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Generalized Langevin theory for inhomogeneous fluids: The equations of motion

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We use the generalized Langevin approach to study the dynamical correlations in an *inhomogeneous* system. The equations of motion (formally exact) are obtained for the number density, momentum density, energy density, stress tensor, and heat flux. We evaluate all the relevant sum rules appearing in the frequency matrix exactly in terms of microscopic pair potentials and an external field. We show using functional derivatives how these microscopic sum rules relate to more familiar, though now *nonlocal*, hydrodynamiclike quantities. The set of equations is closed by a Markov approximation in the equations for stress tensor and heat flux. As a result, these equations become analogous to Grad's 13-moment equations for low-density fluids and constitute a generalization to inhomogeneous fluids of the work of Schofield and Akcasu-Daniels. We also indicate how the resulting general set of equations would simplify for systems in which the inhomogeneity is unidirectional, e.g., a liquid-vapor interface.

I. INTRODUCTION

Inhomogeneities in fluids constitute an important area of current research interest in statistical physics. Since homogeneous fluids are well understood,[1,2,3] one can confidently approach the richer domain of nonuniformity.[4,5,6] Surfaces, boundaries, and other anisotropic disturbances of the fluid can have novel physical consequences in both the equilibrium and nonequilibrium fluid structure, e.g., surface tension and capillary waves. In this paper and elsewhere[7] we have begun a study of the dynamics of inhomogeneous fluids, following the classic treatment for homogeneous fluids by Akcasu and Daniels.[1]

Inhomogeneous fluid dynamics have been treated before by Triezenberg[8] and by Jhon *et al.*[5] Triezenberg made use of generalized Langevin theory, while Jhon *et al.* used kinetic theory. In both discussions, the analysis was restricted to a mean-field level description of the time-dependent number density and momentum density fluctuations, in a liquid-vapor system with a diffuse planar interface. This was because both groups were primarily interested in capillary wave dispersion. We undertake a more complete analysis here, using the generalized Langevin technique.

In this paper, from first principles, we derive and interpret the equations of motion for an inhomogeneous fluid. The derivation is presented in Sec. II, making use of the Zwanzig-Mori generalized Langevin Method.[9] Thus we must *choose* a subset of dynamical variables and then *project* all the dynamics of the system onto that subset. With a good understanding of what the relevant dynamical variables are, we obtain equations in a tractable and understandable form; an inappropriate or incomplete choice of the relevant variables may result in loss of some physical subtleties.

An important part of the *dynamics* is governed by the frequency matrix which requires evaluation of *static* correlation functions called "sum rules". It is this aspect of the Zwanzig-Mori projection operator formalism which puts the completely intractable Liouville equation into a form which is amenable to interpretation. The physical content of the theory then resides in the calculation and interpretation of these sum rules.

We identify the set of relevant microscopic variables as number density, momentum density, energy density, stress tensor, and heat current vector in analogy to Grad's 13-moment method.[10] This is an obvious choice which follows from noting that number, momentum, and energy are conserved, the remaining variables being the fluxes entering the conservation laws. We refine this set further by rearranging it, as we will show, introducing *microscopic* quantities analogous to temperature, entropy, viscous stress tensor, and so on. Essentially, we construct from the above an orthogonal set of fluctuating variables; the orthogonalization procedure is standard,[1,2] e.g., by projecting density fluctuations out of the energy density we obtain a microscopic temperaturelike variable, in the manner of Schofield[2] and Akcasu-Daniels.[1] This process is done while appealing to the general theory of the thermodynamic fluctuations.[11] Thus the dynamical variables are constructed with a well-defined limiting behavior.

Then, having obtained a basis set of variables we calculate the microscopic sum rules which determine the frequency matrix. These results are summarized in Appendix B. The actual calculation is straightforward, though tedious; it is in the interpretation of the sum rules, in Sec. III, that some interesting physics is seen. By extending the work of Schofield[2] on homogeneous fluids, we express the microscopic sum rules in terms of functional derivatives, which in spite of their nonlocality, appear familiar due to similarity to various coefficients in the thermohydrodynamic equations, e.g., the heat capacity. This makes the connection to hydrodynamics apparent.

We can then interpret the equations we have obtained as generalized hydrodynamical equations for a nonuniform fluid. We stress, however, that these are formally exact, microscopic equations following from first principles. Approximations must be made in order to solve them.

A nonuniform fluid of particular interest is that of a liquid-vapor system with a diffuse planar interface. In such a system symmetry is only broken in one direction, for example, the z direction; the remaining symmetry in the xy plane allows us to make many simplifications. It is easy to see how the starting equations of the van der Waals-type theories of Felderhof[12] and Turski-Langer[13] follow from the general structure of the equations we have obtained. We study the liquid-vapor system in Sec. IV, and use its characteristic symmetry to introduce approximations in the same section.

Because the equations we obtain are quite general, they are complex. However, because we have cast them in a form akin to hydrodynamic equations, our insight into possible approximations is sharpened by experience with hydrodynamics. We close the set of equations by a Markov approximation in the equations for viscous stress tensor and purely dissipative heat flux. We can approximate the sum rules in a clear, unambiguous way by referring to their calculated microscopic forms. Thus we can realistically approach the problem of nonuniform fluid dynamics.

Elsewhere[7] we use the dynamical equations to investigate transverse current correlations in a liquid-vapor system with a diffuse planar interface. An expression for the transverse current-current correlation function is obtained. This correlation function is explicitly determined by new, nonlocal, elastic moduli and new, nonlocal, frequency-dependent viscosities. These describe "shearing" and "stretching" of the interface. The nonlocal moduli introduced are simply related to the local "macroscopic" moduli recently introduced by Baus.[14]

We discuss the results of this paper in Sec. V, and indicate a number of further problems we are now pursuing. We have also included a summary on notations in Appendix A. The main results of this paper, the equations of motion, are given in Sec. III C.

II. DERIVATION OF THE EQUATIONS OF MOTION FROM FIRST PRINCIPLES

A. Generalized Langevin equation formalism

We now discuss the form of the Zwanzig-Mori generalized Langevin equation.[9,1,8] Consider a multidimensional dynamical variable $\delta\vec{A}(1t)$.[15] The classical mechanical equation of motion for this variable is

$$\begin{aligned}\frac{d}{dt}\delta\vec{A}(1t) &= -[H,\delta\vec{A}(1t)]_{\mathrm{PB}}\\ &\equiv i\mathscr{L}\delta\vec{A}(1t)\;,\end{aligned} \tag{2.1}$$

where H is the Hamiltonian and Poisson brackets appear because we are in the classical regime. Equation (2.1) defines the Liouville operator $\mathscr{L}$.

Through the use of projection operators it can be shown that Eq. (2.1) is equivalent to the generalized Langevin equation:

$$\frac{d}{dt}\delta\vec{A}(1t)-i\overleftrightarrow{\Omega}(1\bar{2})\cdot\delta\vec{A}(\bar{2}t)+\int_0^t\overleftrightarrow{\phi}(1,\bar{2},t-u)\cdot\delta\vec{A}(\bar{2}u)du=\vec{f}(1t)\ . \tag{2.2}$$

This decomposition is quite easy to understand; it is a formal separation of the total "force" into three parts: a driving force, a systematic force, and a random force.

The driving force $i\overleftrightarrow{\Omega}\cdot\delta\vec{A}$ is, in effect, a collisionless mean-field term since it describes the instantaneous response of the fluid. The frequency matrix $\overleftrightarrow{\Omega}$ is the term about which we have the most assured knowledge. This is because it is determined by *static* correlations in the fluid, i.e.,

$$i\overleftrightarrow{\Omega}(12)=\left\langle\frac{d}{dt}\delta\vec{A}\delta\vec{A}\right\rangle(1\bar{3})\cdot\langle\delta\vec{A}\delta\vec{A}\rangle^{-1}(\bar{3}2)\ . \tag{2.3}$$

The random force $\vec{f}$ is the thermal "noise" of the system. It is formally given by

$$\vec{f}(1t)=e^{t(1-\mathcal{P})i\mathcal{L}}(1-\mathcal{P})\frac{d}{dt}\delta\vec{A}(1t)\ , \tag{2.4}$$

and has the convenient property[9]

$$\langle\vec{f}(1t)\delta\vec{A}(2)\rangle=0\ . \tag{2.5}$$

The projection operator $\mathcal{P}$ is defined by

$$\mathcal{P}\vec{B}(1t)\equiv\langle\vec{B}(1t)\delta\vec{A}(\bar{3})\rangle\cdot\langle\delta\vec{A}\delta\vec{A}\rangle^{-1}(\bar{3}\bar{2})\cdot\delta A(\bar{2})\ , \tag{2.6}$$

a projection onto the space of the multidimensional dynamical variable $\delta\vec{A}$.

The remaining term in Eq. (2.2) is the systematic force. Because of the convolution over time, it described the "memory" of the system. The complicated kernel, $\overleftrightarrow{\phi}$, called the damping matrix, determines the non-Markovian behavior of the inhomogeneous fluid. It is formally related to the random force $\vec{f}$ via the fluctuation dissipation relation,

$$\overleftrightarrow{\phi}(12,t')=\langle\vec{f}(1t)\vec{f}(\bar{3})\rangle\cdot\langle\delta\vec{A}\delta\vec{A}\rangle^{-1}(\bar{3}2)\ . \tag{2.7}$$

Equations (2.2)–(2.7) give us an ansatz for the equation of motion of some variable $\delta\vec{A}$. It remains to identify the relevant dynamical variables, from which we construct an orthogonal set of fluctuation variables comprising $\delta\vec{A}$.

B. Relevant dynamical variables

The term best understood in Eq. (2.2) is the frequency matrix, since it is time independent. The damping matrix is sufficiently complicated that in many instances it has to be approximated. It is obvious that if the components of $\delta\vec{A}$ are conserved variables, or linear combinations of conserved variables, the important part of the dynamics will be determined by the frequency matrix $\underline{\Omega}$. If the relevant variables include the conserved variables and their fluxes, then the conserved variables are completely determined by $\underline{\Omega}$. It is only in the fluxes that the random force and the damping matrix appear. Thus we close the equations with a Markov approximation in the equations for the fluxes.

We consider an inhomogeneous fluid consisting of N-structureless classical particles of mass μ, with the Hamiltonian,

$$H=\sum_i\frac{p_i^2}{2\mu}+\tfrac{1}{2}\sum_{i\neq j}V_2(\vec{R}_i,\vec{R}_j)+\sum_i V_1(\vec{R}_i)\ , \tag{2.8}$$

where $\vec{p}_i$ and $\vec{R}_i$ are the momentum and position of the ith particle. The potential energy is in terms of pairwise additive potentials V_2 and an external field V_1.

Using Eq. (2.8), we identify the relevant dynamical variables as the conserved extensive variables and their fluxes, i.e.,

(i) the number density

$$n(1t)\equiv\sum_i \delta(\vec{r}_1-\vec{R}_i)\ , \tag{2.9}$$

(ii) the momentum density

$$\vec{J}(1t)=\sum_i \vec{p}_i\delta(\vec{r}_1-\vec{R}_i)\ , \tag{2.10}$$

(iii) the Hamiltonian density

$$H(1t)\equiv\sum_i \frac{p_i^2}{2\mu}\delta(\vec{r}_1-\vec{R}_i)+\tfrac{1}{2}\sum_{i\neq j} V_2(\vec{R}_i,\vec{R}_j)\delta(\vec{r}_1-\vec{R}_i)+\sum_i V_1(\vec{R}_i)\delta(\vec{r}_1-\vec{R}_i)\ , \tag{2.11}$$

where half the potential energy of each pair of molecules is associated with each molecule,

(iv) the heat current vector

$$\vec{q}(1t)=\sum_i \frac{\vec{p}_i}{\mu}\delta(\vec{r}_1-\vec{R}_i)\left[\frac{p_i^2}{2\mu}+\tfrac{1}{2}\sum_{\substack{j\\(j\neq i)}} V_2(\vec{R}_i,\vec{R}_j)+V_1(\vec{R}_i)\right]-\tfrac{1}{2}\sum_{i\neq j}\frac{\vec{p}_i}{\mu}\cdot\overleftrightarrow{X}(\vec{r}_1;\vec{R}_i,\vec{R}_j)\ , \tag{2.12}$$

and

(v) the stress tensor

$$\overleftrightarrow{S}(1t)=\sum_i \frac{\vec{p}_i\vec{p}_i}{\mu}\delta(\vec{r}_1-\vec{R}_i)-\tfrac{1}{2}\sum_{i\neq j}\overleftrightarrow{X}(\vec{r}_1;\vec{R}_i,\vec{R}_j)\ , \tag{2.13}$$

where in Eqs. (2.12) and (2.13)

$$\overleftrightarrow{X}(\vec{r}_1;\vec{R}_i,\vec{R}_j)\equiv\tfrac{1}{2}\vec{R}_{ij}\vec{\nabla}_{ij}V_2(\vec{R}_i,\vec{R}_j)\int_0^1 d\lambda[\delta(\vec{r}_1-(1-\lambda)\vec{R}_i-\lambda\vec{R}_j)+\delta(\vec{r}_1-\lambda\vec{R}_i-(1-\lambda)\vec{R}_j)]\ , \tag{2.14}$$

with

$$\vec{R}_{ij}\equiv\vec{R}_i-\vec{R}_j\ ,$$

and

$$\vec{\nabla}_{ij}\equiv\frac{\partial}{\partial\vec{R}_{ij}}\ .$$

We have used the conservation equations to introduce $\vec{J}$, $\vec{q}$, and $\overleftrightarrow{S}$, i.e.,

$$\frac{\partial}{\partial t}n(1t)\equiv-\frac{1}{\mu}\vec{\nabla}_1\cdot\vec{J}(1t)\ , \tag{2.15}$$

$$\frac{\partial}{\partial t}H(1t)\equiv-\vec{\nabla}_1\cdot\vec{q}(1t)\ , \tag{2.16}$$

and

$$\frac{\partial\vec{J}}{\partial t}(1t)\equiv-\vec{\nabla}_1\cdot\overleftrightarrow{S}(1t)-n(1t)\vec{\nabla}_1V_1(1)\ . \tag{2.17}$$

It is more convenient to look at fluctuations of these quantities about their equilibrium values, e.g., $\delta n=n-\langle n\rangle$, and to take their appropriate linear combinations so that the resulting variables are orthogonal at time $t=0$. So, the components of $\delta\vec{A}$ consist of the number of density fluctuation, the momentum density, the "temperature" fluctuation

$$\delta\theta(1t)\equiv\mathscr{C}_v^{-1}(1\bar{2})\delta H(\bar{2}t)-\mathscr{C}_v^{-1}(1\bar{3})\langle\delta H\delta n\rangle(\overline{34})K(\overline{42})\delta n(\bar{2}t)\ , \tag{2.18}$$

the orthogonalized heat current vector

$$\vec{Q}(1t)\equiv\vec{q}(1t)-\langle\vec{q}\,\vec{J}\,\rangle(1\bar{3})\cdot\langle\vec{J}\,\vec{J}\,\rangle^{-1}(\overline{32})\cdot\vec{J}(\bar{2}t)\ , \tag{2.19}$$

and finally the orthogonalized stress tensor fluctuation

$$\delta\overleftrightarrow{\pi}(1t)\equiv\delta\overleftrightarrow{S}(1t)-\delta\overleftrightarrow{\sigma}(1t)\ , \tag{2.20}$$

where

$$\delta\overleftrightarrow{\sigma}(1t)\equiv\langle\delta\overleftrightarrow{S}\delta\theta\rangle(1\bar{3})\mathscr{C}_v(\overline{32})\delta\theta(\bar{2}t)+\langle\delta\overleftrightarrow{S}\delta n\rangle(1\bar{3})K(\overline{32})\delta n(\bar{2}t)\ , \tag{2.21}$$

is the "thermodynamic" pressure fluctuation. We have also introduced the quantitites

$$K(12)\equiv\langle\delta n\delta n\rangle^{-1}(12) \tag{2.22}$$

and

$$\mathscr{C}_v(12)\equiv\langle\delta\theta\delta\theta\rangle^{-1}(12)\ . \tag{2.23}$$

The physical reasons for orthogonalizing the variables are quite evident. In the Hamiltonian density fluctuations, we project out density fluctuations leaving only that fluctuation unique to the Hamiltonian density fluctuation. Conceptually, this is the temperature fluctuation. In the heat current vector and the stress tensor fluctuation, we have projected out the conserved parts of each leaving a purely viscous stress tensor and a purely dissipative heat flux. Thus we can define a thermodynamic pressure fluctuation in the following way: that part of the stress tensor which is made up of the (conserved) temperature and density fluctuations.

So, the multidimensional dynamical variable is

$$\delta\vec{A}(1t)\equiv(\delta n,\vec{J},\delta\theta,\delta\vec{\pi},\vec{Q})$$
$$=(\delta n,J_\alpha,\delta\theta,\delta\pi_a,Q_\alpha) \tag{2.24}$$

(see the Appendix on notation). This is not a unique representation. We have constructed $\delta\vec{A}$ in a way closely analogous to the variables of hydrodynamics. In hydrodynamics an alternative representation to density temperature is pressure entropy. This suggests an alternative representation for $\delta\vec{A}$ which we will explore at a greater length in Sec. III.

C. Equations of motion, in terms of the sum rules

With $\delta\vec{A}$ given by Eq. (2.24), it is straightforward to obtain the frequency matrix. We have

$$\left\langle \frac{d\delta\vec{A}}{dt}\delta\vec{A}\right\rangle(13)=\begin{bmatrix} 0 & \langle\delta\dot{n}J_\alpha\rangle(13) & 0 & 0 & 0\\ \langle\dot{J}_\alpha\delta n\rangle(13) & 0 & \langle\dot{J}_\alpha\delta\theta\rangle(13), & \langle\dot{J}_\alpha\delta\pi_a\rangle(13) & 0\\ 0 & \langle\delta\dot{\theta}J_\alpha\rangle(13) & 0 & 0 & \langle\delta\dot{\theta}Q_\alpha\rangle(13)\\ 0 & \langle\delta\dot{\pi}_aJ_\alpha\rangle(13) & 0 & 0 & \langle\delta\dot{\pi}_aQ_\alpha\rangle(13)\\ 0 & 0 & \langle\dot{Q}_\alpha\delta\theta\rangle(13), & \langle\dot{Q}_\alpha\delta\pi_a\rangle(13) & 0\end{bmatrix}, \tag{2.25}$$

where $\langle\dot{Q}_\alpha\delta n\rangle(12)$ vanishes, because of the defining relationships Eqs. (2.15) and (2.19), and

$$\langle\dot{A}B\rangle(12)=-\langle A\dot{B}\rangle(12)\ . \tag{2.26}$$

We have also used the fact that $\vec{J}$ and $\vec{Q}$ are "odd" in momentum while the other variables are even. In addition, as constructed,

$$\langle\delta\vec{A}\delta\vec{A}\rangle^{-1}(32)=\begin{bmatrix} K(32) & 0 & 0 & 0 & 0\\ 0 & \langle J_\alpha J_\gamma\rangle^{-1}(32) & 0 & 0 & 0\\ 0 & 0 & \mathscr{C}_v(32) & 0 & 0\\ 0 & 0 & 0 & \Sigma_{ab}^{-1}(32) & 0\\ 0 & 0 & 0 & 0 & \mathscr{Q}_{\alpha\gamma}^{-1}(32)\end{bmatrix}, \tag{2.27}$$

with

$$\Sigma_{ab}(12)\equiv\langle\delta\pi_a\delta\pi_b\rangle(12)\ , \tag{2.28}$$

and

$$\mathscr{Q}_{\alpha\gamma}(12)\equiv\langle Q_\alpha Q_\gamma\rangle(12)\ . \tag{2.29}$$

Now recalling from Eqs. (2.3) that the frequency matrix is given by the product of these matrices, we obtain the equations of motion, Eq. (2.2), as

$$\delta\dot{n}(1t)\equiv\langle\delta\dot{n}J_\alpha\rangle(1\bar{3})\langle J_\alpha J_\gamma\rangle^{-1}(\overline{32})J_\gamma(\bar{2}t)\ , \tag{2.30}$$

$$\dot{J}_\alpha(1t)=\langle\dot{J}_\alpha\delta n\rangle(1\bar{3})K(\overline{32})\delta n(\bar{2}t)+\langle\dot{J}_\alpha\delta\theta\rangle(1\bar{3})\mathscr{C}_v(\overline{32})\delta\theta(\bar{2}t)$$
$$+\langle\dot{J}_\alpha\delta\pi_a\rangle(1\bar{3})\Sigma_{ab}^{-1}(\overline{32})\delta\pi_b(\bar{2}t)\ , \tag{2.31}$$

$$\delta\dot{\theta}(1t)=\langle\delta\dot{\theta}J_\alpha\rangle(1\bar{3})\langle J_\alpha J_\gamma\rangle^{-1}(\overline{32})J_\gamma(\bar{2}t)+\langle\delta\dot{\theta}Q_\alpha\rangle(1\bar{3})\mathcal{D}_{\alpha\gamma}^{-1}(\overline{32})Q_\gamma(\bar{2}t)\,, \tag{2.32}$$

$$\begin{aligned}\delta\dot{\pi}_a(1t)=&\langle\delta\dot{\pi}_aJ_\alpha\rangle(1\bar{3})\langle J_\alpha J_\gamma\rangle^{-1}(\overline{32})J_\gamma(\bar{2}t)+\langle\delta\dot{\pi}_aQ_\alpha\rangle(1\bar{3})\mathcal{D}_{\alpha\gamma}^{-1}(\overline{32})Q_\gamma(\bar{2}t)\\&-\int_0^t\phi_{ab}^{\pi}(1\bar{2},t-u)\delta\pi_b(\bar{2}u)du-\int_0^t\phi_{\alpha\gamma}^{\pi Q}(1\bar{2},t-u)Q_\gamma(\bar{2}u)du+f_a^{\pi}(1t)\,,\end{aligned} \tag{2.33}$$

and

$$\begin{aligned}\dot{Q}_\alpha(1t)=&\langle\dot{Q}_\alpha\delta\theta\rangle(1\bar{3})\mathscr{C}_v(\overline{32})\delta\theta(\bar{2}t)+\langle\dot{Q}_\alpha\delta\pi_a\rangle(1\bar{3})\Sigma_{ab}^{-1}(\overline{32})\delta\pi_b(\bar{2}t)\\&-\int_0^t\phi_{\alpha\gamma}^{Q}(1\bar{2},t-u)Q_\gamma(\bar{2}u)du-\int_0^t\phi_{ab}^{Q\pi}(1\bar{2},t-u)\delta\pi_b(\bar{2}u)du+f_\alpha^{Q}(\bar{2}u)\,.\end{aligned} \tag{2.34}$$

The random force and damping matrix terms are absent in Eqs. (2.30), (2.31), and (2.32) due to conservation laws. The sum rules appearing in Eqs. (2.30)–(2.34) are given in Appendix B.

For convenience we now introduce the simple sum rule

$$\langle J_\alpha J_\gamma\rangle(12)=\mu\beta^{-1}\delta_{\alpha\gamma}n(1)\delta(12)\,, \tag{2.35}$$

where β is the inverse temperature measured in energy units, which implies

$$\langle J_\alpha J_\gamma\rangle^{-1}(12)=\frac{\delta_{\alpha\gamma}\delta(12)}{\mu\beta^{-1}n(1)}\,. \tag{2.36}$$

Using this and the defining relationships, Eqs. (2.15)–(2.23), we obtain

$$\delta\dot{n}(1t)=-\frac{1}{\mu}\nabla_{1,\alpha}J_\alpha(1t)\,, \tag{2.37}$$

$$\dot{J}_\alpha(1t)=-\beta^{-1}n(1)\nabla_{1,\alpha}K(1\bar{2})\delta n(\bar{2}t)-\nabla_{1,\gamma}[\langle\delta S_{\gamma\alpha}\delta\theta\rangle(1\bar{3})\mathscr{C}_v(\overline{32})]\delta\theta(\bar{2}t)-\nabla_{1,\gamma}\delta\pi_{\gamma\alpha}(1t)\,, \tag{2.38}$$

$$\delta\dot{\theta}(1t)=-\langle\delta\theta\delta S_{\alpha\gamma}\rangle(1\bar{2})\overline{\nabla}_{2,\alpha}\left[\frac{J_\gamma(\bar{2}t)}{\mu\beta^{-1}n(\bar{2})}\right]-\mathscr{C}_v^{-1}(1\bar{2})\overline{\nabla}_{2,\alpha}Q_\alpha(\bar{2}t)\,, \tag{2.39}$$

$$\begin{aligned}\delta\dot{\pi}_a(1t)=&-{}^a\Sigma_{\alpha\gamma}(1\bar{2})\overline{\nabla}_{2,\alpha}\left[\frac{J_\gamma(\bar{2}t)}{\mu\beta^{-1}n(\bar{2})}\right]+\langle\delta\dot{\pi}_aQ_\alpha\rangle(1\bar{3})\mathcal{D}_{\alpha\gamma}^{-1}(\overline{32})Q_\gamma(\bar{2}t)\\&-\int_0^t\phi_{ab}^{\pi}(1\bar{2},t-u)\delta\pi_b(\bar{2}u)du-\int_0^t\phi_{a\gamma}^{\pi Q}(1\bar{2},t-u)Q_\gamma(\bar{2}u)du+f_a^{\pi}(1t)\,,\end{aligned} \tag{2.40}$$

and

$$\begin{aligned}\dot{Q}_\alpha(1t)=&-\mathcal{D}_{\alpha\gamma}(1\bar{2})\overline{\nabla}_{2,\gamma}\delta\theta(\bar{2}t)+\langle\dot{Q}_\alpha\delta\pi_a\rangle(1\bar{3})\Sigma_{ab}^{-1}(\overline{32})\delta\pi_b(\bar{2}t)\\&-\int_0^t\phi_{\alpha\gamma}^{Q}(1\bar{2},t-u)Q_\gamma(\bar{2}u)du-\int_0^t\phi_{ab}^{Q\pi}(1\bar{2},t-u)\delta\pi_b(\bar{2}u)du+f_\alpha^{Q}(1t)\,.\end{aligned} \tag{2.41}$$

These are the exact equations of motion for an inhomogeneous fluid. We note that Eqs. (2.37), (2.38), and (2.39) are completely equivalent to Eqs. (2.15), (2.16), and (2.17). In Sec. III A we evaluate and interpret the sum rules appearing in Eqs. (2.37)–(2.41).

III. INTERPRETATION OF THE EQUATIONS OF MOTION

A. Discussion of relevant sum rules

The evaluation of the sum rules appearing in Eqs. (2.37)–(2.41) is straightforward but often long and tedious. The procedure for obtaining some of them has been given in the literature.[5] We list our results in Appendix B. We stress the microscopic nature of these sum rules, i.e., their explicit dependence upon the molecular interaction. We note, in particular, that a knowledge of the four-body distribution function is sufficient to give all the sum rules and thus all the mean-field level (without the damping matrix) dynamics. This is because we have assumed a pairwise additive interaction. More generally, if we assume an s-body, nonadditive interaction it is easy to see that we will require the $2s$-body distribution function, We have also calculated sum rules which are first and second order in time. These will be reported elsewhere as they are not explicitly relevant for our discussion in this paper, though they can be used to increase our understanding of the damping matrix.[3,5]

To interpret these sum rules we appeal to the general theory of thermodynamic fluctuations[11] as well as the work of Schofield[2] on homogeneous fluids. Our rationale for interpreting $\delta\theta$, defined by Eq. (2.18), as the temperature fluctuation follows from the general theory of fluctuations. There the temperature fluctuation is seen to be a linear combination of the energy and density fluctuations, orthogonal to the density fluctuations. Its correlation with itself is $(k\beta^2)^{-1}$ times the inverse of the heat capacity (k is Boltzmann's constant). Thus we define $\delta\theta$ and $\mathscr{C}_v$ by Eqs. (2.18) and (2.23).

We can relate $\mathscr{C}_v(12)$ to functional derivatives as follows. We rewrite Eq. (2.18) as

$$\delta H(1t)=[\mathscr{C}_v(1\bar{2})]\delta\theta(\bar{2}t) +[\langle\delta H\delta n\rangle(1\bar{3})K(\overline{32})]\delta n(\bar{2}t)\,. \tag{3.1}$$

Then, noting the implied integrations over barred variables, we have

$$\left.\frac{\delta H(1)}{\delta\theta(2)}\right|_{n(2)}=\mathscr{C}_v(12)\,, \tag{3.2}$$

and

$$\left.\frac{\delta H(1)}{\delta n(2)}\right|_{\theta(2)}=\langle\delta H\delta n\rangle(1\bar{3})K(\bar{3}2)\,. \tag{3.3}$$

Thus it is reasonable to call $\mathscr{C}_v(12)$ the nonlocal heat capacity per unit volume of the inhomogeneous fluid.

Similarly one can examine the thermodynamic pressure fluctuation, from Eq. (2.21):

$$\delta\sigma_a(1t)=[\langle\delta S_a\delta\theta\rangle(1\bar{3})\mathscr{C}_v(\overline{32})]\delta\theta(\bar{2}t) +[\langle\delta S_a\delta n\rangle(1\bar{3})K(\overline{32})]\delta n(\bar{2}t)\,,$$

from which we obtain

$$\left.\frac{\delta\sigma_a(1)}{\delta\theta(2)}\right|_{n(2)}=\langle\delta S_a\delta\theta\rangle(1\bar{3})\mathscr{C}_v(\bar{3}2) \tag{3.4}$$

and

$$\left.\frac{\delta\sigma_a(1)}{\delta n(2)}\right|_{\theta(2)}=\langle\delta S_a\delta n\rangle(1\bar{3})K(\bar{3}2)\,. \tag{3.5}$$

We can alternatively approach this problem directly from the grand partition function.

We introduce the following quantities: the energy density, from Eq. (2.11),

$$E(1)\equiv\langle H(1)\rangle=\tfrac{3}{2}\beta^{-1}n(1)+V_1(1)n(1) +\tfrac{1}{2}V_2(1\bar{4})n_2(1\bar{4})\,, \tag{3.6}$$

and the pressure tensor from Eq. (2.13),

$$P_{\alpha\gamma}(1)\equiv\langle S_{\alpha\gamma}(1)\rangle=\delta_{\alpha\gamma}\beta^{-1}n(1)-\tfrac{1}{2}\int d^3r\frac{r_\alpha r_\gamma}{r}\frac{dV_2(r)}{dr}\int_0^1 d\lambda\, n_2(1'1'')\,, \tag{3.7}$$

with

$$\vec{1}'\equiv\vec{1}+(1-\lambda)\vec{r}\,,$$

$$\vec{1}''\equiv\vec{1}-\lambda\vec{r}\,,$$

and

$$n_s(1\cdots s)\equiv\left\langle\sum_{i,j\cdots k}{}'\,\delta(\vec{r}_1-\vec{R}_i)\cdots\delta(\vec{r}_s-\vec{R}_k)\right\rangle\,, \tag{3.8}$$

the s-body distribution function. The prime on the summation means that $i,j \cdots k$ are all distinct.

We can write Eq. (3.8) more explicitly as

$$n_s(1\cdots s)=\frac{1}{\mathscr{Z}}\sum_{N=s}^{\infty}\frac{\zeta^N}{(N-s)!}\exp[-\beta V_N(\vec{r}_1\cdots\vec{r}_s,\vec{\bar{R}}_{s+1}\cdots\vec{\bar{R}}_N)]\ , \tag{3.9}$$

with

$$\mathscr{Z}\equiv\sum_{N=0}^{\infty}\frac{\zeta^N}{N!}\exp[-\beta V_N(\vec{\bar{R}}_1\cdots\vec{\bar{R}}_N)]\ , \tag{3.10}$$

the grand partition function. Here, V_N is the total potential from Eqs. (2.8), while ζ is the fugacity.

From these we obtain the relationships

$$\left.\frac{\delta n_2(12)}{\delta n(3)}\right|_{\beta}=\langle\delta n_2\delta n\rangle(12,\bar{4})K(\bar{4}3) \tag{3.11}$$

and

$$\left.\frac{\delta n_2(12)}{\delta(-\beta[n(3)])}\right|_{n(3)}=\tfrac{1}{2}N_4(12,\bar{4}3)V_2(\bar{4}3)\ . \tag{3.12}$$

Note that $\delta/(\delta\beta[n(1)])$ is the functional variation with respect to the temperature of an ensemble *with a prescribed density profile, n(1).*

We now introduce the reduced distribution functions appearing in Appendix B and Eqs. (3.11) and (3.12):

$$\langle\delta n_2\delta n\rangle(12,3)\equiv n_3(123)-n_2(12)n(3)+n_2(12)[\delta(13)+\delta(23)]\ , \tag{3.13}$$

$$\begin{aligned}\langle\delta n_2\delta n_2\rangle(12,34)\equiv{}& n_4(1234)-n_2(12)n_2(34)+n_3(123)[\delta(14)+\delta(24)]\\&+n_3(124)[\delta(13)+\delta(23)]+n_2(12)[\delta(13)\delta(24)+\delta(14)\delta(23)]\ ,\end{aligned} \tag{3.14}$$

$$N_3(1,23)\equiv n_3(123)-\frac{n_2(12)n_2(13)}{n(1)}+n_2(12)\delta(23)\ , \tag{3.15}$$

and

$$N_4(12,34)\equiv\langle\delta n_2\delta n_2\rangle(12,34)-\langle\delta n_2\delta n\rangle(12,\bar{5})K(\overline{56})\langle\delta n\delta n_2\rangle(\bar{6},34)\ . \tag{3.16}$$

Now from Eqs. (3.6) and (3.7) and Eqs. (3.11) and (3.12) we obtain the following:

$$\begin{aligned}\frac{\delta E(1)}{\delta(-\beta[n(2)])}&=\tfrac{3}{2}\beta^{-2}n(1)\delta(12)+\tfrac{1}{4}V_2(1\bar{3})N_4(1\bar{3},\bar{4}2)V_2(\bar{4}2)\\&=\mathscr{C}_v(12)\end{aligned} \tag{3.17}$$

and

$$\begin{aligned}\frac{\delta E(1)}{\delta n(2)}&=\tfrac{3}{2}\beta^{-1}\delta(12)+V_1(1)\delta(12)+\tfrac{1}{2}V_2(1\bar{3})\langle\delta n_2\delta n\rangle(1\bar{3},\bar{4})K(\bar{4}2)\\&=\langle\delta H\delta n\rangle(1\bar{3})K(\bar{3}2)\ .\end{aligned} \tag{3.18}$$

Also,

$$\begin{aligned}\frac{\delta P_{\alpha\gamma}(1)}{\delta(-\beta[n(2)])}&=\delta_{\alpha\gamma}\beta^{-2}n(1)\delta(12)-\tfrac{1}{2}\int d^3r\frac{r_\alpha r_\gamma}{r}\frac{dV_2(r)}{dr}\int_0^1 d\lambda\,N_4(1'1'',\bar{3}2)V_2(\bar{3}2)\\&=\langle\delta S_{\alpha\gamma}\delta\theta\rangle(1\bar{3})\mathscr{C}_v(\bar{3}2)\ ,\end{aligned} \tag{3.19}$$

and

$$\frac{\delta P_{\alpha\gamma}(1)}{\delta n(2)} = \delta_{\alpha\gamma}\beta^{-1}\delta(12) - \tfrac{1}{2}\int d^3r \frac{r_\alpha r_\gamma}{r}\frac{dV_2(r)}{dr}\int_0^1 d\lambda \langle \delta n_2 \delta n \rangle (1'1'',\bar{3})K(\bar{3}2)$$

$$= \langle \delta S_{\alpha\gamma}\delta n \rangle (1\bar{3})K(\bar{3}2) \,. \tag{3.20}$$

From Eq. (3.20) and the definitions Eqs. (2.15) and (2.17), it is easy to see that

$$-\beta^{-1}n(1)\nabla_{1,\gamma}K(12) = -\nabla_{1,\alpha}\left[\frac{\delta P_{\alpha\gamma}(1)}{\delta n(2)}\right] - [\nabla_{1,\gamma}V_1(1)]\delta(12) \,. \tag{3.21}$$

Thus the results in Eqs. (3.17)–(3.20) explicitly confirm the prescriptions given in Eqs. (3.2)–(3.5).

B. Pressure-entropy representation

We now briefly discuss another representation for $\delta\vec{A}$, using the variables of Eqs. (2.9)–(2.13), and call it the pressure-entropy representation. We introduce a microscopic variable analogous to the entropy fluctuations, $\delta\Lambda$, as[2]

$$(k\beta)^{-1}\delta\Lambda(1t) = \mathscr{C}_v(1\bar{2})\delta\theta(\bar{2}t) + (k\beta)^{-1}\langle \delta\Lambda\delta n \rangle (1\bar{3})K(\bar{3}\bar{2})\delta n(\bar{2}t) \,, \tag{3.22}$$

which has been appropriately normalized. From the criteria of the general theory of thermodynamic fluctuations we must have[11]

$$\langle \delta\Lambda\delta\sigma_a \rangle (12) \equiv 0 \tag{3.23}$$

so that

$$-\mathscr{C}_v(1\bar{3})\langle \delta\theta\delta\sigma_a \rangle (\bar{3}2) = (k\beta)^{-1}\langle \delta\Lambda\delta n \rangle (1\bar{3})K(\bar{3}\bar{4})\langle \delta n\delta\sigma_a \rangle (\bar{4}2) \,, \tag{3.24}$$

which determines $\langle \delta\Lambda\delta n \rangle (12)$.

We also define the correlation of $\delta\Lambda$ with itself as

$$\mathscr{C}_p(12) \equiv (k\beta)^{-2}\langle \delta\Lambda\delta\Lambda \rangle (12)$$

$$= \mathscr{C}_v(12) + (k\beta)^{-2}\langle \delta\Lambda\delta n \rangle (1\bar{3})K(\bar{3}\bar{4})\langle \delta n\delta\Lambda \rangle (\bar{4}2) \,. \tag{3.25}$$

Note that from Eq. (3.22) and the prescription of Eqs. (3.1)–(3.5), we can relate $\delta\Lambda/\delta n\,|_\theta$ to $\langle \delta\Lambda\delta n \rangle K$ (and to $K\langle \delta n\delta\Lambda \rangle$ also). Also recall that for a homogeneous system $K^{-1}(12)$ is directly related to the isothermal compressibility.[11] We will not pursue this interpretation further at this time, however, now we can see that Eq. (3.25) is in the form of the familiar thermodynamic identity between the heat capacities.[11]

We relate $\mathscr{C}_p(12)$ to a functional derivative as follows. We formally write

$$\delta\theta(1t) = \langle \delta\theta\delta\Lambda \rangle (1\bar{3})\langle \delta\Lambda\delta\Lambda \rangle^{-1}(\bar{3}\bar{2})\delta\Lambda(\bar{2}t) + \langle \delta\theta\delta\sigma_a \rangle (1\bar{3})\langle \delta\sigma_a\delta\sigma_b \rangle^{-1}(\bar{3}\bar{2})\delta\sigma_b(\bar{2}t) \,,$$

which we rearrange as

$$\delta\Lambda(1t) = [(k\beta)^{-1}\langle \delta\Lambda\delta\Lambda \rangle (1\bar{2})]\delta\theta(\bar{2}t) + [\,\cdots\,]_b(1\bar{2})\delta\sigma_b(\bar{2}t) \,. \tag{3.26}$$

As above then, we write

$$(k\beta)^{-1}\left.\frac{\delta\Lambda(1)}{\delta\theta(2)}\right|_{\sigma_a(2)} = (k\beta)^{-1}\langle \delta\Lambda\delta\Lambda \rangle (12) = \mathscr{C}_p(12) \,. \tag{3.27}$$

Thus we call $\mathscr{C}_p(12)$ the generalized nonlocal heat capacity per unit volume at constant thermodynamic pressure.

C. Equations of motion recast: hydrodynamic form

Now, from the discussion above, we can write the equations of motion for $\delta\vec{A} \equiv (\delta n, \vec{J}, \delta T, \delta\overleftrightarrow{\pi}, Q)$, where we have properly normalized variables as

$$\delta T(1t) \equiv \frac{1}{k\beta^2}\delta\theta(1t) \tag{3.28}$$

and

$$C_v(12) \equiv k\beta^2 \mathscr{C}_v(12) \;. \tag{3.29}$$

The equations of motion are

$$\delta\dot{n}(1t) = -\frac{1}{\mu}\nabla_{1,\alpha}J_\alpha(1t) \;, \tag{3.30}$$

$$\dot{J}_\alpha(1t) = -\beta^{-1}n(1)\nabla_{1,\alpha}K(1\bar{2})\delta n(\bar{2}t) + k\beta^2\nabla_{1,\gamma}\frac{\delta P_{\gamma\alpha}(1)}{\delta\beta(n(\bar{2}))}\delta T(\bar{2}t) - \nabla_{1,\gamma}\delta\pi_{\gamma\alpha}(1t) \;, \tag{3.31}$$

$$\delta\dot{T}(1t) = \frac{\beta}{\mu}C_v^{-1}(1\bar{3})\frac{\delta P_{\alpha\gamma}(\bar{2})}{\delta\beta(n(\bar{3}))}\bar{\nabla}_{2,\alpha}\left[\frac{J_\gamma(\bar{2}t)}{n(\bar{2})}\right] - C_v^{-1}(1\bar{2})\bar{\nabla}_{2,\alpha}Q_\alpha(\bar{2}t) \;, \tag{3.32}$$

$$\begin{aligned}\delta\dot{\pi}_a(1t) = {} & \frac{-\beta}{\mu}\,{}^{a}\Sigma_{\alpha\gamma}(1\bar{2})\bar{\nabla}_{2,\alpha}\left[\frac{J_\gamma(\bar{2}t)}{n(\bar{2})}\right] + \langle\delta\dot{\pi}_a Q_a\rangle(1\bar{3})\mathscr{Q}_{\alpha\gamma}^{-1}(\overline{32})Q_\gamma(\bar{2}t) \\ & - \int_0^t \phi_{ab}^{\pi}(1\bar{2},t-u)\delta\pi_b(\bar{2}u)du - \int_0^t \phi_{a\gamma}^{\pi Q}(1\bar{2},t-u)Q_\gamma(\bar{2}u)du + f_a^{\pi}(1t) \;,\end{aligned} \tag{3.33}$$

and

$$\begin{aligned}\dot{Q}_\alpha(1t) = {} & -k\beta^2\mathscr{Q}_{\alpha\gamma}(1\bar{2})\bar{\nabla}_{2,\gamma}\delta T(\bar{2}t) + \langle\dot{Q}_\alpha\delta\pi_a\rangle(1\bar{3})\Sigma_{ab}^{-1}(\overline{32})\delta\pi_b(\bar{2}t) \\ & - \int_0^t \phi_{\alpha\gamma}^{Q}(1\bar{2},t-u)Q_\gamma(\bar{2}u)du - \int_0^t \phi_{ab}^{Q\pi}(1\bar{2},t-u)\delta\pi_b(\bar{2}u)du + f_\alpha^{Q}(1t) \;.\end{aligned} \tag{3.34}$$

For completeness, we must add to these the equation for the density profile,[8]

$$K(1\bar{2})\bar{\nabla}_{2,\alpha}n(\bar{2}) = -\beta\nabla_{1,\alpha}V_1(1) \;. \tag{3.35}$$

These are the exact dynamical equations for an inhomogeneous fluid. All the static correlation functions are known exactly in terms of the microscopic interaction; these sum rules are given in Appendix B. In particular, note the correlation function $K(12)$ appearing in Eq. (3.31). $K(12)$ is connected to the direct correlation function by

$$K(12) = \frac{\delta(12)}{n(1)} - C(12) \;,$$

where $C(12)$ is the direct correlation function. Also note its connection to $\delta P/\delta n$ through Eq. (3.21). $K(12)$ is discussed further in Sec. IV C.

An equivalent representation of the dynamics can be obtained similarly, with $\delta\vec{A} \equiv (\delta\overleftrightarrow{\sigma}, \vec{J}, \delta\Lambda, \delta\overleftrightarrow{\pi}, \vec{Q})$, as

$$\delta\dot{\sigma}_a(1t) = \frac{-\beta}{\mu}\langle\delta\sigma_a\delta\sigma_{\alpha\gamma}\rangle(1\bar{2})\bar{\nabla}_{2,\alpha}\left[\frac{J_\gamma(\bar{2}t)}{n(\bar{2})}\right] + k\beta^2\frac{\delta P_a(1)}{\delta\beta(n(\bar{3}))}C_v^{-1}(\overline{32})\bar{\nabla}_{2,\alpha}Q_\alpha(\bar{2}t) \;, \tag{3.36}$$

$$\dot{J}_\alpha(1t) = -\delta n(1t)\nabla_{1,\alpha}V_1(1) - \nabla_{1,\gamma}\delta\sigma_{\gamma\alpha}(1t) - \nabla_{1,\gamma}\delta\pi_{\gamma\alpha}(1t) \;, \tag{3.37}$$

$$\delta\dot{\Lambda}(1t) = -k\beta\nabla_{1,\alpha}Q_\alpha(1t) \;, \tag{3.38}$$

$$\begin{aligned}\delta\dot{\pi}_a(1t) = {} & \frac{-\beta}{\mu}\,{}^{a}\Sigma_{\alpha\gamma}(1\bar{2})\bar{\nabla}_{2,\alpha}\left[\frac{J_\gamma(\bar{2}t)}{n(\bar{2})}\right] + \langle\delta\dot{\pi}_a Q_\alpha\rangle(1\bar{3})\mathscr{Q}_{\alpha\gamma}^{-1}(\overline{32})Q_\gamma(\bar{2}t) \\ & - \int_0^t \phi_{ab}^{\pi}(1\bar{2},t-u)\delta\pi_b(\bar{2}u)du - \int_0^t \phi_{a\gamma}^{\pi Q}(1\bar{2},t-u)Q_\gamma(\bar{2}u)du + f_a^{\pi}(1t) \;,\end{aligned} \tag{3.39}$$

and

$$\dot{Q}_\alpha(1t) = -k\beta^2 \mathscr{D}_{\alpha\gamma}(1\bar{3})\bar{\nabla}_{3,\gamma}\left[C_p^{-1}(\overline{32})\frac{1}{k\beta}\delta\Lambda(\bar{2}t) - C_v^{-1}(\overline{34})\frac{\delta P_a(\bar{5})}{\delta\beta[u(\bar{4})]}\langle \delta\sigma_a\delta\sigma_b\rangle^{-1}(\overline{52})\delta\sigma_b(\bar{2}t)\right]$$

$$+\langle \dot{Q}_\alpha \delta\pi_a\rangle(1\bar{3})\Sigma_{ab}^{-1}(\overline{32})\delta\pi_b(\bar{2}t) - \int_0^t \phi^{Q}_{\alpha\gamma}(1\bar{2},t-u)Q_\gamma(\bar{2}u)du$$

$$-\int_0^t \phi^{Q\pi}_{ab}(1\bar{2},t-u)\delta\pi_b(\bar{2}u)du + f^{Q}_{\alpha}(1t)\;, \tag{3.40}$$

where

$$C_p(12) \equiv k\beta^2 \mathscr{C}_p(12)\;. \tag{3.41}$$

This set of equations also provides an exact description of nonuniform fluid dynamics; the set is completely equivalent to Eqs. (3.30)–(3.34). In an inhomogeneous system where inhomogeneity is unidirectional, $\delta\sigma_{\alpha\gamma}$ will simplify. This makes the pressure-entropy representation more tractable.

IV. BROKEN SYMMETRY ONLY IN Z DIRECTION

A. Approximate form of the damping matrix

We now consider a liquid-vapor system with a diffuse planar interface in the xy plane. Since the translational symmetry is broken only in the z direction, many simplifications result. Specifically, the external field can be chosen to be gravitational:

$$V_1(1) = \mu g z_1\;. \tag{4.1}$$

After formal calculations we usually take the limit $g \to 0^+$ so that fluid behavior is determined by intrinsic quantities alone.

Now, it is easy to see from Eq. (2.21) and Appendix B that

$$\delta\sigma_{\alpha\gamma} = \mathrm{diag}[\delta\sigma_{xx}, \delta\sigma_{xx}, \delta\sigma_{zz}]\;. \tag{4.2}$$

Similarly, from Eq. (3.19),

$$\frac{\delta P_{\alpha\gamma}}{\delta\beta} = \mathrm{diag}\left[\frac{\delta P_{xx}}{\delta\beta}, \frac{\delta P_{xx}}{\delta\beta}, \frac{\delta P_{zz}}{\delta\beta}\right]\;. \tag{4.3}$$

Baus[14] has discussed the characteristic symmetries of the elastic moduli. Following that work we can write

$$\Sigma_{ab} = \begin{bmatrix} \Sigma_{11} & \Sigma_{12} & \Sigma_{13} & 0 & 0 & 0 \\ \Sigma_{21} & \Sigma_{11} & \Sigma_{13} & 0 & 0 & 0 \\ \Sigma_{31} & \Sigma_{31} & \Sigma_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & \Sigma_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & \Sigma_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & \Sigma_{66} \end{bmatrix}\;. \tag{4.4}$$

We note that Eq. (4.2) implies the same form for

$$\Sigma'_{ab} \equiv \Sigma_{ab} + \langle \delta\sigma_a \delta\sigma_b\rangle\;. \tag{4.5}$$

We also emphasize the property

$$\Sigma_{ab}(12) = \Sigma_{ba}(21)\;, \tag{4.6}$$

which follows from the definition, Eq. (2.28). The moduli introduced by Baus can be obtained exactly from Appendix B, i.e.,

$$C_{ab}(12) \equiv \frac{\beta}{2}[\Sigma'_{ab}(12) + \Sigma'_{ba}(12)]\;, \tag{4.7}$$

where $C_{ab}(12)$ are the elastic moduli. The macroscopic moduli introduced and discussed by Baus are recovered in a straightforward fashion from the connection

$$C_{ab}(z) \equiv C_{ab}(\overline{12})\delta(\bar{z}_2 - z)\;. \tag{4.8}$$

In order to close the set of equations of motion for $\delta\vec{A}$, we use Markov approximation on the memory kernels. In the manner of Akcasu and Daniels,[1] who used the direction of the wave vector $\vec{k}$ in a homogeneous system, we use the unidirectional broken symmetry in the z direction to approximate the damping matrix, ϕ^{π}_{ab} and $\phi^{Q}_{\alpha\gamma}$. The symmetry of the damping matrix is recognized by examining the system in the steady state; see, for example, Eqs. (4.14)–(4.16). Then a local approximation in space and time and the use of unidirectional inhomogeneity as well as isotropy of the bulk phases leads to the parametrization

$$\phi^{\pi}_{ab}(12,t')\simeq\delta(12)\delta(t')\mathrm{diag}[\omega_{66}(1),\omega_{66}(1),\omega_{66}(1),\omega_{44}(1),\omega_{44}(1),\omega_{66}(1)]\ , \tag{4.9}$$

and

$$\phi^{Q}_{\alpha\gamma}(12,t')\simeq\delta(12)\delta(t')\mathrm{diag}[\omega_{xx}(1),\omega_{xx}(1),\omega_{zz}(1)]\ , \tag{4.10}$$

for the memory kernels. One way to approximately evaluate various ω's in Eqs. (4.9) and (4.10) is to use higher-order sum rules. We shall not do that here. Equations (4.9) and (4.10) close the set of equations, (3.30)–(3.34) or (3.36)–(3.40).

B. Approximate forms of the sum rules

The sum rules given in Appendix B require a knowledge of the three- and four-body distribution functions. Some approximations can be made to simplify these expressions.

From the definition of $N_3(1,23)$, Eq. (3.15), it is easy to see that it is zero unless points $\vec{2}$ and $\vec{3}$ are close. Thus to an excellent approximation we can write

$$N_3(1,\overline{23})f(\overline{2},\overline{3})\simeq N_3(1,\overline{23})f(\overline{2},\overline{2})=0 \tag{4.11}$$

for an arbitrary function $f(2,3)$, because

$$N(1,2\overline{3})=0 \tag{4.12}$$

exactly, from Eq. (3.15). This results in a great simplification to all the sum rules involving $N_3(1,23)$: e.g., from Appendix B

$$\mathscr{Q}_{\alpha\gamma}(12)\simeq\frac{5}{2\mu\beta^3}\delta_{\alpha\gamma}\delta(12)n(1)\ . \tag{4.13}$$

We can use Eq. (4.13) to investigate thermal conductivity. In the steady state,[15] we write for Eq. (3.34), using Eq. (4.10) above,

$$\begin{aligned}0=&-\mathscr{Q}_{\alpha\gamma}(12)\overline{\nabla}_{2,\gamma}\{\delta T(\overline{2}t)\}k\beta^2\\&-\omega_{\alpha\alpha}\{Q_\alpha(1t)\}\ ,\end{aligned} \tag{4.14}$$

with *no* implied summation over α. In Eq. (4.14) we have neglected coupling between the heat mode and the viscosity. Thus, using Eq. (4.13) we obtain

$$\{Q_\alpha(1t)\}=-\kappa_\alpha(1)\nabla_{1,\alpha}\{\delta T(1t)\}\ , \tag{4.15}$$

again with no impled summation of α, where κ_α is the thermal conductivity tensor

$$\kappa_\alpha(1)\equiv\frac{5kn(1)}{2\mu\beta\omega_{\alpha\alpha}(1)}\ , \tag{4.16}$$

which is the same form as that given by Grad.[10] [In Eqs. (4.14) and (4.15), $\{\cdots\}$ indicates a steady-state average; $\{f^{Q}_{\alpha}\}=0$.]

Actually, of course this is how we recognize the symmetric forms of Eq. (4.9) and (4.10), through examination of the steady-state form of Eqs. (3.33) and (3.34).[1] Similarly we can approximate $N_4(12,34)$. Here we use the generalized Kirkwood superposition approximation[16] (GKSA). We define

$$g(12\cdots s)\equiv\frac{n_s(12\cdots s)}{n(1)n(2)\cdots n(s)}\ . \tag{4.17}$$

Then the GKSA is

$$g(123)\simeq g(12)g(13)g(23)\ , \tag{4.18}$$

$$g(1234)\simeq g(12)g(13)g(14)g(23)g(24)g(34)\ . \tag{4.19}$$

We also note, from the form of the sum rules given in Appendix B, that we only need $N_4(12,34)$ for those configurations where $\vec{1}$ and $\vec{2}$ are close and where $\vec{3}$ and $\vec{4}$ are close. Then, using the definition of $N_4(12,34)$, Eq. (3.16), it is straightforward to obtain

$$
\begin{aligned}
N_4(12,34) \simeq{} & n(1)n(2)g(12)[\delta(13)\delta(24)+\delta(14)\delta(23)] \\
& -n(1)n(2)g(12)h(34)\{\, n(3)[\delta(14)+\delta(24)]+n(4)[\delta(13)+\delta(23)]\,\} \\
& -n(1)n(2)n(3)n(4)g(12)g(34)[h(13)+h(23)+h(14)+h(24)]\,,
\end{aligned}
\tag{4.20}
$$

where

$$h(12)\equiv g(12)-1\,. \tag{4.21}$$

Equation (4.20) can be used to put the calculated sum rules into more tractable form. In particular, the following approximation scheme emerges for $C_v(12)$. Recall,

$$C_v(12)=\tfrac{3}{2}kn(1)\delta(12)+\frac{k\beta^2}{4}V_2(1\bar{3})N_4(1\bar{3},\bar{4}2)V_2(\bar{4}2)\,. \tag{4.22}$$

Let us look in the homogeneous limit at

$$C_v \equiv \frac{1}{\Omega}C_v(\overline{12})\,, \tag{4.23}$$

where Ω is the volume. Using the form of $N_4(12,34)$ from Eq. (4.20) we obtain

$$
\begin{aligned}
C_v \simeq \tfrac{3}{2}kn + 2\pi k\beta^2 n^2 \Bigg[& \int_0^\infty dr\, r^2 g(r)[V_2(r)]^2 - 8\pi n \left[\int_0^\infty dr\, r^2 g(r)V_2(r) \right] \\
& \times \left[\int_0^\infty dr'(r')^2 h(r')V_2(r') \right. \\
& \left. \quad + 4\pi n \int_0^\infty dr'(r')^2 h(r') \int_0^\infty dr''(r'')^2 g(r'')V_2(r'') \right] \Bigg]\,.
\end{aligned}
\tag{4.24}
$$

This then leads us to the following local approximation of the nonlocal heat capacity:

$$
\begin{aligned}
C_v(12) \simeq \big(\tfrac{3}{2}kn(1) + \tfrac{1}{2}k\beta^2\{ & [V_2(1\bar{4})]^2 n_2(1\bar{4}) - 2V_2(1\bar{4})n_2(1\bar{4})h(\overline{45})n(\bar{5})V_2(\overline{45}) \\
& - 2V_2(1\bar{4})n_2(1\bar{4})h(1\bar{5})n_2(\overline{56})V_2(\overline{56})\,\}\big)\delta(12)\,.
\end{aligned}
\tag{4.25}
$$

Thus we see how an approximation scheme for the sum rules is approached, and have given two examples of explicit approximations.

C. Connections to previous work

We now briefly return to Eqs. (3.30)–(3.34) to note limiting cases, and so make connections to previous work.

With $\delta\theta=\delta\pi_a=Q_a=0$ we recover the dynamical mean-field equations for the density and the momentum density obtained by Triezenberg[8] and by Jhon *et al.*[5] Because both theories are isothermal, they essentially involve only the kernel $K(12)$. We note though that

$$K(12)=\frac{\delta(12)}{n(1)}-C(12)\,,$$

where $C(12)$ is the direct correlation function,[17] is the sum rule upon which much of the crucial equilibrium structure of the inhomogeneous fluid is determined. For example, the preeminent quantity involved in the equilibrium structure of the liquid-vapor interface is surface tension. Surface tension is determined in one form by $K(12)$.[8] This has been shown to be equivalent to a form involving the pairwise additive potential.[5,18] In fact, though, the form of surface tension involving $K(12)$ can be shown to be equivalent to one with a potential composed of *all* the nonadditive many-body interactions.[19] Thus we can see that within the kernel $K(12)$ there is much rich and detailed information on the equilibrium structure.

From our general equations (3.30)–(3.34) we can obtain the starting equations of (i) the van der Waals-type theory of Felderhoff[12] by setting $\delta T=\delta\pi_a=Q_a=0$, and (ii) the hydrodynamiclike theory of Turski-Langer[13] by setting $\delta\pi_a=0$, and making a simple approximation for Q_a. In contrast to these phenomenological theories we obtain microscopic expressions for the various coefficients there, rather than, for example, the square gradient ansatz for $K(12)$.

Finally we note that in the low-density limit we have recovered Grad's 13-moment equations in linearized form.[10] We shall elaborate on these further in a later paper.

V. CONCLUSIONS

In this paper we have focused on the derivation of the exact dynamical equations which, in principle, determine all properties of the inhomogeneous fluid. Because of the (constructed) resemblance of the equations to hydrodynamical equations of motion, we approach these more general equations with an intuition sharpened by experience with hydrodynamics. Thus progress can be made in understanding nonuniform fluid dynamics from a molecular basis.

We have introduced two equivalent sets of dynamical equations. They are analogous to the density-temperature and (thermodynamic) pressure-entropy representations of hydrodynamics. They both result from an identification of the relevant dynamical variables as number density, momentum density, Hamiltonian density, stress tensor, and heat current vector.

We have derived the sum rules, those static correlation function which are the elements of the frequency matrix, in terms of the microscopic interaction. These sum rules are related to functional derivatives which make their meaning more transparent, e.g., leading us to introduce generalized, nonlocal heat capacities.

A liquid-vapor system with a diffuse planar interface is a relatively simple inhomogeneous system. We have used its symmetries through the nonlocal elastic moduli and the thermal conductivity tensor, to obtain approximate forms for the damping matrix. We show the usefulness of such expressions elsewhere,[7] where we derive an expression for the transverse current-current correlation function in terms of the elastic moduli and the damping matrix.

Finally we have outlined an approximation scheme, and explicitly used it to analyze the sum rules $\mathscr{D}_{\alpha\gamma}(12)$ (and thus the thermal-conductivity tensor), and $C_v(12)$. We have also discussed the limiting behavior of the general equations, and thereby their connection to previous work.

The set of dynamical equations that we have derived can be used to tackle many problems in inhomogeneous fluid dynamics. One interesting problem is that of *longitudinal* current correlations, an examination of which should lead to a better understanding of the coupling between bulk phases and the surface "phase". Also with the general equations of motion we can approach the problems of attenuation and dispersion of capillary waves in a careful and complete manner, elucidating, in particular, the role of the heat mode and evaporation condensation.

Yet another problem that we are pursuing is the extension of the derivation presented here to generalized nonlinear hydrodynamics for inhomogeneous systems. Since our variable $\vec{J}$ is akin to $n\vec{v}$ in hydrodynamics, to a certain extent the effect of this bilinearity is contained in our equations (2.37) and (2.38) which are analogous of the continuity equation and equation of motion.

We also plan to apply these generalized hydrodynamic equations to the problem of phase separation[20] for a system which is initially quenched into the unstable region of the phase diagram. A useful start for such a study has been made recently.[21]

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APPENDIX A: NOTATION

Below we discuss the conventions we have used in this paper and elsewhere.[7] We use numbers as shorthand for field points in three ways, i.e.,

$$(1)\equiv\begin{cases}(\vec{r}_1) & \\ (\vec{q}z_1) & \text{after partial Fourier} \\ & \text{transformation}, \\ (0z_1) & \text{as above, with } \vec{q}=0,\end{cases}$$

with context telling which of these is implied.

We have used subscripts in four ways:

(i) as the particle label with Roman letters, e.g., $\vec{R}_i, \vec{p}_j$,

(ii) as the field point label 1,2,..., e.g., $\vec{r}_1$, $\vec{y}_3$, or $\nabla_{1,z}$ which is the derivative with respect to z_1,

(iii) as the Cartesian components of a vector, either Greek letters or actual components x, y, and z, e.g., J_α, δS_{xx}, and

(iv) as the components of a tensor; $a,b,\ldots$, i.e.,

$$\delta S_a \equiv \delta S_{\alpha\gamma} ,$$

where $(xx)\equiv 1$, $(yy)\equiv 2$, $(zz)\equiv 3$, $(xz)\equiv 4$, $(yz)\equiv 5$, and $(xy)\equiv 6$. Then quantities like $\Sigma_{13}\equiv {}^{xx}\Sigma_{zz}$ appear.

Rather than explicitly writing out summations and integrals we have adopted the conventions that repeated indices are implicitly summed, and barred variables are implicitly integrated, e.g.,

$$C_{44}(1\bar{3})\equiv \int d3\, C_{44}(13) .$$

In the sum rules, angular brackets $\langle \cdots \rangle$ refer to thermal averages and we write

$$\langle AB\rangle(12)\equiv\langle A(1,t=0)B(2,t=0)\rangle .$$

Steady-state averages are given by $\{ \cdots \}$, e.g.,

$$\{ \delta T(1t) \} .$$

The symbol δ is used as one of the following:

(i) the Dirac delta function, $\delta(12)\equiv\delta(\vec{r}_1-\vec{r}_2)$,

(ii) the fluctuation of a quantity about its equilibrium value, $\delta A(1t)\equiv A(1t)-\langle A(1)\rangle$, and

(iii) in functional derivatives where δ refers to a functional variation, e.g., $\delta E(1)/\delta n(2)$.

Finally we can use a Laplace transform and a partial Fourier transform, respectively, defined as

$$A(1,s)\equiv \int_0^\infty dt\, A(1,t)\exp(-st) ,$$

where $s=i\omega+\epsilon$, and

$$A(\vec{q}z_1,t)\equiv \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dy_1 A(x_1y_1z_1,t)\exp(iq_xx_1+iq_yy_1) .$$

The latter expression we can use only with unidirectional broken symmetry in the z direction. Note we are actually using the same notation for $A(\vec{q}z_1,t)$ and $A(x_1y_1z_1,t)$ [both are $A(1t)$]. Context makes it clear as to what we are referring to.

APPENDIX B: RELEVANT SUM RULES

We list below the relevant sum rules discussed in the text. The first two sum rules appear in Ref. 5; the other results are new:

$$\begin{aligned}\langle\delta n\delta n\rangle(12)&=n_2(12)-n(1)n(2)+n(1)\delta(12)\\ &=K^{-1}(12) ,\end{aligned} \tag{B1}$$

$$\langle J_\alpha J_\gamma\rangle(12)=\mu\beta^{-1}\delta_{\alpha\gamma}n(1)\delta(12) , \tag{B2}$$

$$\begin{aligned}\langle q_\alpha J_\gamma\rangle(12)=&[\tfrac{5}{2}\beta^{-2}+\beta^{-1}V_1(1)]\delta_{\alpha\gamma}\delta(12)n(1)+\frac{\beta^{-1}}{2}\delta_{\alpha\gamma}\delta(12)n_2(1\bar{3})V_2(1\bar{3})\\ &-\frac{\beta^{-1}}{2}X_{\alpha\gamma}(1,2,\bar{3})n_2(2\bar{3}) ,\end{aligned} \tag{B3}$$

where $X_{\alpha\gamma}(1,23)$ is defined in Eq. (2.14),

$$\langle\delta H\delta n\rangle(1\bar{3})K(\bar{3}2)=\tfrac{3}{2}\beta^{-1}\delta(12)+V_1(1)\delta(12)+\tfrac{1}{2}V_2(1\bar{3})\langle\delta n_2\delta n\rangle(1\bar{3},\bar{4})K(\bar{4}2) , \tag{B4}$$

$$\langle\delta S_{\alpha\gamma}\delta n\rangle(1\bar{3})K(\bar{3}2)=\delta_{\alpha\gamma}\beta^{-1}\delta(12)-\tfrac{1}{2}\int d^3r\frac{r_\alpha r_\gamma}{r}\frac{dV_2(r)}{dr}\int_0^1 d\lambda\langle\delta n_2\delta n\rangle(1'1'',\bar{3})K(\bar{3}2) , \tag{B5}$$

$$\langle\delta S_{\alpha\gamma}\delta\theta\rangle(1\bar{3})\mathscr{C}_v(\bar{3}2)=\delta_{\alpha\gamma}\beta^{-2}n(1)\delta(12)-\tfrac{1}{2}\int d^3r\frac{r_\alpha r_\gamma}{r}\frac{dV_2(r)}{dr}\int_0^1 d\lambda\, N_4(1'1'',\bar{3}2)V_2(\bar{3}2) , \tag{B6}$$

$$\begin{aligned}\mathscr{C}_v(12)&=\langle\delta H\delta H\rangle(12)-\langle\delta H\delta n\rangle(1\bar{3})K(\overline{34})\langle\delta n\delta H\rangle(\bar{4}2)\\ &=\tfrac{3}{2}\beta^{-2}n(1)\delta(12)+\tfrac{1}{4}V_2(1\bar{3})N_4(1\bar{3},\bar{4}2)V_2(\bar{4}2) ,\end{aligned} \tag{B7}$$

$$\begin{aligned}\mathcal{Q}_{\alpha\gamma}(12)&=\langle q_\alpha q_\gamma\rangle(12)-\langle q_\alpha J_\nu\rangle(1\bar{3})\langle J_\nu J_\eta\rangle^{-1}(\overline{34})\langle J_\eta q_\gamma\rangle(\bar{4}2)\\&=\frac{5\beta^{-3}}{2\mu}\delta_{\alpha\gamma}\delta(12)n(1)+\frac{\beta^{-1}}{4\mu}\delta_{\alpha\gamma}\delta(12)V_2(1\bar{4})V_2(1\bar{5})N_3(1,\overline{45})\\&\quad-\frac{\beta^{-1}}{4\mu}V_2(1\bar{4})X_{\alpha\nu}(2,1\bar{5})N_3(1,\overline{45})-\frac{\beta^{-1}}{4\mu}V_2(2\bar{4})X_{\alpha\gamma}(1,2\bar{5})N_3(2,\overline{45})\\&\quad+\frac{\beta^{-1}}{4\mu}X_{\alpha\gamma}(1,\overline{34})X_{\nu\gamma}(2,\overline{35})N_3(\bar{3},\overline{45})\;,\end{aligned}\tag{B8}$$

$$\begin{aligned}{}^{\alpha\eta}\Sigma_{\gamma\zeta}(12)&=\langle\delta S_{\alpha\eta}\delta S_{\gamma\zeta}\rangle-\langle\delta\sigma_{\alpha\eta}\delta\sigma_{\gamma\zeta}\rangle\\&=\beta^{-2}\delta(12)n(1)(\delta_{\alpha\gamma}\delta_{\eta\zeta}+\delta_{\alpha\zeta}\delta_{\eta\gamma})+\beta^{-4}\mathscr{C}_v^{-1}(12)n(1)n(2)\delta_{\alpha\eta}\delta_{\gamma\zeta}\\&\quad+\frac{\beta^{-2}}{4}n(1)\delta_{\alpha\eta}\int d^3r'\frac{r'_\gamma r'_\zeta}{r'}\frac{dV_2(r')}{dr'}\int_0^1 d\epsilon\,\mathscr{C}_v^{-1}(1\bar{4})V_2(\overline{43})N_4(\overline{43},2',2'')\\&\quad+\frac{\beta^{-2}}{4}n(2)\delta_{\gamma\zeta}\int d^3r\frac{r_\alpha r_\eta}{r}\frac{dV_2(r)}{dr}\int_0^1 d\lambda\,N_4(1'1'',\overline{43})V_2(\overline{43})\mathscr{C}_v^{-1}(\bar{4}2)\\&\quad+\tfrac{1}{4}\int d^3r\int d^3r'\frac{r_\alpha r_\eta}{r}\frac{dV_2(r)}{dr}\frac{r'_\gamma r'_\zeta}{r'}\frac{dV_2(r')}{dr'}\\&\qquad\times\int_0^1 d\lambda\int_0^1 d\epsilon[N_4(1'1'',2'2'')-\tfrac{1}{4}N_4(1'1'',\overline{65})V_2(\overline{65})\mathscr{C}_v^{-1}(\overline{54})V_2(\overline{43})N_4(\overline{43},2'2'')]\;,\end{aligned}\tag{B9}$$

$$\langle\delta\sigma_a\delta\sigma_b\rangle(12)=\langle\delta S_a\delta\theta\rangle(1\bar{3})\mathscr{C}_v(\overline{34})\langle\delta\theta\delta S_b\rangle(\bar{4}2)+\langle\delta S_a\delta n\rangle(1\bar{3})K(\overline{34})\langle\delta n\delta S_b\rangle(\bar{4}2)\;,\tag{B10}$$

$$\begin{aligned}\mathscr{C}_p(12)&=(k\beta)^{-2}\langle\delta\Lambda\delta\Lambda\rangle(12)\\&=\mathscr{C}_v(12)+(k\beta)^{-2}\langle\delta\Lambda\delta n\rangle(1\bar{3})K(\overline{34})\langle\delta n\delta\Lambda\rangle(\bar{4}2)\;,\end{aligned}$$

with $\langle\delta\Lambda\delta n\rangle$ given by Eq. (3.24) and the sum rules above:

$$\begin{aligned}\langle\delta\dot{\pi}_{\alpha\gamma}Q_v\rangle(12)&=-\frac{\beta^{-3}}{\mu}[\delta_{\alpha\gamma}\nabla_{1,\nu}+\delta_{\gamma\nu}\nabla_{1,\alpha}+\delta_{\alpha\nu}\nabla_{1,\gamma}][\delta(12)n(1)]\\&\quad+\beta^{-2}\delta_{\alpha\gamma}n(1)\mathscr{C}_v^{-1}(1\bar{3})\overline{\nabla}_{3,\eta}\mathcal{Q}_{\eta\nu}(\bar{3}2)\\&\quad+\frac{\beta^{-2}}{2\mu}\delta(12)V_2(1\bar{4})n(1)[\delta_{\alpha\nu}\nabla_{1,\gamma}+\delta_{\gamma\nu}\nabla_{1,\alpha}]\left[\frac{n_2(1\bar{4})}{n(1)}\right]\\&\quad-\frac{\beta^{-2}}{2\mu}X_{\eta\nu}(2,1\bar{4})n(1)[\delta_{\eta\alpha}\nabla_{1,\gamma}+\delta_{\eta\gamma}\nabla_{1,\alpha}]\left[\frac{n_2(1\bar{4})}{n(1)}\right]\\&\quad-\frac{\beta^{-1}}{2\mu}V_2(2\bar{4})[\nabla_{2,\nu}X_{\alpha\gamma}(1,2\bar{5})]N_3(2,\overline{45})\\&\quad+\frac{\beta^{-1}}{2\mu}[\overline{\nabla}_{3,\eta}X_{\alpha\gamma}(1,\overline{34})]X_{\eta\nu}(2,\overline{35})N_3(\bar{3},\overline{45})\\&\quad+\tfrac{1}{4}X_{\alpha\gamma}(1,\overline{76})N_4(\overline{76},\overline{54})V_2(\overline{54})\mathscr{C}_v^{-1}(\overline{43})\overline{\nabla}_{3,\eta}\mathcal{Q}_{\eta\nu}(\bar{3}2)\;.\end{aligned}\tag{B12}$$

From Sec. III,

$$E(1)=\tfrac{3}{2}\beta^{-1}n(1)+V_1(1)n(1)+\tfrac{1}{2}V_2(1\bar{4})n_2(1\bar{4})\;,\tag{B13}$$

$$P_{\alpha\gamma}(1)=\delta_{\alpha\gamma}\beta^{-1}n(1)-\tfrac{1}{2}\int d^3r\frac{r_\alpha r_\beta}{r}\frac{dV_2(r)}{dr}\int_0^1 d\lambda\,n_2(1'1'')\;.\tag{B14}$$

Also, as is shown in Sec. III A,

$$\left.\frac{\delta E(1)}{\delta n(2)}\right|_{\beta} = \langle \delta H \delta n \rangle (1\bar{3}) K(\bar{3}2) \,, \tag{B15}$$

$$\left.\frac{\delta E(1)}{\delta(-\beta[n(2)])}\right|_{n(2)} = \mathscr{C}_v(12) \,, \tag{B16}$$

$$\left.\frac{\delta P_a(1)}{\delta n(2)}\right|_{\beta} = \langle \delta S_a \delta n \rangle (1\bar{3}) K(\bar{3}2) \,, \tag{B17}$$

$$\left.\frac{\delta P_a(1)}{\delta(-\beta[n(2)])}\right|_{n(2)} = \langle \delta S_a \delta \theta \rangle (1\bar{3}) \mathscr{C}_v(\bar{3}2) \,, \tag{B18}$$

where in the equations above

$$\vec{1}\,' \equiv \vec{1} + (1-\lambda)\vec{r} \,,$$

$$\vec{1}\,'' \equiv \vec{1} - \lambda \vec{r} \,,$$

$$\vec{2}\,' \equiv \vec{2} + (1-\epsilon)\vec{r}\,' \,,$$

$$\vec{2}\,'' \equiv \vec{2} - \epsilon \vec{r}\,' \,,$$

and $\langle \delta n_2 \delta n \rangle$, $\langle \delta n_2 \delta n_2 \rangle$, N_3, and N_4 are defined by Eqs. (3.13)–(3.16).

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[*] Address until June 1, 1982: IBM Research Laboratory, San Jose, California 95193.

[1] A. Z. Akcasu and E. Daniels, Phys. Rev. A 2, 962 (1970).

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

[3] J. P. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw-Hill, New York, 1980), Chaps. 5 and 6.

[4] J. K. Percus, *Studies in Statistical Mechanics,* edited by E. Montroll and J. Lebowitz (North-Holland, Amsterdam, 1982).

[5] (a) M. S. Jhon, J. S. Dahler, and R. C. Desai, Adv. Chem. Phys. 46, 279 (1981); (b) M. S. Jhon, R. C. Desai, and J. S. Dahler, J. Chem. Phys. 70, 1544 (1979); (c) 70, 5228 (1979); (d) 68, 5615 (1978).

[6] R. Evans, Adv. Phys. 28, 143 (1979).

[7] M. Grant and R. C. Desai, *Generalized Langevin Theory for Inhomogeneous Fluids: The Transverse Current-Current Correlation Function,* J. Chem Phys. (in press).

[8] D. G. Triezenberg, Ph.D. thesis, University of Maryland, 1973 (unpublished).

[9] (a) R. Zwanzig, in *Lectures in Theoretical Physics,* edited by W. E. Brittin, W. B. Downs, and J. Downs (Interscience, New York, 1961), Vol. III; (b) H. Mori, Prog. Theor. Phys. (Kyoto) 33, 423 (1965); (c) 34, 399 (1965).

[10] H. Grad, Commun. Pure Appl. Math. 2, 331 (1949).

[11] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley, Reading, Mass. 1970), Chaps. 2 and 12.

[12] B. U. Felderhof, Physica (Utrecht) 48, 541 (1970).

[13] L. A. Turski and J. S. Langer, Phys. Rev. A 22, 2189 (1980).

[14] M. Baus, J. Chem. Phys. (in press).

[15] See Appendix A for notation.

[16] G. Stell, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and M. S. Green (Academic, New York, 1976), Vol. 5B, Chap. 3.

[17] Also note the identity, Eq. (3.21).

[18] P. Schofield, Chem. Phys. Lett. 62, 413 (1979).

[19] M. Grant and R. C. Desai, J. Chem. Phys. 72, 1482 (1980).

[20] F. F. Abraham, Phys. Rep. 53, 93 (1979).

[21] S. W. Koch, R. C. Desai, and F. F. Abraham (unpublished).