PHYSICAL REVIEW A VOLUME 14, NUMBER 6 DECEMBER 1976

Dynamics of metastable fluid states in the liquid-solid transition*

J. W. Haus†
National Bureau of Standards, Washington, D. C. 20234

Paul H. E. Meijer
Physics Department, Catholic University of America, Washington, D. C. 20064

(Received 2 March 1976)

A fluctuation theory for the dynamics of metastable fluid states is presented which relies on a limiting form for the static structure factor $S(k)$ previously presented by the authors. The transport coefficients are found to show a divergence in the hydrodynamic regime. In the nonhydrodynamic regime a model is presented which uses an approximate single-particle memory function and a diffusive mode is found; this is compared with fluctuation theory results of other workers. A recent computer experiment has shown numerical agreement with the static model.

I. INTRODUCTION

In this paper we will extend the theory of metastable fluid states below the freezing point. Our theory is based upon the assumption that there exists an order parameter for this transition, and that this order parameter is the $k_0 = 2\pi/a$ Fourier component of the average density. Using a mean-field theory of Brout[1] for the static structure factor, $S(k)$, we are able to obtain expressions for the dynamic structure factor in the hydrodynamic regime (small k) and in the regime near the first peak of $S(k)$.

The history of metastability dates back to the work of Fahrenheit and is linked with the refinements which he made in thermometry.[2] It was Ostwald[3] who identified two types of nonstable states in supersaturated solutions, those which are metastable, that is, stable to all appearances for a seemingly unlimited amount of time unless mechanically disturbed, and those which are labile or unstable states which spontaneously decompose to the thermostatically stable phase. This leads to the question of the boundary between these two states. If a mean field theory is to be believed, such as van der Waals equation,[4] then the thermostatically unstable regions, $\partial P/\partial V > 0$, correspond to the labile region and the metastable region lies between the phase boundary derived from Maxwell's construction and the spinodal boundary, $\partial P/\partial V = 0$. However, experimentally this boundary has not been directly observed; another boundary intervenes which can be described by nucleation theories.[5] This does not render the spinodal concept (i.e., the line at which $\partial P/\partial V$ changes sign) invalid, in fact this unstable region is obtainable in multicomponent glasses and binary mixtures. The spinodal boundary makes its appearance in the stable and metastable regions through anomalous trends of thermostatic and thermodynamic properties.[6] Similarly, in this theory we propose a limit which may not be directly observable, but whose trends will be felt at some distance from the boundary.

Kirkwood and Monroe[7] presented a theory of freezing based on the Kirkwood integral equation. In their theory a nonlinear integral equation of the Hammerstein type is developed for the one-particle distribution function. It is recognized that the fluid state, $\rho(r) = \rho_0$, is always a solution, but for sufficiently low temperatures there are nonconstant solutions for which $\rho(r) = \rho(r+R)$ where $\vec{R}$ is a lattice translation vector. These solutions break the symmetry of the original Hamiltonian and have a lower free energy. To construct a solution a particular Fourier component is singled out as dominant, the components of which correspond to the first peak of the structure factor for the solid, $\langle\rho_{k_0}\rangle$. The radial distribution function, $g^2(r)$, is assumed to be fluidlike and no assumption is made concerning the pair potential $V(r)$. The Fourier component, $\langle\rho_{k_0}\rangle$, is considered to be an order parameter which changes discontinuously at the freezing point.

Brout's theory[1] is similar in content to Kirkwood and Monroe, but he treats the pair correlation function by breaking the potential into hard core and attractive contributions. A variational calculation which relies on local free energy yields a condition for nonconstant solutions for the density. In Sec. III we will discuss the static treatment of Brout using a perturbation theory of Zwanzig.[8] One of the authors[9] has derived the results of Brout using functional differentiation; this presents an alternative to manipulating renormalized vertices in Brout's derivation and makes explicit the mean-field character of the theory.

Kobayashi[10] has extended the theory of Kirkwood and Monroe to include the time dependence of the one-particle distribution function. The equation is a Vlasov equation whose solution has been extensively studied by van Kampen and by Case.[11] The condition chosen for the instability boundary of the fluid was that the damping of the density mode be zero. In Kobayashi's theory the fluctuation is nonpropagating and damps with a temperature dependence

$$\gamma = T^{-1/2}\rho \frac{\partial G(k_0, T_L)}{\partial T_L}(T - T_L)\,, \tag{1.1}$$

where T is the temperature, T_L is the density dependent limit of stability, ρ is the density, and

$$G(k,T) = \frac{4\pi}{k^3}\int dr \frac{dV(r)}{dr} g^2(r)\,(kr\cos kr - \sin kr)\,, \tag{1.2}$$

$V(r)$ and $g^2(r)$ have the same meaning as above. In the static limit Kobayashi's theory reduces to the nonlinear theory of Kirkwood and Monroe and the dynamics of the Kobayashi theory is not consistent in the hydrodynamic regime. The reason for this lies in the terms neglected in the equation of motion for the one-particle distribution function to produce a Vlasov equation. The poles of the Vlasov equation are not caused by collisions between particles which must satisfy conservation laws, but from single-particle phase interference due essentially to the distributions of velocities for the individual particles.[9] This requires restricting the theory to the nonhydrodynamic regime. We will again discuss this theory in Sec. IV as a comparison with our own and the results of others. We note that this mode has been the object of study in supercooled liquids via neutron and x-ray scattering.

In a rigorous way Penrose and Lebowitz[12] have outlined an approach to describing metastable states in statistical mechanics. An important condition of this method is the restriction of phase space to be locally in some long-lived state and to ignore the global aspects of the phase space which require that the free energy be convex. Recently this approach to metastable states has been applied to a lattice system with short-range potential.[13] Gates[14] has shown rigorously that for certain kernels in the nonlinear equations of the mean-field theory of freezing there is a nonconstant solution and a freezing transition. A special case of this theory is the Kirkwood and Monroe theory and it is formulated in terms of a variation principle which yields an integral equation used by van Kampen.[15] Ravechê and Stuart[16] have provided molecular approach to crystallization based on the equilibrium BBGKY hierarchy. They provide solutions for hard-core systems which are represented as nonlinear eigenvalue problems and the branching eigenvalues represented the limit of stability for the fluid and solid phases.

In Sec. II we will present a synopsis of the Zwanzig-Mori projection operator technique. Section III will be devoted to a discussion of the static structure factor and in Sec. IV the results of the theory will be given for the transport coefficients and for the memory function; the memory function derived by Schneider *et al.*[17] and Mitra and Shukla[18] will also be discussed. It is emphasized by the authors that the possibility of reaching this boundary may be prevented by a freezing-in of fluctuations, such as would occur in a glassy state of simple liquids, as well as by nucleation and growth mechanisms.

II. ZWANZIG-MORI PROJECTION OPERATOR TECHNIQUE

A. Zwanzig-Mori formalism

We wanted to use a theoretical framework which would allow us to compare all the present theories which have been developed. The Zwanzig-Mori projection operator technique has been widely employed to study the properties of correlation functions.[19] In this formalism a subspace of dynamical variables or vectors is chosen from a Hilbert space. The dynamical variables we will be using are Fourier components of the microscopic density,

$$\rho_k = |\Omega|^{-1}\sum_{i\in\Omega} e^{i\vec{k}\cdot\vec{r}_i}\,; \tag{2.1}$$

the particle current density

$$J_k = |\Omega|^{-1}\sum_{i\in\Omega}\frac{p_i}{M} e^{i\vec{k}\cdot\vec{r}_i}\,, \tag{2.2}$$

and the energy density

$$E_k = |\Omega|^{-1}\sum_{i\in\Omega}\left(\frac{p_i^2}{2M} + \Phi_i\right) e^{i\vec{k}\cdot\vec{r}_i}\,, \tag{2.3}$$

where Ω is the physical space containing the particle with metric volume $|\Omega|$; $\vec{r}_i$, $\vec{p}_i$, and M are the ith particle's position, momentum, and mass, respectively, and

$$\Phi_j = \frac{1}{2}\sum_{\substack{i\in\Omega\\ i\neq j}} V(r_{ij})\,.$$

We begin with the Liouville equation for the evolution of the set of dynamical variables, $\vec{A}$, and by introducing an inner product between two dynamical variables a and b which we denote by (a,b). The Liouville equations for the dynamical variables is cast into the form of generalized

Langevin equations. A projection operator is defined which projects a dynamical quantity, $\vec{B}$, on to the subspace of dynamical variables

$$\underline{P}\vec{B} = (\vec{B}, \vec{A})(\vec{A}, \vec{A})^{-1}\vec{A} . \qquad (2.4)$$

This subspace is often referred to as the relevant or slow variable subspace. It is called slow because the variables one chooses satisfy conservation laws which require a long time compared to interparticle collisions in which to dissipate a local fluctuation.

It is important to note that the generalized Langevin equation has as a generalized force a quantity which lies in the subspace orthogonal to the dynamical variables

$$\vec{f}_1(t) = \exp[t(\underline{I} - \underline{P})iL](\underline{I} - \underline{P})iL\vec{A} , \qquad (2.5)$$

$\underline{I}$ is unit operator, and iL is the Liouville operator.

The details of this procedure are omitted, but they are covered in detail by the authors quoted in Ref. 19.

The equations which are developed are formally exact. A specific inner product is obtained by assuming an ensemble subject to initial constraints upon the dynamical variables used in the calculation. At this point of the analysis the equations become approximations to the exact development of the system's dynamical behavior. However, in the analysis no assumption is made concerning the stability of the states used in the average. We only require that the states be stationary. This will be discussed as it relates to metastable states below.

Since the phase space states are stationary, the correlation matrix $\Xi_0(t)$, will be time translatable. We use this property to Laplace transform the correlation matrix from time space, t, to its inverse space, z. The result is expressed as

$$\underline{\Xi}_0(z) = (\vec{A}(z), \vec{A})(\vec{A}, \vec{A})^{-1} . \qquad (2.6)$$

The equation of motion for the matrix is an alegbraic relation in this space yielding the solution

$$\underline{\Xi}_0(z) = [z\underline{I} - i\underline{\Omega}_0 + \underline{\Xi}_1(z)\underline{\Delta}_1^2]^{-1} , \qquad (2.7)$$

where

$$\underline{\Xi}_1(z) = (\vec{f}_1(z), \vec{f}_1)/(\vec{f}_1, \vec{f}_1)$$

and

$$\underline{\Delta}_1 = (\vec{f}_1, \vec{f}_1)/(\vec{A}, \vec{A}) .$$

The process of projecting onto subspaces (orthogonal to each other) may be continued with the subspace $\vec{f}_1$; the variables $\vec{f}_1(t)$ satisfy a modified Liouville equation which is amenable to the same algorithm. This procedure can be repeated to obtain a continued fraction representation for the correlation matrix. The result for a subspace containing a single dynamical variable is written

$$\Xi_0(z) = 1/\{z + \Delta_1^2/[z + \Delta_2^2/(z + \cdots , \qquad (2.8)$$

where

$$\Delta_j^2 = (f_j, f_j)/(f_{j-1}, f_{j-1}) ,$$

$$f_j = e^{it(I-P_{j-1})L}(\mathrm{I} - P_{j-1})iL f_{j-1} ,$$

and

$$PB = (B, f_j)(f_j, f_j)^{-1} f_j . \qquad (2.9)$$

This equation is solved in the appendix for the case of an ideal gas. It involves only equal time correlations instead of the more complicated time translated correlations, but it is difficult to assess at what point the continued fraction may be truncated. We shall be interested in approximations for $\Xi_1(z)$ in what follows. A metastable state is locally an equilibrium state and small fluctuations will not decay to the globally stable phase in general. If the constrained canonical ensemble used in the Zwanzig-Mori theory is allowed to implicitly delete that part of the phase space which would correspond to the globally stable phase, then the properties of equilibrium fluids can with equal validity be applied to metastable fluids. We have only required that the system be stationary and that the correlation functions preserve Galilean invariance; this is an implicit restriction of the phase space solution which, as we shall see in what follows, has an instability at a sufficiently low temperature. Below the limit temperature a fluid solution cannot exist and nonconstant solutions are required.

B. Transport coefficients

In the hydrodynamic regime (i.e., long wavelengths) Eqs. (2.1)–(2.3) comprise the usual set of coupled dynamical variables. They are conserved variables and slowly varying in this regime. The generalized Langevin equation is required to satisfy the fluctuation dissipation theorem which relates space- and time-dependent transport coefficients to correlations of the generalized forces. In the hydrodynamic regime we neglect nonlocal contributions to the transport coefficients.

The volume viscosity, $\tilde{\eta}_v$, shear viscosity, $\tilde{\eta}_s$, and thermal conductivity, $\tilde{\lambda}_L$, have the Kubo formulas:

$$\tilde{\eta}_s = (Mk_BT)^{-1}\int_0^\infty \langle J^y(t)J^y\rangle dt , \qquad (2.10\mathrm{a})$$

$$\tilde{\eta}_v = (Mk_BT)^{-1}\int_0^\infty \langle J^v(t)J^v\rangle dt , \qquad (2.10\mathrm{b})$$

$$\tilde{\lambda}_L = (3k_B T^2)^{-1} \int_0^\infty \langle \vec{S}(t) \cdot \vec{S} \rangle \, dt \,, \tag{2.10c}$$

where

$$J^y(t) = \frac{d}{dt} e^{iLt} \left(\sum_{i \in \Omega} P_i^y r_i^x \right) , \tag{2.11a}$$

$$J^v(t) = \frac{d}{dt} e^{iLt} \frac{1}{3} \left(\sum_{i \in \Omega} \vec{P}_i \cdot \vec{r}_i \right) , \tag{2.11b}$$

and

$$\vec{S}(t) = \frac{d}{dt} e^{iLt} \left(\sum_{i \in \Omega} (H_i - h_i) \vec{r}_i \right) . \tag{2.11c}$$

All these variables have been defined in Eqs. (2.1)–(2.3) with the exception of h_i which is the enthalpy per particle.

It is useful at this juncture to define the relaxation time[20] for a pair of fluctuating variables $\{a, b\}$

$$\tau_{ab} = \Xi_0^{ab}(0) \,; \tag{2.12}$$

in the Zwanzig-Mori formalism this is

$$\tau_{ab} = \{ [-i \underline{\Omega}_0 + \underline{\Xi}_1(0) \underline{\Delta}_1^2]^{-1} \}^{ab} \,. \tag{2.13}$$

Schofield[21] has expressed the relaxation time for density fluctuations as

$$\tau_{\rho\rho} = \rho^3 C_v \beta_L^2 / \tilde{\lambda}_L k^2 \,. \tag{2.14}$$

C_v is the specific heat and β_L is the thermal expansion coefficient.

III. STATIC MODEL

In a recent paper[22] we have presented the results of a mean-field theory developed by Brout[1]:

$$S(k) \equiv \langle \rho_k \rho_{-k} \rangle = \frac{\langle \rho_k \rho_{-k} \rangle_r}{1 + \beta \tilde{\phi}_L(k) \langle \rho_k \rho_{-k} \rangle_r} \,, \tag{3.1}$$

where $\tilde{\phi}_L(k)$ is the Fourier transform of $\phi_L(R) g_r^2(R)$, $\phi_L(R)$ being a long-ranged attractive part of the total pair potential and the subscript "r" denoting a property of the reference system attributed to a short-ranged repulsive potential. A perturbation scheme for the Lennard-Jones potential used in the calculation has been amply discussed by Andersen, Weeks, and Chandler.[23] The procedure for computing $S(k)$ is summarized as follows: We equate the properties of the repulsive reference system to those of a hard-core system with a temperature-dependent diameter, $d(T)$; the diameter is chosen by any number of criteria[22,24] and the Percus-Yevick approximation is used to represent the hard-core system.[25] The zeros of the denominator of Eq. (3.1) are related to the limit of (meta-) stability for the one-phase system. If we initially have a low-density system and temperature between the triple and critical point temperatures and we isothermally raise the density, Brout has pointed out that the first instability will occur at wave number, $k = 0$. This is the limit of stability for the gas phase; at this point, the system spontaneously decomposes into a liquid-gas two-phase system. This boundary of infinite compressibility has been termed the spinodal boundary.[26] Below this boundary the system is thermostatically unstable to any fluctuations in the system. The scaling properties and pseudocritical exponents of a mean-field Ising system near this boundary were recently discussed by Compagner.[27]

As we further increase the density isothermally, a second zero is found, this time at the wave number corresponding to the first peak of the structure factor, k_0. The instability is not accompanied by a divergence of the thermostatic compressibility; hence, the boundary is not called the spinodal boundary. From computer experiments of Matsuda and Hiwatari[28] the evidence indicates that the equation of state does not contain van der Waals loops and that the boundary, if one exists, must certainly occur for densities and pressures higher than the equilibrium solid density and pressure. The glass phase is not associated with some hidden order parameter in this static theory of metastable states, but it may be due to the slowing down of the local structural rearrangement and thus, would be considered a relaxation phenomenon connected with the time scale of the fluid state.[29]

To summarize the results of this theory: taking note of the success of using the hard sphere structure factor to fit a variety of data including argon[30] and liquid metals[31] which have very different representations for pair potentials, we found that the first peak of $S(k)$ was overenhanced by the attractive interaction, but out of this region the agreement was quite good. It is worth noting that molecular beam experiments on argon have shown an overenhanced first peak in (111) (their electron diffraction pattern[32]) and metallic alloy glasses have shown a sharp first peak, as well as, a split second peak[33]; the splitting of the second peak is evidence that there are important correlations in the system which are not taken into account in the mean-field theory. The compressibility is finite contrary to suggestions by previous authors[34]; as the limit of stability is approached at constant density,

$$S(k) = S_0 / [(k - k_0)^2 + \kappa^2], \quad \kappa^2 = \kappa_0^2 (T - T_L) \tag{3.2}$$

and for a density $\rho = 0.84/\sigma^3$, σ being the Lennard-Jones range parameter, $T_L = 55.5$ K. This form for $S(k)$ was suggested by Schneider and coworkers[17] in their theory of the freezing instability; their results used a molecular dynamics computation and the random-phase approximation yielding $T_L = 64$ K. Another result derived by Mitra and Shukla[18] based on a scaling generalization of the Schneider theory (presented below) yields $T_L = 69.5$ K.

Recent experiments on supercooled fluids[35] have observed no anomaly in $S(q_0)$ down to temperatures $(T - T_L)/T_L \simeq 0.044$–$0.09$, where T_L is obtained by extrapolation of the quasielastic linewidth to zero. However, our numerical work on the mean-field approximation has suggested the requirement that $(T - T_L)/T_L < 0.02$ for marginal observation of the anomaly. This puts a severe restriction on the ability to test this theory for real systems, but perhaps not for a computer fluid.

A recent computer experiment by Mandell *et al.*[36] has observed crystal nucleation in a Lennard-Jones fluid. Large fluctuations in the structure factor at vector position $\vec{k}_0$ were observed, and the limit of metastability they observed for the system was in agreement with our model.

We feel that before this theory may be pursued in greater depth that a formalism should be developed which allows a systematic improvement of the theory, such as have been presented for lattice theories.[37] There are similarities of the inhomogeneities caused by fluctuations in a metastable system and inhomogeneities introduced in a random system which are worthwhile pursuing. Further generalizations might include nonadditive effects which certainly play a role in water, but will also be present in weakly quantum systems,[38] and considerations of properties of liquid and plastic crystals where an interaction is present between angular and translational order parameters.[39] In closing we stress that the form of the structure factor in Eq. (3.2) puts very stringent conditions on the convergence of the functionals representing the transport coefficients and memory kernels.

IV. DYNAMICS

A. Transport coefficients

In Sec. II we discussed generalized transport coefficients which are wave-number and frequency dependent. These expressions are too difficult to carry out in practice, but we will consider some limiting cases which simplify the computations.

The simplification we are concerned with here is the hydrodynamic or small wave number regime used to derive Eq. (2.10). The technique used to study these coefficients was developed for a one component van der Waals gas by Mountain and Zwanzig[40] and for two components by Deutch and Zwanzig.[41] A less phenomenological approach than theirs was developed by DeSobrino[42] and Kawasaki[43] and applied to one- and two-component systems. DeSobrino's calculations are based on the nonequilibrium BBGKY equation for a van der Waals gas. His equilibrium results are identical to van Kampen's results.[15] The nonequilibrium properties are primarily due to the short-ranged repulsive interaction with modifications to the system properties from the longer-ranged and weak attractive interaction. Kawasaki reformulated these results in a way which lends itself to application to the freezing instability presented in Sec. III.

We argue that the kinetic-energy and repulsive short-ranged potential-energy contributions will not lead to any anomaly in the transport coefficients. What may be said about the long-ranged attractive contribution? As an example, consider the shear viscosity

$$\tilde{\eta}_s = \tilde{\eta}_s^r + \Delta\tilde{\eta}_s \,. \tag{4.1}$$

$\tilde{\eta}_s^r$ is the part from nonanomalous contributions, and

$$\Delta\tilde{\eta}_s = (k_B T)^{-1} \int_0^{\infty} \left\langle \frac{1}{2} \sum_{\substack{i\in\Omega \\ j\in\Omega \\ i\neq j}} \left(\frac{\partial}{\partial r_{ij}^x} [\phi_L(r_{ij}) r_{ij}^y] \right)(t) \times \frac{1}{2} \sum_{\substack{i\in\Omega \\ j\in\Omega \\ i\neq j}} \left(\frac{\partial}{\partial r_{ij}^x} [\phi_L(r_{ij}) r_{ij}^y] \right)(0) \right\rangle dt \tag{4.2}$$

now, since $\phi_L(R)$ is Fourier transformable

$$r^\alpha \frac{\partial \phi_L(r)}{\partial r^\beta} = \int d^3k \frac{\partial}{\partial k^\alpha} [k^\beta \phi_L(k)] e^{i\vec{k}\cdot\vec{r}} \tag{4.3}$$

and

$$|\Omega|^{-2} \sum_{\substack{i\in\Omega \\ j\in\Omega}} e^{i\vec{k}\cdot\vec{r}_{ij}} = \rho_k \rho_{-k} - \frac{\rho}{|\Omega|} \,. \tag{4.4}$$

The last term in Eq. (4.4) may be neglected, so that

$$\Delta\tilde{\eta}_s = (k_B T)^{-1} \int_0^{\infty} \int d^3k \int d^3k' \, \frac{k^x k^{x'}}{4} \frac{\partial \phi_L(k)}{\partial k^y} \frac{\partial \phi_L(k')}{\partial k^{y'}} \times \langle \rho_k^{(t)} \rho_{-k}^{(t)} \rho_{k'} \rho_{-k'} \rangle \, dt \,. \tag{4.5}$$

The four-point density functional in the integrand of Eq. (4.5) is now simplified by the following assumptions:

$$\rho_k(t) = \rho_k e^{-t/\tau_L^r} \,, \tag{4.6}$$

$$\langle \rho_k \rho_{-k} \rho_{k'} \rho_{-k'} \rangle \simeq 2 \langle \rho_k \rho_{-k} \rangle^2 \delta_{k,\pm k'} + \langle \rho_k \rho_{-k} \rangle \langle \rho_{k'} \rho_{-k'} \rangle \,. \tag{4.7}$$

The first assumption recognized that a coarse graining has taken place in the statistical description of the density whose time dependence is governed by a diffusive mode. τ_L^r is related to generalized thermal diffusivity of the reference system. The second assumption decoupled the four-point functional and corresponds to a Gaussian approximation.[44]

Substituting Eq. (3.2) for $\langle\rho_k\rho_{-k}\rangle$, note that for $\kappa = 0$ our integrals are divergent. We will approximate the integrals whose main contribution is at wave numbers near k_0 by the integrand evaluated at k_0, then using

$$I_1 = \int_0^\infty \frac{dk}{k^2+bk+c} = \frac{2}{\sqrt{\Delta}}\left(\tan^{-1}\frac{|b|}{\sqrt{\Delta}} + \frac{\pi}{2}\right), \tag{4.8}$$

$\Delta = 4c - b^2$. In our case $c = \kappa^2 + k_0^2$ and $b = -2k_0$. The most divergent contribution to the shear viscosity which is proportional to $-dI_1/dc$ is

$$\Delta\tilde{\eta}_s = A/\kappa^3 . \tag{4.9}$$

A is a constant which depends on temperature and density, but has no anomalous behavior. The expression for the volume viscosity, $\tilde{\eta}_v$, proceeds in exactly the same manner. The anomalous part is again a functional of the density to which we apply assumptions [Eqs. (4.6) and (4.7)]. The contribution of the long-ranged attractive potential to the volume current density is

$$\Delta J^v = \frac{1}{6}\int d^3k\left(3\hat{\phi}_L(k) - \vec{\mathrm{k}}\cdot\frac{\vec{\partial}}{\partial k}\hat{\phi}_L(k)\right) \times[\rho_k(t)\rho_{-k}(t) - \langle\rho_k(t)\rho_{-k}(t)\rangle], \tag{4.10}$$

$$\Delta\tilde{\eta}_v = B/\kappa^3 . \tag{4.11}$$

B is a temperature- and density-dependent constant.

The thermal conductivity has a heat current whose long-ranged contribution is

$$\Delta\vec{\mathrm{S}} = -\frac{1}{2}\int d^3k\left(2\hat{\phi}_L(k)\vec{\mathrm{J}}_{-k} - \vec{\mathrm{k}}\cdot\vec{\mathrm{J}}_{-k}\,\frac{\partial\vec{\hat{\phi}}_L(k)}{\partial k}\right)\rho_k . \tag{4.12}$$

The particle current $\vec{\mathrm{J}}_{-k}$ contains both longitudinal and transverse components. In the wave-number regime with which we are concerned, the relaxation time of the currents is diffusive. The reference-state relaxation time is taken as τ_v^r. We assume that the current has the time dependence

$$J_k^T(t) = J_k^T e^{-t/\tau_v^r} , \tag{4.13}$$

decoupling the four-point functional

$$\langle J_{-k}^T(t)\,\rho_k(t)\,J_{-k'}^T\,\rho_{k'}\rangle \simeq \langle J_{-k}^T(t)\,J_k^T\rangle\langle\rho_k(t)\,\rho_{-k}\rangle\delta_{k,\pm k'} \tag{4.14}$$

and noting that

$$\langle J_{-k}^T J_k^T\rangle = k_B T\rho/M , \tag{4.15}$$

we find

$$\Delta\tilde{\lambda}_L = C/\kappa . \tag{4.16}$$

C is a constant which depends upon temperature and density. From Eq. (4.16) we can infer that the density relaxation time [Eq. (2.14)] will behave as

$$\tau_{\rho\rho} \sim \kappa/k^2 \tag{4.17}$$

and we may expect a kinetic speeding-up very close to the boundary. In an actual experiment a large viscosity attributed to the reference system may interfere in the measurement of this effect, but from Eq. (3.2) this will mean that

$$\tau_{\rho\rho} \sim (T - T_L)^{1/2}/k^2 , \tag{4.18}$$

$$\Delta\lambda \sim (T - T_L)^{-1/2} , \tag{4.19}$$

$$\Delta\tilde{\eta}_{s,v} \sim (T - T_L)^{-3/2} . \tag{4.20}$$

Thus, the light-scattering spectrum from this system has a central mode whose peak grows and half-width narrows as $(T - T_L)^{-1/2}$. The half-width and height of the Brillouin peaks change as $(T - T_L)^{-3/2}$, but the sound velocity has no anomalous behavior. The total intensity being related to thermostatic quantities also has no anomalous behavior.

B. Nonhydrodynamic regime

The technique of Sec. IV A is not conducive to analytic methods in the nonhydrodynamic regime. In the hydrodynamic regime we were able to neglect the effect of the projection operator on the time dependence of the memory function, and to employ a Markoff approximation. Also, the continued fraction technique is not easily handled by analytical methods. For these reasons, in the large k regime it is better to use approximations which have been developed for the correlation matrix $\tilde{\Xi}_1(z)$. This approach has been discussed by Ortoleva and Nelkin.[45] One approximation is the ideal gas memory function related to its correlation function by

$$\tilde{\Xi}^0(k,z) = [z + \Delta_1^2\tilde{\Xi}_1^0(k,z)]^{-1} . \tag{4.21}$$

Here, we assume a one-variable subspace where for an ideal gas, $\Delta_1^2 = k^2V_T^2$, and the thermal velocity is $V_T = (k_BT/M)^{1/2}$. For an interacting system we have

$$\Delta_1^2 = k^2V_T^2/S(k) \tag{4.22}$$

and substituting the ideal-gas memory function yields

$$\tilde{\Xi}(k,z)=\frac{\tilde{\Xi}^0(k,z)}{1+C(k)[z\tilde{\Xi}^0(k,z)-1]}\,, \tag{4.23}$$

where

$$C(k)=[S(k)-1]/S(k)\,. \tag{4.24}$$

This result has been called the simple collective model by Ortoleva and Nelkin and it is equivalent to the random-phase approximation used by Schneider *et al.*[17] The dispersion relation for this approximation is determined by the zeros in the denominator,

$$z\tilde{\Xi}^0(k,z)=-[S(k)-1]^{-1}\,, \tag{4.25}$$

the most important mode being the smallest nonpropagating zero, they found that

$$z=i\omega+\gamma\simeq-\frac{k_0V_T}{\sqrt{\pi}S_0}\,[\kappa^2+(k-k_0)^2]\,. \tag{4.26}$$

Kobayashi's theory is similar in form, but the equation was derived by an entirely different approach, the denominator of his expression has the form

$$1+G(k)[z\tilde{\Xi}^0(k,z)-1]\,, \tag{4.27}$$

$G(k)$ being given by Eq. (1.2). This theory does not rely on a divergence of the static structure factor, but it is restricted to large wave numbers as discussed earlier. The $G(k)$ here plays the role of Δ_1^2 in the Zwanzig-Mori theory.

Another approximation used by Mitra and Shukla,[18] but originally derived by Pathak and Singwi,[46] may be brought under the Zwanzig-Mori formalism by scaling the ideal-gas memory function[47]

$$\tilde{\Xi}^{SC}(k,z)=\mu^{-1}\Xi^0(k,z/\mu)\,, \tag{4.28}$$

where

$$\begin{aligned}\mu&=[(\omega_l^2-\omega_0{}^2)/2\omega_0^2S(k)]^{1/2}\,,\\ \omega_0^2&=k^2k_BT/MS(k)\,.\end{aligned} \tag{4.29}$$

and

$$\omega_l^2=\frac{3k^2k_BT}{M}+\rho\frac{1}{M}\int d^3r\,g^2(r)(1-\cos kr^x)\frac{\partial^2\phi}{\partial r^{x2}}\,. \tag{4.30}$$

ω_l^2 and ω_0^2 are related to the zeroth, second, and fourth moments of $\Xi_0(k,T)$. In this manner we are able to write an expression for the dispersion relation and rigorously fit the first four frequency moments of the correlation function. The dispersion relation for this model is

$$z\tilde{\Xi}^0(k,z/\mu)=-\mu/[S(k)-1]\,. \tag{4.31}$$

μ is defined in Eq. (4.29). As before

$$z=i\omega+\gamma\simeq\frac{-k_0VT}{\sqrt{\pi}\,S_0}\,[\kappa^2+(k-k_0)^2]\mu\,. \tag{4.32}$$

Another approximation which we shall consider is the memory function for the self-motion of a single atom. The correlation function for this case is

$$\Xi(k,z)=\frac{\Xi^{SM}(k,z)}{1+C(k)[z\Xi^{SM}(k,z)-1]}\,, \tag{4.33}$$

$\Xi^{SM}(k,z)$ is the self-part of the density autocorrelation function:

$$\Xi^{SM}(k,z)=\int_0^\infty dt\,e^{-zt}\langle e^{i\vec{k}\cdot\vec{r}_1}e^{iLt}e^{-i\vec{k}\cdot\vec{r}_1}\rangle\,. \tag{4.34}$$

For this case we will formulate an approximation which should yield a correct short time description. An approximation which can be thought of as being a compromise to the ideal-gas and scaled-ideal-gas theories. Our approach is to split the Liouville operator into its kinetic and potential energy contributions

$$iL=iL_0+iL_1,\quad iL_0=\sum_l\frac{p_l\,\partial/\partial r_l}{M},\quad iL_1=\sum_l\dot{p}_l\frac{\partial}{\partial p_l}\,. \tag{4.35}$$

Making use of this decomposition and noting that the iL_0 operates on an eigenfunction, we rewrite this expression neglecting noncommutativity between iL_0 and iL_1,

$$\begin{aligned}\Xi^{SM}(z)&\simeq\int_0^\infty dt\;e^{-zt}\langle e^{iL_1t}e^{-ikp_1^xt/M}\rangle\\ &=\int_0^\infty dt\,e^{-zt}\langle e^{ik\dot{p}_1^xt^2/M}\rangle\langle e^{-ikp_1^xt/M}\rangle\,,\end{aligned} \tag{4.36}$$

expand the first average in the integrand into moments of t^2, and exponentiate the first nonzero moment; we find that

$$\Xi^{SM}(z)\simeq\int_0^\infty dt\,e^{-zt}\exp(-k^2\langle\dot{p}_1^x\dot{p}_1^x\rangle t^4/M^2)\langle e^{-ikp_1^xt/M}\rangle\,. \tag{4.37}$$

Evaluating the exponent gives

$$\langle\dot{p}_1^x\dot{p}_1^x\rangle=\left\langle\frac{\partial\Phi}{\partial r_1^x}\,\frac{\partial\Phi}{\partial r_1^x}\right\rangle=k_BT\left\langle\frac{\partial^2}{\partial r_1^{x2}}\Phi\right\rangle\,, \tag{4.38}$$

where we have made use of

$$e^{-\beta H}\frac{\partial\Phi}{\partial r_1^x}=-\beta\frac{\partial}{\partial r_1^x}\,e^{-\beta H}\,. \tag{4.39}$$

If we assume a central pair potential, then

$$\left\langle\frac{\partial^2\Phi}{\partial r_1^{x2}}\right\rangle=\rho\int d^3r\left(g^2(r)\frac{\partial^2}{\partial r^{x2}}\,\phi(r)\right)\,. \tag{4.40}$$

Again we will consider the most divergent part of this expression due to the attractive part of the potential which we take as being Fourier transformable, then

$$\left\langle \frac{\partial^2 \Phi_L}{\partial r_1^{x^2}} \right\rangle = \rho \int d^3k\, S(k) k^{x^2} \hat{\phi}_L(k)$$

$$\simeq 8\pi^2 \rho k_0^4 S_0 \phi_L(k_0)/K = D/(\kappa\beta M) . \quad (4.41)$$

D is a constant which depends on the density. The self-correlation function reduces to

$$\Xi^{SM}(z) \simeq \int_0^\infty dt\, e^{-zt} \exp\left(\frac{-k^2(Dt^4/\kappa + t^2/2)}{\beta M} \right) . \quad (4.42)$$

Considering the case of small z we may write the integral as

$$\Xi^{SM}(z) \simeq \frac{1}{2R^{1/2}} [\pi^{1/2} e^{Q^2/4} U(0, Q)$$

$$- S e^{Q^2/4} U(\tfrac{1}{2}, Q) + O(S^2)] , \quad (4.43)$$

where $U(a, x)$ are parabolic cylinder functions[48]

$$R = (2k^2 D/\kappa\beta M)^{1/2} , \quad Q = k^2/2\beta M R ,$$

and

$$S = z/R^{1/2} .$$

For $S = 0$ ($z = 0$) the relaxation time is

$$\tau_{\rho\rho} \simeq \frac{S(k)\pi^{1/2}}{2R^{1/2}} U(0, Q) e^{Q^2/4} . \quad (4.44)$$

For the Schneider case,

$$\tau_{\rho\rho} = \Xi^0(k, 0)\, S(k) , \quad (4.45)$$

and the Pathak and Singwi approximation (using a similar technique as above):

$$\tau_{\rho\rho} = \Xi^0(k, 0)\, S(k)/\mu ,$$

$$\mu \simeq [(\rho S_0/k^2)\beta N]^{1/2} \kappa^{1/2} . \quad (4.46)$$

N is a constant which depends on k_0 and the potential. The dispersion equation from Eq. (4.36) is similar to the previous cases already considered in detail. The propagating component is zero and the attenuation is

$$z = i\omega + \gamma \simeq \frac{-2[(k - k_0)^2 + \kappa^2] R^{1/2}}{\pi^{1/2} U(0, Q) e^{Q^2/4}} . \quad (4.47)$$

There is a difference in the models in temperature and wave-number dependence, these differences are in principle testable. Table I presents these three approximations evaluated at $k = k_0$.

TABLE I. Inverse lifetime and relaxation time.

	$\gamma,\ \tau_\rho^{-1}$
Schneider *et al.*	$\sqrt{T}\ \kappa^2$
Pathak and Singwi	$\kappa^{5/2}$
This work	$\kappa^{7/4}$

V. CONCLUSIONS

In this paper we have presented a calculation of the dynamic properties of a fluid as it approaches the limit of stability. The basis for the calculation is the form of the static structure factor suggested by Brout. In the hydrodynamic regime we employed a mode decoupling approximation of four-point functionals to products of two-point functions which allowed us to assess the divergence of the transport coefficients. The form [Eq. (3.2)] for $S(k)$ put stringent requirements on the convergence of the integrals. The transport coefficients were found to diverge under this model in Eqs. (4.8), (4.9), and (4.18). The thermal conductivity determines the height and width of the central Rayleigh peak in a light scattering experiment; this peak is changing in such a manner that the area is constant giving a nondivergent Landau-Placzek ratio. The relaxation time [Eq. (2.1)] corresponds to a critical speeding up.

In the nonhydrodynamic regime, we employed the Zwanzig-Mori formalism to express the results of several researchers. Using the ideal-gas memory function, we recovered the results of Schneider *et al.* A variation on this theory was developed by Pathak and Singwi and is equivalent to the scaled ideal-gas memory function as was pointed out by Rahman. Since the ideal-gas approximation neglects any dependence on the potential in the memory function, we presented a short-time approximation for the self-memory function. This approximation is equivalent to keeping the moments of the single-particle memory function up to fourth order. This should provide a representation somewhere between the ideal gas and the full interaction representation of the system. We expect this to be a valid approximation at large k where the distance probed is short and the corresponding time scale is also short. The relaxation times and the lifetimes of the nonpropagating modes given in Table I yield similar dependences on κ. Temperature, density, and wave-number dependences are significantly different to provide a test in an experimental situation. Each result has been derived not by nucleation considerations, but by a fluctuation approach. The stable and metastable states are not formally different in these theories, but we must be aware that in some sense we are restricting the region of phase space allowed, so that the state of lowest free energy is not obtained. In simple atomic systems this may not be possible by continuous cooling. An approach such as Farges may be useful in providing information about metastability in these systems. Two other systems of interest are: hydrogen-metal systems which have been found to obey a mean-field equation of state and which also show an ordered state[6b] and helium adsorbed on a carbon surface which has an ordering transition.[49] These systems may provide an insight into the physics of a liquid-solid-type phase transition without other order parameters coupling in the theory. Molecular systems, although they are easily supercooled, display couplings between angular order parameters and transverse translational modes which are probably important in suppressing the ability of the system to attain a translationally ordered state or in the case of plastic crystals the temperature of translational ordering is affected by the coupling strength for the order parameters.[50]

APPENDIX

It is well known that for an ideal gas the correlation function is

$$\langle \rho_k(z)\,\rho_{-k}\rangle = (2\pi M k_B T)^{-1/2}\int_{-\infty}^{\infty} dp\,\frac{e^{-\beta p^2/2M}}{z - ikp/M}\,. \tag{A1}$$

However, we will derive this expression using the continued fraction representation of the Zwanzig-Mori formalism. In Sec. II we showed that

$$\frac{\langle \rho_k(z)\rho_{-k}\rangle}{\langle \rho_k\rho_{-k}\rangle} = \cfrac{1}{z + \cfrac{\Delta_1^2}{z + \cfrac{\Delta_2^2}{z + \cdots}}}\,, \tag{A2}$$

where

$$\Delta_n^2 = \langle f_n f_n^*\rangle\langle f_{n-1} f_{n-1}^*\rangle\,. \tag{A3}$$

The f_n are the generalized forces described in Sec. II. Each f_n is orthogonal to all previous f_i, $i<n$, and the weight factor of the inner product is a Gaussian. Therefore, the polynomials for the f_n will be in essence the Hermite polynomials; carrying through the algebra yields:

$$\Delta_n^2 = \tfrac{1}{2} n (ik)^2 (2k_B T/M)\,. \tag{A4}$$

Letting $V_T^2 = 2/\beta M$,

$$\frac{\langle \rho_k(z)\,\rho_{-k}\rangle}{\langle \rho_k\rho_{-k}\rangle} = \cfrac{1}{z - \cfrac{\frac{1}{2}(ik)^2V_T^2}{z - \cfrac{(ik)^2V_T^2}{z - \cfrac{\frac{3}{2}(ik)^2V_T^2}{z - \cdots}}}}\,. \tag{A5}$$

This is the continued fraction for (A1).[51] A direct projection operator calculation of the ideal-gas memory function in this formalism was recently performed by Mountain.[52]

---

*Supported by NSF Grant No. GH 37916.

†NRC-NBS Postdoctoral Research Associate.

[1] R. Brout, *Phase Transitions* (Benjamin, New York, 1965).

[2] See for example, F. Cajori, *A History of Physics* (McMillan, New York, 1899). G. D. Fahrenheit, Philos. Trans. 33, 78–84 (1724–5).

[3] W. Ostwald, Z. Phys. Chem. 22, 289 (1897); 34, 493 (1900).

[4] J. D. van der Waals, Dissertation (Leiden, 1873) (unpublished); P. Weiss, J. Phys. (Paris) 6, 661 (1907).

[5] J. S. Langer, Physica (Utr.) 73, 61 (1974); W. I. Goldburg and J. S. Huang, in *Fluctuations, Instabilities, and Phase Transitions,* edited by T. Riste (Plenum, New York, 1975).

[6] (a) B. Chu, F. J. Schoenes, and M. E. Fisher, Phys. Rev. 185, 219 (1969); (b) G. Alefeld, Comm. Solid State Phys. 6, 53 (1975); (c) J. Schroeder, C. J. Montrose, and P. B. Macedo, J. Chem. Phys. 63, 2907 (1975).

[7] J. G. Kirkwood and E. M. Monroe, J. Chem. Phys. 9, 514 (1941).

[8] R. Zwanzig, J. Chem. Phys. 22, 1420 (1954).

[9] J. W. Haus (unpublished notes).

[10] K. Kobayashi, J. Phys. Soc. Jpn. 27, 1116 (1969).

[11] N. G. van Kampen, Physica (Utr.) 21, 949 (1955); K. M. Case, Ann. Phys. (N.Y.) 7, 349 (1959).

[12] See, J. L. Lebowitz, Physica (Utr.) 73, 48 (1974).

[13] D. Capocaccia, M. Cassandro, and E. Olivieri, Comm. Math. Phys. 39, 185 (1974).

[14] D. J. Gates, Ann. Phys. (N.Y.) 71, (1972).

[15] N. G. van Kampen, Phys. Rev. 135, A366 (1964).

[16] H. J. Raveché and C. A. Stuart, J. Chem. Phys. 63, 1099 (1975).

[17] T. Schneider, R. Brout, H. Thomas, and J. Feder, Phys. Rev. Lett. 25, 1423 (1970); T. Schneider, Phys. Rev. A 3, 2145 (1971).

[18] S. Mitra and G. Shukla, Phys. Status Solidi B 62, K33 (1974).

[19] R. Zwanzig, Lectures in *Theoretical Physics,* edited by W. E. Brittain (Wiley, New York, 1966), Vol. III; H. Mori, Prog. Theor. Phys. 33, 423 (1965); 34, 399 (1965); A. Z. Akcasu and E. Daniels, Phys. Rev. A 2, 962 (1970); C. Murase, J. Phys. Soc. Jpn. 29, 549 (1970); 32, 1205 (1972); M. Weinberg and R. Kapral, Phys. Rev. A 4, 1127 (1971).

[20] P. Schofield, Proc. Phys. Soc. 88, 149 (1966); also in *Physics of Simple Liquids,* edited by H. N. V. Temperley, J. S. Rowlinson, and G. S. Rushbrooke (North-Holland, Amsterdam, 1968), Chap. 13.

[21] M. Suzuki, Prog. Theor. Phys. 43, 882 (1970).

[22] J. W. Haus and P. H. E. Meijer, Physica (Utr.) A 80, 313 (1975).

[23] H. C. Andersen, D. Chandler, and J. D. Weeks, J. Chem. Phys. 54, 5237 (1971); 57, 1930, 2626 (1972); Phys. Rev. A 4, 1597 (1971).

[24] H. C. Andersen, D. Chandler, and J. D. Weeks, J. Chem. Phys. 56, 3812 (1972); J. A. Barker and D. Henderson, *ibid.* 47, 4714 (1967).

[25] E. Thiele, J. Chem. Phys. 38, 1959 (1963); M. S.

Wertheim, Phys. Rev. Lett. 10, 321 (1963); J. Math. Phys. 5, 643 (1964).

[26] J. D. van der Waals, Z. Phys. Chem. 5, 133 (1890).

[27] A. Compagner, Physica (Utr.) 72, 115 (1974).

[28] H. Matsuda and Y. Hiwatari, in *Cooperative Phenomena,* edited by H. Haken and M. Wagner (Springer-Verlag, Berlin, 1973), p. 250.

[29] A. R. Cooper and P. K. Gupta, J. Am. Cer. Soc. 58, 350 (1975).

[30] J. L. Yarnell *et al.*, Phys. Rev. A 7, 2130 (1973).

[31] N. W. Ashcroft and J. Lekner, Phys. Rev. 145, 83 (1960); I. H. Umar and W. H. Young, J. Phys. F 4, 525 (1974).

[32] J. Farges, B. Raoult, and G. Torchet, J. Chem. Phys. 59, 3454 (1973).

[33] G. S. Cargill, III, J. Appl. Phys. 41, 12 (1970).

[34] For example, J. G. Eberhart and H. C. Schnyders, J. Phys. Chem. 77, 2730 (1973); J. J. van Laar, Proc. Kon. Akad. Amsterdam 13, 454 (1910); 13, 636 (1910); 11, 765 (1909).

[35] D. I. Page, D. H. Saunderson, and C. G. Windsor, J. Phys. C 6, 212 (1973); D. G. Carlson, J. Feder, and A. Segmüller, Phys. Rev. A 9, 400 (1974); L. Bosio and C. G. Windsor, Phys. Rev. Lett. 35, 1652 (1975).

[36] M. J. Mandell, J. P. McTague, and A. Rahman, J. Chem. Phys. 64, 3699 (1976).

[37] T. Morita and T. Tanaka, Phys. Rev. 145, 298 (1966).

[38] D. Shalatin, J. Chem. Phys. 58, 5120 (1973).

[39] K. Kobayashi, J. Phys. Soc. Jpn. 29, 101 (1970).

[40] R. Mountain and R. Zwanzig, J. Chem. Phys. 48, 1451 (1968).

[41] J. M. Deutsch and R. Zwanzig, J. Chem. Phys. 46, 1612 (1967).

[42] L. DeSobrino, Can. J. Phys. 45, 363 (1967); 46, 2821 (1968).

[43] K. Kawasaki, Prog. Theor. Phys. 41, 1190 (1969).

[44] R. A. Ferrell, Phys. Rev. Lett. 24, 1169 (1970).

[45] P. Ortoleva and M. Nelkin, Phys. Rev. A 2, 187 (1970).

[46] K. N. Pathak and K. S. Singwi, Phys. Rev. A 2, 2427 (1970).

[47] A. Rahman, in *Statistical Mechanics—New Concepts, New Problems, New Applications,* edited by S. A. Rice, K. F. Freed, and J. C. Light (Chicago U.P., Chicago, 1972), p. 195.

[48] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (National Bureau of Standards, Washington, D.C., 1964), Eq. (19.5.3).

[49] S. Nakajima, in *Cooperative Phenomena,* edited by H. Haken and M. Wagner (Springer-Verlag, New York, 1973), p. 287.

[50] J. A. Pople and F. E. Karasz, Phys. Chem. Solids 18, 28 (1961); 20, 294 (1961).

[51] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (National Bureau of Standards, Washington, D.C., 1964), Eq. (7.1.15).

[52] R. D. Mountain, J. Res. Nat'l. Bur. Stds. A 78, 413 (1974).