to second order in the weak-coupling potential, and a comparison is made with experimental observations of this line.

1. INTRODUCTION

THE shape of the broadened spectral lines emitted or absorbed by neutral and ionized gases is determined primarily by the interparticle forces present in the gas. Consequently, much effort has been devoted to the development of a theory which will accurately predict the shape of these lines. Such a theory would permit the observable characteristics of a given line (shift, width, etc.) to serve as noninterfering probes for a determination of the temperature, density, etc., of the gas.

The most successful line shape calculations have been obtained by the impact theories of Kolb,[1] Griem,[2] and Baranger.[3] These theories use a time-dependent perturbation and employ an impact approximation that is based on a binary-collision model.

The application of these binary-collision-impact (BCI) theories to the Stark broadening in plasmas is plagued by the familiar divergences that result when a binary-collision model is used to treat long-range interactions. Attempts to avoid these divergences by means of impact-parameter cutoffs have led many BCI theories to neglect the long-range electron-atom interactions.

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† The work reported here is based on a dissertation submitted to the University of Florida in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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