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Surface contribution to the dynamic structure function of liquid He

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The liquid-He dynamic structure function $S(\vec{q},\omega)$ at wave vector $\vec{q}$ and frequency ω is calculated within the framework of quantum hydrodynamics of an infinite "slab" of a viscousless, compressible fluid bounded by a free, sharp surface of area A and by a wall at depth V/A, where V is the volume. A simple technique of representing momentum sums to $O(A/V)$ is presented. $S(\vec{q},\omega)$ is thereby represented as $S = S_{\text{bulk}} + S_{\text{rip}} + S^{\text{coh}}_{\text{phon}} + S^{\text{inc}}_{\text{phon}}$, where S_{bulk} is the usual bulk contribution to S, and the last three terms are $O(A/V)$ corrections. S_{rip} is a coherent ripplon contribution which diverges in the long-wavelength limit; $S^{\text{coh}}_{\text{phon}}$ is a δ function at the phonon frequency $\omega = qc$, where c is the sound speed; and $S^{\text{inc}}_{\text{phon}}$ is a broad incoherent function, which behaves as ω^{-3} for $\omega \to \infty$, and which has a square-root integrable divergence at a threshold of $\omega = q_\rho c$, where q_ρ is the component of $\vec{q}$ parallel to the free surface. Both limiting forms of $S^{\text{inc}}_{\text{phon}}$ provide probes of the boundary conditions at the wall. Relevant sum rules are discussed—both formal and explicit verifications of the f-sum rule are presented; the static structure function $S(\vec{q})$ is discussed; finally, a surface tension sum rule analogous to the compressibility sum rule is given.

I. INTRODUCTION

One of the most exciting events in the course of liquid-helium study has been the confirmation of the existence of Landau[1] phonon rotons through direct observation by neutron scattering.[2] Similar investigation of the excitations associated with oscillations of a free surface (so called "ripplons"), initially proposed by Atkins[3] to describe the experimental temperature dependence of the surface tension, is as yet lacking. However, with present-day advances in neutron-scattering technology, it appears likely that the relevant experiment is at hand.

To date, the only calculation of the neutron-scattering cross section for liquid He with surface is that carried out by Saam in 1973.[4] The calculation is based on a quantum-hydrodynamic model, which is expected to yield results applicable to liquid He in the long-wavelength regime, as is the case with the bulk system. Furthermore, within a distorted-wave Born approximation, estimates are obtained for excitation creation by incident neutrons grazing the surface. The experimental advantage of such an arrangement is simply that all volume-dependent contributions to the scattering cross section are eliminated, thereby minimizing the excitation of (bulk) phonon modes. Even though surface and bulk modes are widely separated energetically, such an isolation of surface contributions is evidently necessary for a successful scattering experiment involving basically a single surface bounding a large amount of bulk fluid. The main drawback to such an experiment seems to be that the statistics are so poor that much of the energy dependence of the scattering cross section, and therefore, knowledge of the dynamic behavior of the surface, is lost.

An alternative procedure may be to scatter neutrons through a *composite* of He films adsorbed, for example, on grafoil. Such an arrangement would provide both a small volume-to-surface ratio, as well as a large scattering surface area. Information lost due to the substrate and angular spread of the film orientation is yet to be understood.

One problem, however, with Saam's work is that the f-sum rule is violated by the calculated structure function. Furthermore, boundary conditions on the density fluctuations are specified only at a single (free) surface, which gives rise to ambiguities in $O(A/V)$ contributions to the neutron-scattering cross section.

A major result of the present paper is the calculation of a representation of the dynamic structure function $S(\vec{q},\omega)$ which satisfies the f-sum rule. Furthermore, a physical discussion of the smoothing involved in calculating momentum sums to $O(A/V)$ in order to obtain such a representation is given. Uncertainty broadening and the effects of various boundary conditions are considered. Finally, a variety of useful techniques and results for calculational simplification are presented: (i) use of current-current response functions, (ii) introduction of a convenient scalar product useful for the discussion of completeness and commutation relations, and (iii) discussion of the important sum rules, including the introduction of a new sum rule which has the same relation to the surface tension that the compressibility sum rule has to the sound speed.

Explicitly, we have considered an infinite "slab" of a compressible, viscousless liquid bounded by one free surface and by a wall at a depth V/A, where V is the volume and A is the area of the free surface. For simplicity, we calculate the usual Born approximation to $d^2\sigma/d\Omega\, d\omega$, which is related to $S(\vec{q}, \omega)$ via Van Hove's theorem[5] by

$$\frac{d^2\sigma}{d\Omega\, d\omega} = \frac{N\sigma_a q_f}{8\pi^2 q_i} S(\vec{q}, \omega) . \tag{1.1}$$

Here $d\Omega$ is a solid angle, N is the number of He atoms, σ_a is the bound-atom scattering cross section, and $\hbar q_i$ and $\hbar q_f$ are the initial and final neutron momenta. We thus neglect the multiple scattering effects important at grazing neutron incidence, which have been adequately dealt with in Saam's innovative paper.[4]

We find that $S(\vec{q}, \omega)$ may be represented as a sum of the usual bulk contribution plus $O(A/V)$ terms δS of the form

$$\delta S = S_{\text{rip}} + S_{\text{phon}}^{\text{coh}} + S_{\text{phon}}^{\text{inc}} . \tag{1.2}$$

Here S_{rip} is a δ function peaked at the capillary wave frequency with a factor which approaches infinity in the long-wavelength limit, corresponding to the divergence in the density of ripplon states as the wave vector approaches zero. $S_{\text{phon}}^{\text{coh}}$ is an $O(A/V)$ coherent correction to the phonon δ-function peak at $\omega = qc$, where c is the sound speed. Finally, $S_{\text{phon}}^{\text{inc}}$ is an incoherent broad background extending from $\omega = q_\rho c$ to $\omega = \infty$, where q_ρ is the component of $\vec{q}$ parallel to the surface. Near threshold $\omega = q_\rho c$, $S_{\text{phon}}^{\text{inc}}$ displays an (integrable) square-root divergence, whereas for large frequencies, $S_{\text{phon}}^{\text{inc}}$ has an $O(\omega^{-3})$ dependence on ω. The divergences in both S_{rip} and $S_{\text{phon}}^{\text{inc}}$, together with the fact that they occur at frequencies below the threshold $[\omega = qc\ (|q_z| > 0)]$ for the usual bulk phonon processes, may be important factors in the experimental visibility of these contributions.

In Sec. II we present a description of classical hydrodynamics of a viscousless, compressible liquid with a free surface. State normalization and completeness is expressed via a useful scalar product peculiar to this system. Response functions are also presented. Section III involves quantization of the modes discussed in Sec. II. In Sec. IV we evaluate $S(\vec{q}, \omega)$ in terms of a current-current response function by means of simple techniques developed to represent momentum sums to $O(A/V)$. Finally, in Sec. V, the various sum rules are discussed.

II. CLASSICAL HYDRODYNAMICS

A. Equations of motion

We first give an account of classical hydrodynamics of a compressible, viscousless, irrotational fluid with a free surface. Specifically we assume that the liquid lies between a wall at $z = -L$ and a free surface at $z = \zeta(\vec{\rho}, t) \approx 0$. The system is unbounded in $\vec{\rho}$ directions (parallel to the equilibrium free surface). Assuming that the number density $n(\vec{x}, t)$ undergoes sharp discontinuities at the boundaries we may write n in the form,

$$n(\vec{x}, t) = n_{\text{cont}}(\vec{x}, t)\, \Theta(z+L)\, \Theta(\zeta(\vec{\rho}, t) - z) , \tag{2.1}$$

where n_{cont} is a continuous function of $\vec{x}$. Expressing n_{cont} as

$$n_{\text{cont}}(\vec{x}, t) = n_0 + \delta n_{\text{cont}}(\vec{x}, t) , \tag{2.2}$$

where n_0 is the (constant) bulk density, and linearizing in δn_{cont} and ζ, n may be expressed as

$$n(\vec{x}, t) = [n_0 + \delta n_{\text{cont}}(\vec{x}, t)]\, \Theta(z+L)\, \Theta(-z) + n_0 \zeta(\vec{\rho}, t)\, \delta(z) . \tag{2.3}$$

The density n satisfies a continuity equation

$$\frac{\partial n}{\partial t} + \vec{\nabla} \cdot \vec{J} = 0 , \tag{2.4}$$

where the (number) current $\vec{J}(\vec{x}, t)$ is given in terms of the velocity $\vec{v}(\vec{x}, t)$ by

$$\vec{J} = n\vec{v} . \tag{2.5}$$

In linearized form we have

$$\vec{J} = n_0 \Theta(z+L)\, \Theta(-z)\, \vec{\nabla}\phi(\vec{x}, t) , \tag{2.6}$$

where ϕ is the velocity potential related to $\vec{v}$ by

$$\vec{v} = \vec{\nabla}\phi . \tag{2.7}$$

Linearization of the continuity equation [Eq. (2.4)] leads to

$$\frac{\partial\, \delta n_{\text{cont}}}{\partial t} + n_0 \Delta\phi = 0 , \quad -L \leq z \leq 0 , \tag{2.8}$$

$$\frac{\partial \phi}{\partial z} - \frac{\partial \zeta}{\partial t} = 0 , \quad z = 0 , \tag{2.9}$$

$$\frac{\partial \phi}{\partial z} = 0 , \quad z = -L . \tag{2.10}$$

The linearized Navier-Stokes equations for the fluid of particles in an external potential $U(\vec{x}, t)$ (per particle mass m) may be expressed as

$$c^2 \delta n_{\text{cont}} + \frac{n_0 \partial\phi}{\partial t} = -n_0 U , \quad -L \leq z \leq 0 . \tag{2.11}$$

Finally we have a boundary condition at $z = 0$ expressing Laplace's[6] relation of the pressure just inside the free surface to the curvature of the surface [the pressure at $z > \zeta(\vec{\rho}, t)$ is equal to zero]:

$$mc^2 \delta n_{\text{cont}} = -\sigma \Delta_\rho \zeta , \quad z = 0 , \tag{2.12}$$

where σ is the surface tension.

Equations (2.8)–(2.12) are a complete set of equations determining n and ϕ. They may be succinctly expressed in terms of a Lagrangian L:

$$L = -H - H_{\text{ext}} - \int d^3x\, mn \frac{\partial \phi}{\partial t}, \tag{2.13}$$

where the energies H and H_{ext} are

$$H = \int d^3x \left[\left(\frac{mn_0 v^2}{2} + \frac{mc^2 \delta n_{\text{cont}}^2}{2n_0} \right) \Theta(-z)\,\Theta(z+L) + \frac{\sigma \vec{\nabla}_\rho \zeta \cdot \vec{\nabla}_\rho \zeta\, \delta(z)}{2} \right], \tag{2.14}$$

$$H_{\text{ext}} = \int d^3x\, nm\, U. \tag{2.15}$$

(Variations are carried out with respect to δn_{cont}, ϕ, and ζ.)

B. Homogeneous solutions

We now list the homogeneous ($U=0$) solutions of Eqs. (2.8)–(2.12). The equations admit two types of solutions, corresponding to (i) sound waves reflecting between $z=-L$ and $z=0$ and to (ii) capillary waves localized near $z=0$. As is easily verified by direct substitution into Eqs. (2.8)–(2.12), the sound waves with wave vector $(\vec{k}_\rho, k_z)$ are of the form

$$\phi_s = e^{i\vec{k}_\rho\cdot\vec{\rho} - ikct} \sin(k_z z + \gamma), \tag{2.16}$$

where the boundary conditions [Eqs. (2.9) and (2.12)] are satisfied by

$$\gamma = \tan^{-1}(\sigma k_z k_\rho^2 / \rho_0 c^2 k^2), \tag{2.17}$$

and the boundary condition [Eq. (2.10)] is fulfilled by requiring that k_z satisfy the transcendental equation,

$$k_z L - \gamma = (j + \tfrac{1}{2})\pi, \quad j = 0, 1, 2, \ldots \tag{2.18}$$

($\rho_0 = mn_0$ and $k^2 = k_\rho^2 + k_z^2$). For $k_\rho \gg L^{-1}$ the capillary waves are given by

$$\phi_c = \exp(i\vec{k}_\rho \cdot \vec{\rho} - i\omega_{k_\rho} t) E_{k_\rho}(z), \tag{2.19}$$

where

$$E_{k_\rho}(z) = \left(\frac{\sigma k_\rho^2}{2\rho_0 \omega_{k_\rho}^2} + \frac{\rho_0 c^2}{\sigma k_\rho^2} \right)^{-1/2} e^{\kappa_z z}, \tag{2.20}$$

$$\kappa_z = \left[k_\rho^2 + \left(\frac{\sigma k_\rho^2}{2\rho_0 c^2} \right)^2 \right]^{1/2} - \frac{\sigma k_\rho^2}{2\rho_0 c^2}, \tag{2.21a}$$

$$\to k_\rho \quad (k_\rho \to 0), \tag{2.21b}$$

$$\omega_{k_\rho}^2 = c^2(k_\rho^2 - \kappa_z^2), \tag{2.22a}$$

$$= (\sigma/\rho_0) k_\rho^2 \kappa_z, \tag{2.22b}$$

$$= \frac{-\sigma^2 k_\rho^4/c^2 + (\sigma^4 k_\rho^8/c^4 + 4\rho_0^2 \sigma^2 k_\rho^6)^{1/2}}{2\rho_0^2}, \tag{2.22c}$$

$$\to (\sigma/\rho_0) k_\rho^3 \quad (k_\rho \to 0). \tag{2.22d}$$

We now discuss the orthogonalization, normalization, and completeness relations which the above state functions satisfy. We have found it convenient to introduce a singular weight function $\mu_{k_\rho}(z)$ defined by

$$\mu_{k_\rho}(z) \equiv \Theta(z+L)\,\Theta(-z) + (\rho_0 c^2/\sigma k_\rho^2)\,\delta(z). \tag{2.23}$$

Then, as is shown in the Appendix, the functions $E_{k_\rho}(z)$ and

$$\left(\frac{2}{L - d\gamma/dk_z} \right)^{1/2} \sin(k_z z + \gamma)$$

are orthogonal and normalized to unity under the scalar product defined for functions f_1 and f_2 as

$$\langle f_1 | f_2 \rangle \equiv \int_{-\infty}^{+\infty} dz\, f_1(z) f_2(z)\, \mu_{k_\rho}(z). \tag{2.24}$$

Furthermore, the completeness relation is expressed by the statement that the sum $\delta_{k_\rho}(z, z')$ given by

$$\delta_{k_\rho}(z,z') = E_{k_\rho}(z) E_{k_\rho}(z') + \sum_{k_z} \frac{2}{L - d\gamma/dk_z} \sin(k_z z + \gamma) \sin(k_z z' + \gamma) \tag{2.25}$$

makes up a δ function for the scalar product [Eq. (2.24)]. More precisely, defining

$$\delta(z,z') \equiv \delta_{k_\rho}(z,z')\,\mu_{k_\rho}(z'), \tag{2.26}$$

it is possible to show (see Appendix) that if $f(z)$ is a continuous function on the interval $-L \leq z \leq 0$, and if $F(z)$ is given by

$$F(z) \equiv \int_{-\infty}^{+\infty} dz'\, \delta(z,z') f(z'), \tag{2.27}$$

then for $-L \leq z \leq 0$, $F(z) = f(z)$ and is continuous at $z=0$ and $z=-L$, which is necessary for the construction of useful Green's functions. Furthermore, it is possible to show that

$$\Theta(-z)\,\Theta(z+L)\,\delta(z,z') = \Theta(-z)\,\Theta(z+L)\,\delta(z-z'), \tag{2.28a}$$

$$\Theta(-z)\,\Theta(z+L) \frac{\partial}{\partial z} \delta(z,z') = \Theta(-z)\,\Theta(z+L) \frac{\partial}{\partial z} \delta(z-z'). \tag{2.28b}$$

We finally remark as to the physical origin of the seemingly strange scalar product [Eq. (2.24)]. Defining the density fluctuation δn as

$$\delta n \equiv n - n_0 \Theta(z+L)\,\Theta(-z), \tag{2.29}$$

Eqs. (2.3) and (2.12) easily give for $\vec{k}_\rho$-Fourier components

$$\delta n_{\vec{k}_\rho} = \mu_{k_\rho} \delta n_{\text{cont}\,\vec{k}_\rho}. \tag{2.30}$$

Thus the orthogonality relations given above are seen to be simply a statement of the orthogonality of $\delta n_{\vec{k}_\rho,\omega}$ and $\phi_{\vec{k}_\rho,\omega'}$:

$$\int_{-\infty}^{+\infty} dz\, \delta n_{\vec{k}_\rho,\omega}\, \phi_{\vec{k}_\rho,\omega'} = 0\,, \tag{2.31}$$

for unequal frequencies ω and ω'. The relation [Eq. (2.31)] is expected to hold generally, e.g., for more reasonable systems in which the (equilibrium) density varies smoothly through the surface region at $z \approx 0$. (For an interesting attempt at an approximation to such a system see Edwards, Eckhart, and Gasparini, 1974.[7]) (See also Ref. 8.)

C. Green's functions

Making use of the completeness relations given above we can construct a retarded Green's function $G^R(x,x')$ which satisfies the velocity potential boundary conditions obtained from Eqs. (2.9), (2.10), (2.12),

$$\left(\frac{\partial}{\partial z}\Delta_\rho - \frac{\rho_0 c^2}{\sigma}\Delta_x\right) G^R(x,x') = 0, \quad z=0, \tag{2.32a}$$

$$\frac{\partial}{\partial z} G^R(x,x') = 0\,, \quad z=-L\,, \tag{2.32b}$$

and which also solves

$$\Box_x G^R(x,x') = \delta^{(2)}(\vec{\rho}-\vec{\rho}\,')\,\delta(z,z')\,\delta(t-t')\,. \tag{2.33}$$

We obtain

$$G^R(x,x') = c^2 \int \frac{d^2k_\rho d\omega}{(2\pi)^3} e^{i\vec{k}_\rho\cdot(\vec{\rho}-\vec{\rho}\,')-i\omega(t-t')} \mu_{k_\rho}(z') \left(\frac{E_{k_\rho}(z)\,E_{k_\rho}(z')}{(\omega+i\eta)^2-\omega_{k_\rho}^2} + \sum_{k_z} \frac{2}{L-d\gamma/dk_z}\,\frac{\sin(k_z z+\gamma)\sin(k_z z'+\gamma)}{(\omega+i\eta)^2-k^2c^2}\right). \tag{2.34}$$

The various functions induced by an external potential $m\,U(x)$ are then given by

$$\phi_{\text{ind}}(x) = \int d^4x' \frac{1}{c^2}\frac{\partial}{\partial t} G^R(x,x')\,U(x')\,, \tag{2.35}$$

$$\delta n_{\text{cont}}^{\text{ind}}(x) = \int d^4x' \left(-\frac{n_0}{c^2}\right)\Delta_x G^R(x,x')\,U(x')\,, \tag{2.36}$$

$$\zeta_{\text{ind}}(\vec{\rho},t) = \int d^4x' \frac{1}{c^2}\frac{\partial}{\partial z} G^R(x,x')\,U(x')\bigg|_{z=0}\,. \tag{2.37}$$

Note that the properties of $\delta(z,z')$ as regards continuity (discussed in Sec. II B) ensures that the integral reproduction of $U(x)$ in Eq. (2.11) is continuous at the boundaries. This is vital as otherwise an infinite fictitious force appears at $z=0$ or $z=-L$.

With δn_{ind} given by

$$\delta n_{\text{ind}} = \Theta(-z)\,\Theta(z+L)\,\delta n_{\text{cont}}^{\text{ind}} + n_0\zeta_{\text{ind}}\delta(z)\,, \tag{2.38}$$

the density-density response function $D^R(x,x')$ takes on the symmetric form

$$D^R(x,x') = \frac{\hbar n_0}{m}\int \frac{d^2k_\rho d\omega}{(2\pi)^3} e^{i\vec{k}\cdot(\vec{\rho}-\vec{\rho}\,')-i\omega(t-t')}\mu_{k_\rho}(z)\,\mu_{k_\rho}(z') \times\left(\frac{\omega_{k_\rho}^2}{c^2}\frac{E_{k_\rho}(z)\,E_{k_\rho}(z')}{(\omega+i\eta)^2-\omega_{k_\rho}^2} + \sum_{k_z}\frac{2}{L-d\gamma/dk_z}\frac{k^2\sin(k_z z+\gamma)\sin(k_z z'+\gamma)}{(\omega+i\eta)^2-k^2c^2}\right). \tag{2.39}$$

The induced density is then given by

$$\delta n_{\text{ind}} = \hbar^{-1}\int d^4x'\, D^R(x,x')\, m U(x')\,. \tag{2.40}$$

III. QUANTIZATION OF THE HYDRODYNAMIC MODES

We now construct a quantum hydrodynamic theory corresponding to the classical system considered in Sec. II. The results are similar to those obtained independently by Saam,[9] except that here we have a boundary condition specified at $z=-L$ in order to obtain a well-defined accounting of the photon modes.

The simplest approach to quantization is to expand the operators δn and ϕ in terms of the state functions given in Sec. II as

$$\delta n(\vec{x},t) = \left(\frac{\hbar n_0}{mcA}\right)^{1/2} \sum_{\vec{k}_\rho} e^{i\vec{k}_\rho\cdot\vec{\rho}}\mu_{k_\rho}(z)\left[\left(\frac{\omega_{k_\rho}}{2c}\right)^{1/2} E_{k_\rho}(z)\,[r_{\vec{k}_\rho}\exp(-i\omega_{k_\rho}t) + r^\dagger_{-\vec{k}_\rho}\exp(i\omega_{k_\rho}t)] + \sum_{k_z}\frac{k^{1/2}}{(L-d\gamma/dk_z)^{1/2}}\sin(k_z z+\gamma)(b_{\vec{k}_\rho,k_z}e^{-ikct} + b^\dagger_{-\vec{k}_\rho,k_z}e^{ikct})\right], \tag{3.1}$$

$$\phi(\vec{x},t) = -i\left(\frac{\hbar c}{mn_0 A}\right)^{1/2}\sum_{\vec{k}_\rho} e^{i\vec{k}_\rho\cdot\vec{\rho}}\left[\left(\frac{c}{2\omega_{k_\rho}}\right)^{1/2} E_{k_\rho}(z)[r_{\vec{k}_\rho}\exp(-i\omega_{k_\rho}t) - r^\dagger_{-\vec{k}_\rho}\exp(i\omega_{k_\rho}t)] + \sum_{k_z}\frac{k^{-1/2}}{(L-d\gamma/dk_z)^{1/2}}\sin(k_z z+\gamma)(b_{\vec{k}_\rho,k_z}e^{-ikct} - b^\dagger_{-\vec{k}_\rho,k_z}e^{ikct})\right]. \quad (3.2)$$

[$\delta n_{\text{cont}}(\vec{x},t)$ may be obtained from the expression (3.1) for $\delta n(\vec{x},t)$ by replacing $\mu_{k_\rho}(z)\to 1$)]. If the operators $r_{\vec{k}_\rho}$ and $b_{\vec{k}}$ obey the commutation relations,

$$[r_{\vec{k}_\rho}, r^\dagger_{\vec{k}'_\rho}] = \delta_{\vec{k}_\rho\vec{k}'_\rho}, \quad (3.3a)$$

$$[b_{\vec{k}}, b^\dagger_{\vec{k}'}] = \delta_{\vec{k}\vec{k}'} \text{ (all others vanish)}, \quad (3.3b)$$

then direct evaluation yields

$$[\phi(\vec{x}), n(\vec{x}')] = (\hbar/im)\delta^{(2)}(\vec{\rho}-\vec{\rho}')\delta(z,z'). \quad (3.4)$$

Equation (2.28) then implies that

$$[\vec{J}(\vec{x}), n(\vec{x}')] = (\hbar/im)n(\vec{x})\vec{\nabla}_x\delta^{(3)}(\vec{x}-\vec{x}'). \quad (3.5)$$

Furthermore, substitution into Eq. (2.14) gives H up to a c number as

$$H = \sum_{\vec{k}}\hbar kc b^\dagger_{\vec{k}} b_{\vec{k}} + \sum_{\vec{k}_\rho}\hbar\omega_{k_\rho} r^\dagger_{\vec{k}_\rho} r_{\vec{k}_\rho}. \quad (3.6)$$

Finally, the retarded density-density response function defined by

$$iD^R(x,x') \equiv \langle 0|[n(x), n(x')]|0\rangle\Theta(t-t'), \quad (3.7)$$

where $|0\rangle$ designates the ground state, is found to be identical to Eq. (2.39).

Note that unlike the usual situation in the bulk system,[10] the operators ϕ and n are not canonical conjugates over the entire space, since $\delta(z,z')$ does not behave as $\delta(z-z')$ everywhere (even for z infinitesimally outside of the interval $-L\le z\le 0$), nevertheless the fundamental relation [Eq. (3.5)] obtains. In fact the operators ϕ and δn_{cont} are not uniquely defined for all z, since the equations of motion apply only for $-L\le z\le 0$. However, the various representations are expected to be equivalent as regards physically observable quantities, and the above representation is chosen primarily for its simplicity.

IV. CALCULATION OF $S(\vec{q},\omega)$

We now obtain a representation for $S(\vec{q},\omega)$ to $O(A/V)$. $S(\vec{q},\omega)$ may be expressed[4] in terms of ground-state expectation values of density operators as

$$S(\vec{q},\omega) = \frac{1}{2\pi N}\int d^3x\int d^3x'\, e^{-i\vec{q}\cdot(\vec{x}'-\vec{x})} \times\int dt e^{-i\omega t}\langle 0|\delta n(\vec{x}')\,\delta n(\vec{x},t)|0\rangle, \quad (4.1a)$$

$$= \frac{1}{2\pi N}\int dt e^{-i\omega t}\langle 0|\delta n(\vec{q})\,\delta n^\dagger(\vec{q},t)|0\rangle, \quad (4.1b)$$

$$= \frac{1}{N}\sum_\alpha \delta(\omega - E_\alpha/\hbar)\,|\langle\alpha|\delta n^\dagger(\vec{q})|0\rangle|^2, \quad (4.1c)$$

where the sum runs over all excited states $|\alpha\rangle$ with energy E_α (above the ground-state energy). (Operators expressed in terms of $\vec{q}$ will denote Fourier transforms throughout this section.) We have found that the calculation is considerably simplified by expressing $S(\vec{q},\omega)$ in terms of current operators. This is basically due to the simplicity of the operator $\vec{J}$ [Eq. (2.6)] as compared to the density n [Eq. (2.3)]. Two integrations of Eq. (4.1b) by parts and use of the continuity equation [Eq. (2.4)] directly yield $S(\vec{q},\omega)$ in the form

$$S(\vec{q},\omega) = \frac{1}{2\pi N\omega^2}\int dt e^{-i\omega t}\langle 0|\vec{q}\cdot\vec{J}(\vec{q})\vec{q}\cdot\vec{J}^\dagger(\vec{q},t)|0\rangle, \quad (4.2a)$$

$$= \frac{1}{N\omega^2}\sum_\alpha\delta(\omega - E_\alpha/\hbar)\,|\langle\alpha|\vec{q}\cdot\vec{J}^\dagger(\vec{q})|0\rangle|^2. \quad (4.2b)$$

Since the operator $\vec{J}$ in the quantum hydrodynamic model (Sec. III) is linear in the creation and annihilation operators, only single-excitation states contribute to the sum in Eq. (4.2b). Thus the significant states of $\{|\alpha\rangle\}$ are $|\vec{k}_\rho\rangle$ for ripplons and $|\vec{k}\rangle$ for phonons:

$$|\vec{k}_\rho\rangle = r^\dagger_{\vec{k}_\rho}|0\rangle, \quad (4.3a)$$

$$|\vec{k}\rangle = b^\dagger_{\vec{k}}|0\rangle. \quad (4.3b)$$

A. $S_{\text{rip}}(\vec{q},\omega)$

Calculation of the ripplon contribution $S_{\text{rip}}(\vec{q},\omega)$ to $S(\vec{q},\omega)$ is nearly trivial. Equations (2.6) and (3.2) determine the matrix element,

$$\langle 0|\vec{q}\cdot\vec{J}(\vec{q})|\vec{k}_\rho\rangle = -i\left(\frac{\hbar c^2 n_0}{2mA\omega_{k_\rho}}\right)^{1/2} \times \int d^3x\, e^{-i\vec{q}\cdot\vec{x}} E_{k_\rho}(z) \times [i\vec{q}_\rho\cdot\vec{k}_\rho + q_z\kappa_z(k_\rho)]e^{i\vec{k}_\rho\cdot\vec{\rho}}, \tag{4.4}$$

where the z integration is from $z=-L$ to $z=0$. Carrying out the indicated integrations and substituting Eq. (4.4) into Eq. (4.2b) leads directly to

$$S_{\mathrm{rip}}(\vec{q},\omega) = \frac{A}{V}\frac{\hbar}{2m\omega_{q_\rho}}\frac{q_z^2\kappa_z^2+q_\rho^4}{(q_z^2+\kappa_z^2)[q_\rho^2+(\sigma q_\rho^2/2\rho_0c^2)^2]^{1/2}} \times \delta(\omega-\omega_{q_\rho}), \tag{4.5}$$

where $\kappa_z=\kappa_z(q_\rho)$ and ω_{q_ρ} are given in Eqs. (2.21) and (2.22).

For $q_\rho \ll \rho_0c^2/\sigma$ (the "incompressibility limit," corresponding to $c\to\infty$), $S_{\mathrm{rip}}(\vec{q},\omega)$ becomes independent of q_z and we obtain the important, simple limiting expression:

$$S_{\mathrm{rip}}(\vec{q},\omega) \to \frac{A}{V}\frac{\hbar q_\rho}{2m\omega_{q_\rho}}\delta(\omega-\omega_{q_\rho}). \tag{4.6}$$

Note that the factor of the δ function in Eq. (4.6) diverges as $q_\rho^{-1/2}$ as $q_\rho\to 0$, corresponding to the long-wavelength infinity in the density of ripplon states.

B. $S_{\mathrm{phon}}(\vec{q},\omega)$

Determination of the $O(A/V)$ phonon contribution $S_{\mathrm{phon}}(\vec{q},\omega)$ to $S(\vec{q},\omega)$ is considerably more difficult than in the ripplon case, as we now have a troublesome sum (over k_z) to contend with. Furthermore $S_{\mathrm{phon}}(\vec{q},\omega)$ contains $O(1/L)$ oscillations in the variable q_z which are probably physically uninteresting. Finally, at fixed $\vec{q}_\rho$, $S_{\mathrm{phon}}(\vec{q},\omega)$ is nonzero only for ω equal to one or another of the discrete frequencies corresponding to the modes delineated by Eq. (2.18). This discreteness is again uninteresting from an experimental point of view. Thus, in order to obtain a reasonable form for S_{phon} we average out the q_z oscillations by representing the summands (to appear) in terms of δ functions and principal-value function of q_z. Finally, the discrete dependence of $S_{\mathrm{phon}}(\vec{q},\omega)$ upon ω is smoothed out by replacing

$$\sum_{k_z}\frac{1}{L-d\gamma/dk_z} \to \frac{1}{\pi}\int_0^\infty dk_z. \tag{4.7}$$

We emphasize that this procedure yields an averaged representation of $S_{\mathrm{phon}}(\vec{q},\omega)$ to $O(A/V)$, rather than a strict "thermodynamic limit" of the function.

Equations (2.6) and (3.2) determine the matrix element,

$$\langle 0|\vec{q}\cdot\vec{J}(\vec{q})|\vec{k}\rangle = -i\left(\frac{\hbar cn_0}{mAk}\right)^{1/2}\left(L-\frac{d\gamma}{dk_z}\right)^{-1/2} \times\int d^3x\, e^{-i\vec{q}\cdot\vec{x}}[i\vec{q}_\rho\cdot\vec{k}_\rho\sin(k_zz+\gamma) + q_zk_z\cos(k_zz+\gamma)]e^{i\vec{k}_\rho\cdot\vec{\rho}}. \tag{4.8}$$

Carrying out the simple $\vec{\rho}$ integration and substituting into Eq. (4.2b) gives

$$S_{\mathrm{phon}}(\vec{q},\omega) = \frac{\hbar c^2}{L\omega^3 m}\sum_{k_z}\frac{\delta(\omega-kc)}{L-d\gamma/dk_z}\left|\int_{-L}^0 dz\, e^{-iq_zz}[iq_\rho^2\sin(k_zz+\gamma) + q_zk_z\cos(k_zz+\gamma)]\right|^2, \tag{4.9}$$

where k is given by

$$k^2=q_\rho^2+k_z^2. \tag{4.10}$$

Integrating over z we obtain after minor rearrangement

$$S_{\mathrm{phon}}(\vec{q},\omega) = \frac{\hbar c^2}{L\omega^3 m}\sum_{k_z}\frac{\delta(\omega-kc)}{L-d\gamma/dk_z}[(q_\rho^2+q_zk_z)^2\Delta^2(q_z-k_z)+(q_\rho^2-q_zk_z)^2\Delta^2(q_z+k_z) + (-q_\rho^4+q_z^2k_z^2)\Delta(q_z-k_z)\Delta(q_z+k_z)2\cos(Lk_z-2\gamma)], \tag{4.11}$$

where $\Delta(Q)$ is defined by

$$\Delta(Q) \equiv (\tfrac{1}{2}\sin QL)/Q. \tag{4.12}$$

We now smooth the $O(1/L)$ q_z oscillations by representing the products of Δ functions in Eq. (4.11) in terms of δ functions and principal-value functions of q_z. $\Delta^2(q_z-k_z)$ is given by

$$\Delta^2(q_z-k_z) = -\tfrac{1}{4}(e^{i(q_z-k_z)L}-2+e^{-i(q_z-k_z)L})/(q_z-k_z)^2. \tag{4.13}$$

This function is sharply peaked at $q_z=k_z$, whereas for $|q_z-k_z|\gg 1/L$, is given by $1/[2(q_z-k_z)^2]$ (averaging over the q_z oscillations). Thus we represent $\Delta^2(q_z-k_z)$ as

$$\Delta^2(q_z-k_z) = \tfrac{1}{2}L\pi\delta(q_z-k_z) + [2(q_z-k_z)^2]^{-1}, \tag{4.14}$$

where the second term is a double-pole principal-value function which satisfies

$$\int_{-\infty}^{+\infty} dq_z \frac{1}{(q_z - k_z)^2} = 0 . \quad (4.15)$$

The coefficient factor of the δ function in Eq. (4.14) is determined by integrating Eq. (4.13) over $-\infty < q_z < +\infty$. Similarly, $\Delta(q_z - k_z)\Delta(q_z + k_z)$ is represented by

$$\Delta(q_z - k_z)\Delta(q_z + k_z) = \frac{\pi}{4}\frac{\sin Lk_z}{k_z}[\delta(q_z - k_z) + \delta(q_z + k_z)] + \frac{\cos Lk_z}{2(q_z - k_z)(q_z + k_z)} , \quad (4.16)$$

which is consistent with Eq. (4.14) in the limit $k_z \to 0$. This function [Eq. (4.16)] as appearing in the sum [Eq. (4.11)] is considerably simplified, since application of the boundary condition [Eq. (2.18)] yields

$$\Delta(q_z - k_z)\Delta(q_z + k_z) 2\cos(Lk_z - 2\gamma) = \frac{\pi}{2k_z}[\delta(q_z - k_z) + \delta(q_z + k_z)] \times \cos\gamma \sin\gamma - \frac{\sin^2\gamma}{(q_z - k_z)(q_z + k_z)} . \quad (4.17)$$

Finally, the replacement [Eq. (4.7)] is made, smoothing out the discrete dependence of $S_{\text{phon}}(\vec{q}, \omega)$ upon ω. The integral over k_z is now easily carried out, and after considerable algebraic rearrangement $S_{\text{phon}}(\vec{q}, \omega)$ is obtained in the simple form:

$$S_{\text{phon}} = S_{\text{bulk}} + S_{\text{phon}}^{\text{coh}} + S_{\text{phon}}^{\text{inc}} , \quad (4.18)$$

where S_{bulk} is the usual

$$S_{\text{bulk}} = (\hbar q/2mc)\delta(\omega - qc) . \quad (4.19)$$

The $O(A/V)$ contributions to $S_{\text{phon}}(\vec{q}, \omega)$ consist of coherent (δ function) and incoherent parts given by

$$S_{\text{phon}}^{\text{coh}}(\vec{q}, \omega) = \frac{A}{V}\frac{\hbar q}{2mc}\frac{(q_z^2 - q_\rho^2)(\sigma q_\rho^2/\rho_0 c^2)}{q^4 + (\sigma q_z q_\rho^2/\rho_0 c^2)^2}\delta(\omega - qc) , \quad (4.20)$$

$$S_{\text{phon}}^{\text{inc}}(\vec{q}, \omega) = \frac{A}{V}\frac{\hbar\omega^2}{\pi m c^4 k_z} \times \left(\frac{q_\rho^2 q^2 - q_z^2\omega^2/c^2}{(\omega^2/c^2 - q^2)[\omega^4/c^4 + (\sigma k_z q_\rho^2/\rho_0 c^2)^2]} + \frac{2q_z^2}{(\omega^2/c^2 - q^2)^2}\right)\Theta(k_z) , \quad (4.21)$$

where k_z is given here by

$$k_z = (\omega^2/c^2 - q_\rho^2)^{1/2} . \quad (4.22)$$

$S_{\text{phon}}^{\text{inc}}$ is plotted as a function of ω in Fig. 1 for $q_\rho = 0.3$ Å^{-1}, $q_z = 0.4$ Å^{-1}, and depth $L = V/A = 50$ Å.

Note that near the threshold at $\omega = q_\rho c$ (which lies below the coherent phonon threshold at $\omega = qc$), $S_{\text{phon}}^{\text{inc}}$ manifests a divergent (though integrable) behavior:

$$S_{\text{phon}}^{\text{inc}}(\vec{q}, \omega) \to \frac{A}{V}\frac{\hbar q_\rho^2}{\pi m c^2 q_z^2}\frac{\Theta(\omega^2/c^2 - q_\rho^2)}{(\omega^2/c^2 - q_\rho^2)^{1/2}} , \quad \omega \to q_\rho c . \quad (4.23)$$

Furthermore, at large ω,

$$S_{\text{phon}}^{\text{inc}} \to \frac{A}{V}\frac{\hbar c q_z^2}{\pi m \omega^3} , \quad \omega \to \infty , \quad (4.24)$$

which implies that the second ω moment of $S(\vec{q}, \omega)$ does not exist within this model. Both limiting forms [Eqs. (4.23) and (4.24)] are manifestations of the existence of a wall at $z = -L$. This can be seen most easily by letting $\sigma \to \infty$ in Eq. (4.21), which replaces the free surface at $z \approx 0$ by a (second) wall. In this case the $\omega \to q_\rho c$ and $\omega \to \infty$ limits of $S_{\text{phon}}^{\text{inc}}$ are equal to the expressions in Eqs. (4.23) and (4.24) multiplied by a factor of 2. These considerations lead to a simple separation of $S_{\text{phon}}^{\text{inc}}$ as

$$S_{\text{phon}}^{\text{inc}} = S_{\text{wall}}^{\text{inc}} + S_{\text{free}}^{\text{inc}} , \quad (4.21'\text{a})$$

where $S_{\text{wall}}^{\text{inc}}$ and $S_{\text{free}}^{\text{inc}}$ are contributions due to the boundary conditions at $z = -L$ and $z = 0$, respectively, and are given by

$$S_{\text{wall}}^{\text{inc}} = \frac{A}{V}\frac{\hbar\omega^2 q_z^2 \Theta(k_z)}{\pi m c^4 k_z(\omega^2/c^2 - q^2)^2} , \quad (4.21'\text{b})$$

$$S_{\text{free}}^{\text{inc}} = \frac{A}{V}\frac{\hbar\omega^2 k_z}{\pi m c^4}\left(\frac{q^4 + (\sigma q_z q_\rho^2/\rho_0 c^2)^2}{\omega^4/c^4 + (\sigma k_z q_\rho^2/\rho_0 c^2)^2}\right)\frac{\Theta(k_z)}{(\omega^2/c^2 - q^2)^2} . \quad (4.21'\text{c})$$

Note that the divergences at $\omega = qc$ in $S_{\text{phon}}^{\text{inc}}$ are only apparent as they occur in principal-value functions and are simply a reflection of the $O(1/L)$ "uncertainty broadening" of $S(\vec{q}, \omega)$ vs q_z. This corresponds to a width $\Delta\omega = O(q_z c/qL)$ in $S(\vec{q}, \omega)$ at

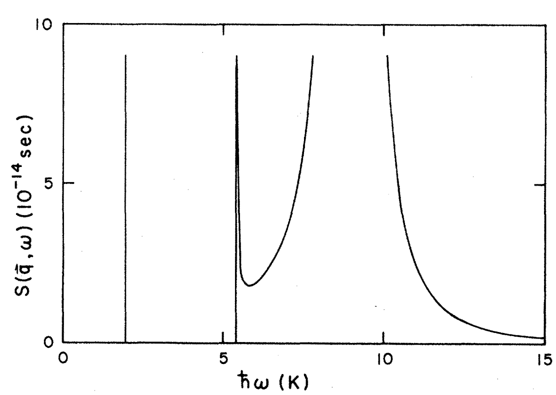

FIG. 1. $S(\vec{q}, \omega)$ as a function of ω at $q_\rho = 0.3$ Å^{-1}, $q_z = 0.4$ Å^{-1}, and depth $L = V/A = 50$ Å. Line at $\hbar\omega = 1.94$ K represents the ripplon δ function contribution $S_{\text{rip}}(\vec{q}, \omega)$. Divergence in $S(\vec{q}, \omega)$ at $\hbar\omega = \hbar q_\rho c = 5.41$ K, the tail at large ω, and the shoulders of the "uncertainty broadened" bulk phonon peak centered at $\hbar\omega = \hbar qc = 9.01$ K are clearly indicated.

fixed $\vec{q}$. For a similar use of principal-value functions in another context, see Ref. 11.

At this point, comparison with the work of Saam[4,9] is possible. Equations (34) and (36) of Ref. 4 give $S(\vec{q},\omega)$ for a liquid of depth L for scattering in which the angle between the neutron beam and free surface is not infinitesimal and for which the present paper is applicable. As is easily seen, $S^{\text{coh}}_{\text{phon}}(\vec{q},\omega)$ is missing. This is possibly related to the fact that the completeness relation published in Ref. 9 [Eq. (25)] is invalid for the important regime $z\approx z'\approx 0$ [compare with Eq. (A19) of the Appendix]. However, as calculational details are omitted from Ref. 4, the error is difficult to pinpoint. Furthermore, as no boundary condition is specified at depth L into the liquid, Saam's result has no contribution analogous to Eq. (4.21′b). Both of these omissions lead to a violation of the f-sum rule as computed from Eqs. (34) and (36) of Ref. 5. This fact, however, does not invalidate the small-angle scattering results which constitute the main import of Saam's paper.

V. SUM RULES

We now consider the interesting ω moments of $S(\vec{q},\omega)$. A system of particles in an external field interacting via two-body forces is known[4] to yield the "f-sum rule" for $S(\vec{q},\omega)$,

$$S_1(\vec{q})\equiv\int_0^\infty d\omega\,\omega\,S(\vec{q},\omega)=\frac{\hbar q^2}{2m}\,. \tag{5.1}$$

It is important to prove that Eq. (5.1) is satisfied by the quantum hydrodynamic model discussed in this paper, as otherwise little confidence can be placed in the results of Sec. IV. We first give a very simple formal demonstration (along the lines of a proof in Pines and Nozieres,[4] 1966) that the f-sum rule is satisfied by the quantum hydrodynamic model of a fluid with free surface. Secondly, we explicitly prove that the representation of $S(\vec{q},\omega)$ in Eqs. (4.5), (4.19)–(4.21) satisfies the f-sum rule.

The formal proof is as follows. Equation (3.5) immediately allows evaluation of the commutator,

$$\frac{im}{\hbar}[J_j(\vec{q}),\,\delta n^\dagger(\vec{q})]=\int d^3x\int d^3x'\,e^{-i\vec{q}\cdot(\vec{x}-\vec{x}')}n_0\Theta(-z)\times\Theta(z+L)\frac{\partial}{\partial x_j}\delta^{(3)}(\vec{x}-\vec{x}')\,, \tag{5.2a}$$

$$=iq_jN, \tag{5.2b}$$

where Eq. (5.2b) follows upon integration by parts, since the δ function contributions (in J_z) at $z=0$ and $z=-L$ cancel. Thus, since

$$\vec{q}\cdot\vec{J}(\vec{q})=(1/\hbar)[\delta n(\vec{q}),H]\,, \tag{5.3}$$

we have

$$[[\delta n(\vec{q}),H],\delta n^\dagger(\vec{q})]=\hbar^2q^2N/m\,. \tag{5.4}$$

But the commutator in Eq. (5.4) may also be expressed as

$$\begin{aligned}[[\delta n(\vec{q}),H],\delta n^\dagger(\vec{q})]&=\langle 0|\Big([\delta n(\vec{q}),H]\sum_\alpha|\alpha\rangle\langle\alpha|\delta n^\dagger(\vec{q})\\&\qquad-\delta n^\dagger(\vec{q})\sum_\alpha|\alpha\rangle\langle\alpha|[\delta n(\vec{q}),H]\Big)|0\rangle\\&=\sum_\alpha E_\alpha[|\langle 0|\delta n(\vec{q})|\alpha\rangle|^2+|\langle\alpha|\delta n(\vec{q})|0\rangle|^2]\,, &(5.5\text{a})\\&=2\hbar S_1(\vec{q})\,, &(5.5\text{b})\end{aligned}$$

by Eq. (4.1c), as the two sums in Eq. (5.5a) are equal. Thus, Eqs. (5.5b) and (5.4) imply that the f-sum rule [Eq. (5.1)] is satisfied.

We now explicitly prove that the representation [Eqs. (4.5), (4.19)–(4.21)] satisfies Eq. (5.1). The only nontrivial integral is $S^{\text{inc 1}}_{\text{phon}}$ given by

$$\begin{aligned}S^{\text{inc 1}}_{\text{phon}}(\vec{q},\omega)&\equiv\int_{q_\rho c}^\infty d\omega\,\omega\,S^{\text{inc}}_{\text{phon}}(\vec{q},\omega)\,, &(5.6)\\&=\frac{A}{V}\frac{\hbar}{2\pi m}\int_{-\infty}^{+\infty}dk_z\\&\qquad\times\frac{(k_z^2+q_\rho^2)(q_\rho^2q^2-q_z^2k^2)}{[(k_z+i\eta)^2-q_z^2][k^4+(\sigma k_zq_\rho^2/\rho_0c^2)^2]}\,, &(5.7)\end{aligned}$$

where $k^2=q_\rho^2+k_z^2$. The integrand of Eq. (5.7) has two poles in the upper half plane given by the zeros of

$$k^4+(\sigma k_zq_\rho^2/\rho_0c^2)^2=(k_z-i\kappa_z)(k_z-i\kappa_c)\times(k_z+i\kappa_z)(k_z+i\kappa_c)\,, \tag{5.8}$$

where $\kappa_z(q_\rho)$ is the inverse capillary wave damping length [Eq. (2.21)] and κ_c is defined by

$$\kappa_c\equiv\left[q_\rho^2+\left(\frac{\sigma q_\rho^2}{2\rho_0c^2}\right)^2\right]^{1/2}+\frac{\sigma q_\rho^2}{2\rho_0c^2}\,. \tag{5.9}$$

Completing the integral [Eq. (5.7)] in the upper plane, the pole at $k_z=i\kappa_z$ contributes

$$S^1_{i\kappa_z}=\frac{A}{V}\frac{\hbar 2\pi i(\omega^2_{q_\rho}/c^2)(q_\rho^2q^2-q_z^2\omega^2_{q_\rho}/c^2)}{2\pi m(-k_z^2-q_z^2)(-i\sigma q_\rho^2/\rho_0c^2)(2i\kappa_z)2i[q_\rho^2+(\sigma q_\rho^2/2\rho_0c^2)^2]^{1/2}}=-\frac{A}{V}\frac{\hbar}{4m}\frac{q_\rho^4+q_z^2\kappa_z^2}{(\kappa_z^2+q_z^2)[q_\rho^2+(\sigma q_\rho^2/2\rho_0c^2)^2]^{1/2}}=-\tfrac{1}{2}S^1_{\text{rip}}(\vec{q})\,, \tag{5.10}$$

where the f sum $S^1_{\text{rip}}(\vec{q})$ from the ripplon branch is easily found from Eq. (4.5). The integral about the pole at $k_z=i\kappa_c$ is calculated similarly, and after an amount of algebra it is found that

$$S^1_{i\kappa_c}+S^{\text{coh}\,1}_{\text{phon}}=-\tfrac{1}{2}S^1_{\text{rip}}\,, \tag{5.11}$$

where the f-sum $S^{\text{coh}\,1}_{\text{phon}}$ is found from Eq. (4.20). Thus we have for arbitrary $\vec{q}$

$$\int_0^\infty d\omega\,\omega[S_{\text{rip}}(\vec{q},\omega)+S^{\text{coh}}_{\text{phon}}(\vec{q},\omega)+S^{\text{inc}}_{\text{phon}}(\vec{q},\omega)]=0\,, \tag{5.12}$$

which leaves the f sum "exhausted" by $S_{\text{bulk}}(\vec{q},\omega)$.

We now briefly discuss the static structure function $S(\vec{q})$ given by

$$S(\vec{q})\equiv\int_0^\infty d\omega\,S(\vec{q},\omega)\,. \tag{5.13}$$

Although a closed-form expression for $S(\vec{q})$ at arbitrary $\vec{q}$ may be obtained from the representation [Eqs. (4.5), (4.19)–(4.21)] for $S(\vec{q},\omega)$, the calculation is quite tedious and is omitted here. However, for small q_ρ ($q_\rho\ll\rho_0c^2/\sigma$), the ripplon branch must dominate the $O(A/V)$ contributions to $S(\vec{q})$ in order to satisfy the f-sum rule, since $\omega_{q_\rho}\ll q_\rho c$. Thus we have simply from Eqs. (4.6) and (4.19)

$$S(\vec{q})\to\frac{\hbar q}{2mc}+\frac{A}{V}\frac{\hbar q_\rho}{2m\omega_{q_\rho}}\,. \tag{5.14}$$

Note that the second term diverges as $q_\rho\to 0$. [In fact for depth $L=V/A\approx 50$ Å and $q_z\approx 0.1$ Å^{-1} the ripplon contribution in Eq. (5.14) is of the same order of magnitude as that from the bulk phonons (see Fig. 2).]

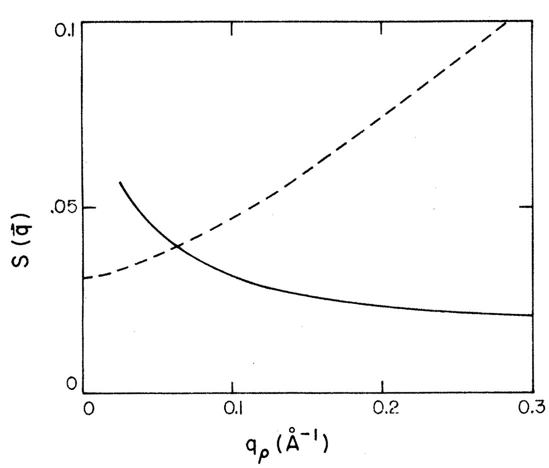

FIG. 2. Ripplon (solid curve) and bulk phonon (dashed curve) contributions to the static structure function $S(\vec{q})$ vs q_ρ for $q_z=0.1$ Å^{-1} at depth $L=V/A=50$ Å.

Finally, we remark that it is a simple matter to obtain a long-wavelength "surface-tension sum rule" analogous to the compressibility sum rule. Equations (2.22) and (4.6) directly yield

$$\int_0^\infty d\omega\,\omega^{1/3}S(\vec{q},\omega)=\frac{A}{V}\frac{\hbar}{2m}\left(\frac{\rho_0}{\sigma}\right)^{1/3}\quad(q\to 0)\,. \tag{5.15}$$

Furthermore, ω^α moments of $S(\vec{q},\omega)$ for $\alpha<\frac{1}{3}$ diverge in the long-wavelength limit. In particular, the compressibility sum rule is violated at $O(A/V)$. Note that for q_ρ comparable to L^{-1}, ω_{q_ρ} becomes dependent upon L in the form[10]

$$\omega^2_{q_\rho}=(\sigma/\rho_0)q_\rho^3\tanh(q_\rho L)\,. \tag{5.16}$$

Thus for very low wavelengths ($q_\rho\ll L^{-1}$), the sum rule [Eq. (5.15)] is replaced by

$$\int_0^\infty d\omega\,\omega^{1/2}S(\vec{q},\omega)=\frac{A}{V}\frac{\hbar}{2m}\left(\frac{\rho_0}{L\sigma}\right)^{1/4}\,, \tag{5.17}$$

as Eq. (4.6) is still valid.

APPENDIX: ORTHONORMALIZATION AND COMPLETENESS

The orthogonality of the state functions given in Sec. II is easily proven as follows. Let ϕ_1 and ϕ_2 be two $\vec{k}_\rho$ solutions with frequencies ω_1 and ω_2. Then since ϕ_1 and ϕ_2 satisfy the wave equation, we have

$$\left(-\frac{\omega_1^2}{c^2}+\frac{\omega_2^2}{c^2}\right)\int_{-L}^0 dz\,\phi_1\phi_2=\int_{-L}^0 dz\left(\phi_2\frac{\partial^2\phi_1}{\partial z^2}-\phi_1\frac{\partial^2\phi_2}{\partial z^2}\right)$$
$$=\left(\frac{\phi_2\partial\phi_1}{\partial z}-\frac{\phi_1\partial\phi_2}{\partial z}\right)_{z=0}$$
$$=(\omega_1^2-\omega_2^2)\left(\frac{\rho_0}{\sigma k_\rho^2}\right)\phi_1(0)\,\phi_2(0)\,, \tag{A1}$$

where the last equation follows from Eqs. (2.8), (2.9), and (2.12). Thus, if $\omega_1\neq\omega_2$, ϕ_1 and ϕ_2 are orthogonal under the scalar product [Eq. (2.24)].

Normality is most easily proven by direct evaluation. For the capillary waves we have

$$I_c\equiv\int dz\,\mu_{k_\rho}(z)\,E^2_{k_\rho}(z)=E^2_{k_\rho}(0)\left(\frac{1}{2\kappa_z}+\frac{\rho_0c^2}{\sigma k_\rho^2}\right)=1\,. \tag{A2}$$

For the sound waves,

$$I_s \equiv \int dz\, \mu_{k_\rho}(z) \sin^2(k_z z+\gamma)$$

$$= \frac{L}{2} - \frac{1}{2k_z}\sin\gamma\cos\gamma + \frac{\rho_0 c^2}{\sigma k_\rho^2}\sin^2\gamma = \frac{1}{2}\left(L - \frac{d\gamma}{dk_z}\right). \tag{A3}$$

We now produce a completeness relation for the state functions given in Sec. II. Strictly speaking, we give a proof in the large-L limit, although generalization to finite L with the appropriate capillary wave states is evidently possible, albeit complicated. We wish to evaluate the functions $\delta_{k_\rho}(z,z')$ given by Eq. (2.25). For z and z' away from the wall at $-L$, where the state functions are wildly oscillating, the sum S over k_z in Eq. (2.25) may be directly replaced by an integral by means of Eq. (2.18) which implies that

$$\left(L - \frac{d\gamma}{dk_z}\right)\Delta k_z \approx \pi\,, \tag{A4}$$

so that we may replace

$$\sum_{k_z} \frac{2}{L - d\gamma/dk_z} \to \frac{2}{\pi}\int_0^\infty dk_z\,. \tag{A5}$$

As $\sin(k_z z+\gamma)$ may be expressed as

$$\sin(k_z+\gamma) = \tfrac{1}{2}(BB^*)^{-1/2}(Be^{ik_z z} + B^* e^{-ik_z z})\,, \tag{A6}$$

where

$$B = \frac{\sigma k_z k_\rho^2}{\rho_0} - ik^2c^2\,, \tag{A7}$$

S is given by

$$S = \delta(z-z') + I\,, \tag{A8}$$

where

$$I \equiv \frac{1}{2\pi}\int_{-\infty}^{+\infty} dk_z \frac{B^*}{B} e^{-ik_z\xi}\,, \tag{A9}$$

where

$$\xi = z + z'\,. \tag{A10}$$

The singular integral I may be expressed as

$$I = \frac{d}{d\xi} I_1\,, \tag{A11}$$

where

$$I_1 = \frac{i}{2\pi}\int_{-\infty}^{+\infty} dk_z \frac{B^* e^{-ik_z\xi}}{B(k_z - i\eta)}\,. \tag{A12}$$

Evaluation of I_1 by means of contour integration yields

$$I_1 = \begin{cases} 1 - \dfrac{(\sigma k_\rho^2/\rho_0 c^2)e^{\kappa_z\xi}}{[(\sigma k_\rho^2/2\rho_0c^2)^2 + k_\rho^2]^{1/2}}\,, & \xi < 0 \\[2ex] \dfrac{-\sigma k_\rho^2/\rho_0 c^2)e^{\kappa_c\xi}}{[(\sigma k_\rho^2/2\rho_0c^2)^2 + k_\rho^2]^{1/2}}\,, & \xi > 0\,, \end{cases} \tag{A13}$$

where κ_z is the inverse capillary wave damping length given in Eq. (2.21) and κ_c is given by

$$\kappa_c = \left[\left(\frac{\sigma k_\rho^2}{2\rho_0 c^2}\right)^2 + k_\rho^2\right]^{1/2} + \frac{\sigma k_\rho^2}{2\rho_0 c^2}\,. \tag{A14}$$

Differentiating I_1 with respect to ξ, we have for $z+z'<\epsilon$, $0<\epsilon \ll 1/\kappa_z$, and z, z' away from the lower boundary

$$\delta_{k_\rho}(z,z') = \delta(z-z') - \delta(z+z') + (2\sigma k_\rho^2/\rho_0c^2)\Theta(z+z')\,. \tag{A15}$$

For z and z' near $-L$ we must take the highly oscillatory nature of the state functions into account before sums are approximated by integrals. Transforming to

$$\zeta = z + L\,, \quad \zeta' = z' + L\,, \tag{A16}$$

we have S in the form

$$S = \sum_{k_z} \frac{2}{L - d\gamma/dk_z}\cos k_z\zeta\cos k_z\zeta'\,. \tag{A17}$$

Note that the functions $\cos k_z\zeta$ and $\cos k_z\zeta'$ are smooth for ζ and $\zeta' \approx 0$, but are highly oscillatory for $\zeta \approx \zeta' \approx +L$. Replacing the sum by an integral we have for z, $z' \approx -L$,

$$S = \delta(z-z') + \delta(z+z'+2L)\,. \tag{A18}$$

The remaining region of (z,z') space may be considered similarly yielding the final, general result

$$\delta_{k_\rho}(z,z') = \delta(z-z') - \delta(z+z') + \delta(z+z'+2L) + (2\sigma k_\rho^2/\rho_0c^2)\Theta(z+z')\,, \tag{A19}$$

where $-2L-\epsilon < (z+z') < \epsilon$.

We now show that $\delta_{k_\rho}(z,z')$ is a δ function under the scalar product [Eq. (2.24)] for continuous functions $f(z)$ defined in $-L-\epsilon \leq z \leq \epsilon$. For $F(z)$ defined by Eq. (2.27), we must show that $F(z)=f(z)$, $-L-\epsilon \leq z \leq \epsilon$. For $-L<z<0$, the proof is trivial, since only the first δ function in $\delta_{k_\rho}(z,z')$ [Eq. (A19)] contributes. At $z=0$ only the final terms of both $\delta_{k_\rho}(z,z')$ [Eq. (A19)] and $\mu_{k_\rho}(z')$ [Eq. (2.23)] contribute, thus

$$F(0) = (2\sigma k_\rho^2/\rho_0c^2)\,\Theta(0)(\rho_0c^2/\sigma k_\rho^2)\,f(0) = f(0)\,. \tag{A20}$$

At $0<z\leq\epsilon$, the second and final terms of $\delta_{k_\rho}(z,z')$ [Eq. (A19)] contribute and we have

$$F(z) = -f(-z) + (2\sigma k_\rho^2/\rho_0c^2)\Theta(z)(\rho_0c^2/\sigma k_\rho^2)f(0)$$
$$= -f(-z) + 2f(0) \to f(0) \quad \text{as } z\to 0\,. \tag{A21}$$

The lower boundary is handled similarly.

Equation (2.28) may be proven as follows. Equations (2.26), (2.23), and (A19) immediately give $\delta(z,z')$ in the simple useful form

$$\delta(z,z') = 2\delta(z)\,\Theta(z) + \delta(z-z')\,\Theta(-z')\,\Theta(z'+L) - \delta(z+z')\,\Theta(-z') + \delta(z+z'+2L)\,\Theta(z'+L)\,. \tag{A22}$$

Thus,

$$\begin{aligned}\Theta(-z)\,\Theta(z+L)\,\delta(z,z') &= 2\Theta(z)\,\Theta(-z)\,\delta(z') + \delta(z-z')\,\Theta(-z)\,\Theta(-z')\,\Theta(z+L)\,\Theta(z'+L) - \Theta(-z)\,\Theta(-z')\,\delta(z+z') \\ &\quad + \delta(z'+z+2L)\,\Theta(z+L)\,\Theta(z'+L) \\ &= \frac{\frac{1}{2}\delta(z)\,\delta(z')}{\delta(0)} + \delta(z-z')\,\Theta(-z)\,\Theta(-z')\,\Theta(z+L)\,\Theta(z'+L) - \frac{\frac{1}{4}\delta(z)\,\delta(z')}{\delta(0)} + \frac{\frac{1}{4}\delta(z'+L)\,\delta(z+L)}{\delta(0)} \\ &= \Theta(-z)\,\Theta(z+L)\,\delta(z-z')\,, \end{aligned} \tag{2.28a}$$

since

$$\Theta^2(-z) = \Theta(-z) - \frac{\frac{1}{4}\delta(z)}{\delta(0)}\,. \tag{A23}$$

Equation (2.28b) is obtained similarly.

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