AIP | The Journal of Chemical Physics

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Citation: J. Chem. Phys. **78**, 483 (1983); doi: 10.1063/1.444473
View online: http://dx.doi.org/10.1063/1.444473
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v78/i1
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Interfacial hydrodynamics: A microscopic approach

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(Received 20 October 1981; accepted 9 February 1982)

Linearized hydrodynamic equations for a nonuniform anisotropic fluid are obtained from the exact Mori–Zwanzig equations for the conserved densities. In the particular case of a two-phase system with a planar equilibrium interface, these equations can be reduced to the ordinary hydrodynamic equations inside each bulk phase and to surface hydrodynamic equations for the interfacial layer. Surface transport coefficients and surface thermodynamic parameters are hereby obtained as Gibbs surface excess values. All the known phenomenological equations can be recovered by suitable approximations. Various correction terms to the phenomenological results, including Laplace's formula, are found.

I. INTRODUCTION

The basic concepts and equations of hydrodynamics are used in many areas of physics, chemical physics, and of the engineering sciences. The science of hydrodynamics was developed during the nineteenth century on a phenomenological basis and has become, essentially since the beginning of this century, one of the best developed chapters of macroscopic physics.[1] It has been a major concern of statistical mechanics, from its very beginning, to try to provide a microscopic framework within which the approximations which lead from the macroscopic conservation laws to the hydrodynamic equations could be analyzed and their validity discussed. For dilute gases this was achieved through the Chapman–Enskog solution of the Boltzmann equation.[2] From the experimental studies it is known however that the validity of the hydrodynamic equations does not depend on the smallness of the density and that hydrodynamics correctly describes the large scale motions of all fluids, both gases and liquids. In view of the lack of a fundamental kinetic equation for liquids, the present day justification of the hydrodynamic equations for fluids rests not on the classical kinetic theory but on the slightly more formal Mori–Zwanzig projection method.[3] This method has culminated in the formulation of generalized hydrodynamic equations from which the ordinary hydrodynamic equations can be recovered in the limit of low frequencies and large wavelengths. This method has however only been applied to linearized hydrodynamics for systems which are only slightly perturbed from the uniform and isotropic equilibrium state of a one-phase fluid. In practice however, the hydrodynamic equations have also been often applied successfully to fluids perturbed around situations consisting of different fluid phases in equilibrium with each other (e.g., a liquid in equilibrium with its saturated vapor below the critical temperature, a binary fluid mixture below the demixing temperature, etc.).[4] In other words, the statistical mechanical justification has been concerned only with bulk hydrodynamics, whereas many of the applications of hydrodynamics do in fact also involve interfaces between various fluid phases. It is our purpose here to indicate how the methods used to justify the linearized hydrodynamic equations of pure bulk phases[5] can be extended to the case of two-phase systems.[6]

The *statistical mechanical* study of two-phase systems is a fairly recent subject and until now only static equilibrium properties have been considered.[7–9] To our knowledge, the first attempt to treat the dynamic properties of two-phase systems within a full statistical mechanical framework is the recent investigation of Jhon, Desai, and Dahler.[10] Their work, although closely related to the present one, is mainly devoted to the study of the origin of surface waves. Here we want to establish contact between the general methods of statistical mechanics and the full set of equations of phenomenological interfacial hydrodynamics.[1,4,11] We will do this for the particular case of a one-component monoatomic fluid, in the two-phase liquid–vapor region, which is slightly perturbed around a planar equilibrium interface. Elsewhere[12] we have considered the high-frequency elastic properties of this system and here we will focus our attention on its low frequency hydrodynamic behavior.[6]

In the *phenomenological* study of interfacial hydrodynamics, as developed by Levich[4] and Landau,[1] it is assumed that one can use the solutions of the bulk hydrodynamic equations up to the interface and match the bulk solutions at the interface with the aid of boundary conditions for the bulk phase variables. These boundary conditions are however not at our disposal but prescribed by the underlying physical phenomena. These boundary conditions state then that the hydrodynamic variables and their gradients along the interface are continuous, as well as the tangential stresses and the normal heat current, but that the jump in the normal stresses is balanced by the surface pressure when one goes from one bulk phase to the other across the interface.[1,4] In the more refined theory of Bedeaux, Albano, and Mazur[11] the interface is considered as a separate and singular surface phase endowed with specific surface properties, while the hydrodynamic equations are split into coupled bulk and surface hydrodynamic equations. A still different approach was taken by Felderhof[13] and Turski and Langer[14] who used a van der Waals free energy functional in order to obtain hydrodynamic equations for a nonuniform fluid which reduce in a continuous fashion to the bulk hydrodynamic equations when one moves away from the interface. These different

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0021-9606/83/010483-14$02.10

phenomenological approaches will be shown to correspond to different approximations to the statistical mechanical theory developed below. We are moreover able to provide explicit definitions for the various quantities introduced by the phenomenological theories and state the approximations underlying them. We are however not able to justify these approximations.

The present theory starts from the exact evolution equations for the nonequilibrium statistical average of the conserved densities. These equations are obtained in Sec. II by the standard Mori–Zwanzig projection method[3,5,15] suitably extended to the case of a system whose equilibrium state is nonuniform because of the lack of translational invariance, and anisotropic because of the lack of rotational invariance both of which are brought about by the presence of the interface. These equations are put into the form of generalized linearized hydrodynamic equations for a nonuniform anisotropic fluid and merely serve as an exact starting point on which the approximations leading to the hydrodynamic equations can be most easily introduced and discussed. Before introducing these approximations we have opted for a set of hydrodynamic variables consisting of the local density, the local velocity field and the local temperature field and we eliminate the local density in favor of the velocity field with the aid of the linearized continuity equation. The advantage of this set of variables stems from the fact that even in the unperturbed liquid–vapor equilibrium state both the velocity field and the temperature field remain uniform and isotropic constants and their gradients can hence be considered as smooth functions even in the interface region. As for the bulk case,[3,5] we neglect then the transient nonhydrodynamic terms and expand the spatial gradients to the lowest nontrivial order and we obtain in this way in Sec. III the linearized hydrodynamic equations of a nonuniform and anisotropic fluid. These equations describe then the dominant behavior of weak, slow nonequilibrium perturbations occurring on a large spatial scale. With suitable additional approximations they can be reduced to the equations used by Turski and Langer in their phenomenological study of the diffuse liquid–vapor interface.[14] As shown in Sec. IV, the number of local transport coefficients and local thermodynamic parameters appearing in these equations can be considerably reduced by restricting ourselves to the case of a *planar* interface, where the translational invariance of the unperturbed equilibrium state is broken only in the direction normal to the interface, while the system remains also invariant for rotations around this direction. Although the system as a whole is now characterized by an unperturbed state with unidirectional nonuniformity and cylindrical rotational symmetry, we expect the uniformity and spherical symmetry characteristic of bulk phases to be restored rapidly as one moves away from the interface layer into the bulk phases. For temperatures well below the critical temperature, the thickness of the interface *layer* will be of microscopic order and in any case much smaller than the hydrodynamic length scale. Under such circumstances the system can be viewed as composed of two spherically symmetric and uniform bulk phases sandwiching a thin, anisotropic and nonuniform interfacial layer in which the properties of one bulk phase quickly go over into those of the other bulk phase. As indicated in Sec. V, the structural details of the interfacial layer can then, to dominant order in the layer thickness, be eliminated from the hydrodynamic equations by a suitable extension of Gibbs' method of surface thermodynamics. In the next sections, we show how the hydrodynamic equations of the nonuniform anisotropic fluid obtained in Sec. III can be reduced under such circumstances to ordinary linearized hydrodynamic equations in each bulk phase (Sec. VI) and in the interface region to linearized "surface" hydrodynamic equations (Sec. VII). The latter equations have the appearance of hydrodynamic equations for a two-dimensional surface phase described by surface transport properties and surface thermodynamic parameters, which are defined as Gibbs surface excess values of the corresponding local properties. Moreover, these surface hydrodynamic equations contain source terms which couple the bulk phases to this "surface phase." As indicated in Sec. VIII, these equations can be reduced, under suitable approximations, to those of Bedeaux *et al.*[11] while further approximations will turn the *surface hydrodynamic equations* into the *boundary conditions* of Levich[4] and Landau.[1] Even to the lowest order in the interface thickness we find correction terms to the phenomenological results (e.g., Laplace's formula) which involve the time derivative or the surface gradients of the local nonequilibrium curvature of the interface as well as terms involving correlations between a point of the bulk phase and a point inside the interfacial layer. Finally, a number of conclusions are summarized in Sec. IX.

II. EXACT EVOLUTION EQUATIONS FOR NONUNIFORM FLUIDS

We will be concerned with the macroscopic evolution of the spatial densities of those microscopic variables, say $a_j(t)$, which are time invariant $\dot{a}_j(t)=0$. These spatial densities, say $a_j(\mathbf{x},t)$ with $a_j(t)=\int d\mathbf{x}\, a_j(\mathbf{x},t)$, are then known to obey microscopic conservation laws relating their time rate of change $\dot{a}_j(\mathbf{x},t)$ to the spatial gradients ($\nabla=\partial/\partial\mathbf{x}$) of a current density $\mathbf{J}_j(\mathbf{x},t)$ in the form $\dot{a}_j(\mathbf{x},t)=\nabla\cdot\mathbf{J}_j(\mathbf{x},t)$. The average values of macroscopic interest $\langle a_j(\mathbf{x},t)\rangle$ and $\langle\mathbf{J}_j(\mathbf{x},t)\rangle$ will obey then the macroscopic conservation laws $\langle\dot{a}_j(\mathbf{x},t)\rangle=\nabla\cdot\langle\mathbf{J}_j(\mathbf{x},t)\rangle$. The importance of these variables follows from the fact that when the length scale of the gradients of the macroscopic (or average) currents is the largest length scale of the system, the macroscopic conservation equations tell us that the conserved densities will be the slowest macroscopic variables of the system. Such slow macroscopic motions are easily observed and constitute the subject of a large body of studies generally designed as "hydrodynamics." The microscopic foundation of the hydrodynamic equations of a one-phase fluid linearized around a uniform equilibrium state is by now well understood.[2,3,5] Here, we merely repeat the various steps in a setting which is suitable for the study of a nonuniform anisotropic fluid of which the two-phase liquid–vapor system, of interest to us, is a special case.

A. The conserved densities

For a system of N identical particles of mass m interacting through a spherically symmetric pair potential $\phi(|\mathbf{x}|)$, the conserved densities consist of the number density

$$\hat{n}(\mathbf{x},t)=\sum_{j=1}^{N}\delta[\mathbf{x}-\mathbf{x}_j(t)]\ , \tag{2.1}$$

the momentum density

$$\hat{\mathbf{g}}(\mathbf{x},t)=\sum_{j=1}^{N}\mathbf{P}_j\delta[\mathbf{x}-\mathbf{x}_j(t)]\ , \tag{2.2}$$

and the energy density

$$\hat{e}(\mathbf{x},t)=\sum_{j=1}^{N}\left\{\frac{\mathbf{P}_j^2(t)}{2m}+\frac{1}{2}\sum_{\substack{i=1\\ i\neq j}}^{N}\phi[|\mathbf{x}_j(t)-\mathbf{x}_i(t)|]\right\}\delta[\mathbf{x}-\mathbf{x}_j(t)]\ , \tag{2.3}$$

where $\mathbf{x}_j(t)$ and $\mathbf{P}_j(t)$ denote, respectively, the instantaneous position and momentum of particle j while $\delta(\mathbf{x})$ is the Dirac delta function. The angular momentum density is not an independent variable here since it can be obtained from $\hat{g}(\mathbf{x},t)$ as $\mathbf{x}\times\hat{\mathbf{g}}(\mathbf{x},t)$ so that the five microscopic variables $\{\hat{n},\hat{\mathbf{g}},\hat{e}\}$ do indeed lead to the eight conservation laws of the total mass, linear momentum, angular momentum, and energy of the system. The local forms of the microscopic conservation equations can then be written as

$$m\dot{\hat{n}}(\mathbf{x},t)+\nabla\cdot\hat{\mathbf{g}}(\mathbf{x},t)=0\ , \tag{2.4a}$$

$$\dot{\hat{\mathbf{g}}}(\mathbf{x},t)+\nabla\cdot\hat{\sigma}(\mathbf{x},t)=0\ , \tag{2.4b}$$

$$\dot{\hat{e}}(\mathbf{x},t)+\nabla\cdot\hat{\mathbf{J}}(\mathbf{x},t)=0\ , \tag{2.4c}$$

and are seen to introduce a microscopic stress tensor $\hat{\sigma}(\mathbf{x},t)$ and energy current density $\hat{\mathbf{J}}(\mathbf{x},t)$, whose explicit expression in terms of $\phi(|\mathbf{x}|)$ will not be needed here but can be found in the literature.[3,5,15]

B. The evolution equations

The macroscopic evolution equations of the five conserved densities $\{\hat{n},\hat{\mathbf{g}},\hat{e}\}=\{a_j(\mathbf{x},t);j=1,\ldots,5\}$ can be put into a form convenient for the study of linearized hydrodynamics with the aid of the well-known Mori–Zwanzig method.[3,5,15] Writing the microscopic evolution equations (2.4) in the alternative form $\dot{a}_j(\mathbf{x},t)=[H,a_j(\mathbf{x},t)]\equiv iLa_j(\mathbf{x},t)$, where $H=\int d\mathbf{x}\,\hat{e}(\mathbf{x},t)$ is the Hamiltonian and L the Liouville operator, a straightforward application of the Mori–Zwanzig method in $\mathbf{x}-t$ space leads to the following set of equations:

$$\dot{G}_{jj'}(\mathbf{x},\mathbf{x}';t)+\sum_{j_1=1}^{5}\int d\mathbf{x}_1\left[\Omega^{s}_{jj_1}(\mathbf{x},\mathbf{x}_1)G_{j_1j'}(\mathbf{x}_1,\mathbf{x}';t)+\int_0^t dt_1\,\Omega^{d}_{jj_1}(\mathbf{x},\mathbf{x}_1;t_1)G_{j_1j'}(\mathbf{x}_1,\mathbf{x}';t-t_1)\right]=0 \tag{2.5}$$

for the space-time correlation functions or hydrodynamics propagators

$$G_{jj'}(\mathbf{x},\mathbf{x}';t)=\langle\delta a_j(\mathbf{x},t)\delta a_{j'}(\mathbf{x}',0)\rangle_0\ , \tag{2.6}$$

where $\langle\cdots\rangle_0$ denotes a normalized ($\langle 1\rangle_0=1$) average over a stationary equilibrium ensemble describing the two-phase system. As usual, in Eq. (2.6) $\delta a_j=a_j-\langle a_j\rangle_0$ denotes the microscopic equilibrium fluctuation. The evolution equation of the macroscopic deviation from equilibrium, $A_j(\mathbf{x},t)=\langle a_j(\mathbf{x},t)\rangle-\langle a_j(\mathbf{x},t)\rangle_0$ where $\langle\cdots\rangle$ denotes a normalized nonequilibrium average, can then be written[5]:

$$\dot{A}_j(\mathbf{x},t)+\sum_{j'=1}^{5}\int d\mathbf{x}'\left[\Omega^{s}_{jj'}(\mathbf{x},\mathbf{x}')A_{j'}(\mathbf{x}',t)+\int_0^t dt'\,\Omega^{d}_{jj'}(\mathbf{x},\mathbf{x}';t')A_{j'}(\mathbf{x}',t-t')\right]=I_j(\mathbf{x},t)\ , \tag{2.7}$$

where the static $\Omega^{s}_{jj'}$, and dynamic $\Omega^{d}_{jj'}$ memory functions appearing in Eqs. (2.5) and (2.7) are defined as

$$\Omega^{s}_{jj'}(\mathbf{x},\mathbf{x}')=-\sum_{j_1=1}^{5}\int d\mathbf{x}_1\langle\delta\dot{a}_j(\mathbf{x})\delta a_{j_1}(\mathbf{x}_1)\rangle_0K_{j_1j'}(\mathbf{x}_1,\mathbf{x}')\ , \tag{2.8a}$$

$$\Omega^{d}_{jj'}(\mathbf{x},\mathbf{x}';t)=\sum_{j_1=1}^{5}\int d\mathbf{x}_1\langle\delta\dot{a}_j(\mathbf{x})\psi(t)\delta\dot{a}_{j_1}(\mathbf{x}_1)\rangle_0K_{j_1j'}(\mathbf{x}_1,\mathbf{x}')\ , \tag{2.8b}$$

with $a_j(\mathbf{x})$ and $\dot{a}_j(\mathbf{x})$ denoting the initial values ($t=0$) of $a_j(\mathbf{x},t)$ and $\dot{a}_j(\mathbf{x},t)$, respectively. The source term I_j appearing in Eq. (2.7) is defined as

$$I_j(\mathbf{x},t)=\langle\psi(t)\dot{a}_j(\mathbf{x})\rangle_0\ , \tag{2.9}$$

while in Eqs. (2.8) and (2.9) there also appears a projected evolution operator $\psi(t)=Q[\exp(-iQLQt)Q]$ involving a projection operator $Q^2=Q=I-P$ onto the space orthogonal to the conserved densities, i.e.,

$$P=\sum_{j,j'}\int d\mathbf{x}\int d\mathbf{x}'\,\delta a_j(\mathbf{x})K_{jj'}(\mathbf{x},\mathbf{x}')\delta a_{j'}(\mathbf{x}')\ , \tag{2.10}$$

where $K_{jj'}(\mathbf{x},\mathbf{x}')$ is the matrix inverse

$$\sum_{j_1}\int d\mathbf{x}_1K_{jj_1}(\mathbf{x},\mathbf{x}_1)G_{j_1j'}(\mathbf{x}_1,\mathbf{x}')=\delta_{jj'}\delta(\mathbf{x}-\mathbf{x}')=\sum_{j_1}\int d\mathbf{x}_1\,G_{jj_1}(\mathbf{x},\mathbf{x}_1)K_{j_1j'}(\mathbf{x}_1,\mathbf{x}') \tag{2.11}$$

of the static correlation functions $G_{jj'}(\mathbf{x},\mathbf{x}')\equiv G_{jj'}(\mathbf{x},\mathbf{x}';t=0)$ [cf. Eq. (2.6)].

C. The hydrodynamic variables

The above algebra can be simplified considerably by choosing the basic variables ($a_j;j=1,\ldots,5$) such as to diagonalize the static matrix $G_{jj'}\propto\delta_{jj'}$. To this end we take $\{a_j(\mathbf{x},t)\}=\{\hat{n}(\mathbf{x},t),\hat{\mathbf{g}}(\mathbf{x},t),\hat{e}_n(\mathbf{x},t)\}$, where $\hat{e}_n$ is that part of the energy density $\hat{e}$ which is orthogonal to (or in physical terms, thermodynamically independent of) the number density $\hat{n}$, i.e., $G_{ne_n}=\langle\delta\hat{n}\delta\hat{e}_n\rangle_0=0$ or explicitly

$$\hat{e}_n(\mathbf{x},t)=\hat{e}(\mathbf{x},t)-\int d\mathbf{x}_1\int d\mathbf{x}_2\times G_{en}(\mathbf{x},\mathbf{x}_1)K_{nn}(\mathbf{x}_1,\mathbf{x}_2)\hat{n}(\mathbf{x}_2,t)\ , \tag{2.12}$$

where $G_{en}(\mathbf{x},\mathbf{x}')=\langle\delta\hat{e}(\mathbf{x})\delta\hat{n}(\mathbf{x}')\rangle_0$, $G_{nn}(\mathbf{x},\mathbf{x}')=\langle\delta\hat{n}(\mathbf{x})\delta\hat{n}(\mathbf{x}')\rangle_0$, etc. In these variables ($j=n,g_\alpha,e_n;\alpha=x,y,z$) the static matrices $G_{jj'}$ and $K_{jj'}$ become diagonal and can also be written in the alternative forms

$$G_{nn}(\mathbf{x}, \mathbf{x}') = \delta(\mathbf{x} - \mathbf{x}')\rho(\mathbf{x}) + \rho(\mathbf{x}, \mathbf{x}') - \rho(\mathbf{x})\rho(\mathbf{x}') \ , \qquad (2.13)$$

$$K_{nn}(\mathbf{x}, \mathbf{x}') = \frac{\delta(\mathbf{x} - \mathbf{x}')}{\rho(\mathbf{x})} - c(\mathbf{x}, \mathbf{x}') \ , \qquad (2.14)$$

$$G_{g_\alpha g_\beta}(\mathbf{x}, \mathbf{x}') = (mv_0)^2 \delta_{\alpha\beta}\delta(\mathbf{x} - \mathbf{x}')\rho(\mathbf{x}) \ , \qquad (2.15)$$

$$K_{g_\alpha g_\beta}(\mathbf{x}, \mathbf{x}') = \frac{\delta_{\alpha\beta}\delta(\mathbf{x} - \mathbf{x}')}{(mv_0)^2\rho(\mathbf{x})} \ , \qquad (2.16)$$

while $G_{e_n e_n}(\mathbf{x}, \mathbf{x}')$ and $K_{e_n e_n}(\mathbf{x}, \mathbf{x}')$ take on simple forms only in the ideal fluid limit which is not of interest here. In Eqs. (2.13)–(2.16) $\rho(\mathbf{x})$ is the equilibrium density $\rho(\mathbf{x}) = \langle \hat{n}(\mathbf{x}) \rangle_0$, $\rho(\mathbf{x}, \mathbf{x}')$ the equilibrium pair density related to the Ornstein–Zernike direct correlation function $c(\mathbf{x}, \mathbf{x}')$ by Eqs. (2.11), (2.13), and (2.14), while v_0 is the thermal velocity ($v_0^2 = k_B T/m$).

We now choose a set of *hydrodynamical variables* (A_j) corresponding to the above set of conserved densities (a_j). First we take the macroscopic mass density $mn(\mathbf{x}, t)$ with $n(\mathbf{x}, t) = \langle \hat{n}(\mathbf{x}, t) \rangle$ and $\delta n(\mathbf{x}, t) = n(\mathbf{x}, t) - \rho(\mathbf{x})$ denoting the nonequilibrium deviation of the macroscopic number density $n(\mathbf{x}, t)$ from its equilibrium value $\rho(\mathbf{x})$ [not to be confused with the equilibrium fluctuation of the microscopic number density $\delta\hat{n}(\mathbf{x}, t) = \hat{n}(\mathbf{x}, t) - \rho(\mathbf{x})$, $\delta n(\mathbf{x}, t) = \langle \delta\hat{n}(\mathbf{x}, t) \rangle$]. Next we consider the macroscopic momentum density $\mathbf{g}(\mathbf{x}, t) = \langle \hat{\mathbf{g}}(\mathbf{x}, t) \rangle$ and define from it the hydrodynamic velocity field $\mathbf{u}(\mathbf{x}, t)$. For a system at rest we have $\langle \hat{\mathbf{g}}(\mathbf{x}, t) \rangle_0 = 0$ and hence $\mathbf{g}(\mathbf{x}, t)$ is already a nonequilibrium deviation. We therefore can define $\mathbf{u}(\mathbf{x}, t)$ by $\mathbf{u}(\mathbf{x}, t) = \mathbf{g}(\mathbf{x}, t)/m\rho(\mathbf{x})$ instead of $\mathbf{g}(\mathbf{x}, t)/mn(\mathbf{x}, t)$ since the nonlinear term $m\delta n(\mathbf{x}, t)\mathbf{u}(\mathbf{x}, t)$ will be neglected later on anyway, while the present definition [$\mathbf{g}(\mathbf{x}, t) = m\rho(\mathbf{x})\mathbf{u}(\mathbf{x}, t)$] will avoid some more cumbersome notations. Notice that there is no approximation involved in defining $\mathbf{u}(\mathbf{x}, t)$ in this way while in the framework of linearized hydrodynamics our definition reduces to the standard one. Finally, we have to introduce a macroscopic variable corresponding to the energy density $\hat{e}(\mathbf{x}, t)$ or better to that part of the energy density which is thermodynamically independent of the remaining conserved densities, i.e., $\hat{e}_n(\mathbf{x}, t)$ of Eq. (2.12), which is closely related to the local temperature.[16] We therefore introduce the nonequilibrium internal energy density $\epsilon(\mathbf{x}, t)$, according to $\langle \delta\hat{e}_n(\mathbf{x}, t) \rangle = \rho(\mathbf{x})\epsilon(\mathbf{x}, t)$ and associate with it the nonequilibrium deviation of the temperature field $\theta(\mathbf{x}, t)$ through

$$\rho(\mathbf{x})\theta(\mathbf{x}, t) = \int d\mathbf{x}' \, K_{e_n e_n}(\mathbf{x}, \mathbf{x}')\rho(\mathbf{x}')\epsilon(\mathbf{x}', t) \ , \qquad (2.17a)$$

$$\rho(\mathbf{x})\epsilon(\mathbf{x}, t) = \int d\mathbf{x}' \, G_{e_n e_n}(\mathbf{x}, \mathbf{x}')\rho(\mathbf{x}')\theta(\mathbf{x}', t) \ , \qquad (2.17b)$$

which constitute a straightforward generalization to nonuniform fluids of Schofield's definition of the local temperature.[16] Notice from Eq. (2.17) that $G_{e_n e_n}$ plays the role of a local specific heat at constant volume while our notations anticipate once more the linearized situations of interest below [i.e., both $\theta(\mathbf{x}, t)$ and $\epsilon(\mathbf{x}, t)$ are already nonequilibrium deviations]. The set of hydrodynamical variables considered here consists thus of the nonequilibrium deviations of the macroscopic number density $\delta n(\mathbf{x}, t)$, the velocity field $\mathbf{u}(\mathbf{x}, t)$, and the temperature field $\theta(\mathbf{x}, t)$ or internal energy density $\epsilon(\mathbf{x}, t)$.

D. The generalized hydrodynamic equations

With the above choice of variables the set of equations (2.7) takes on a form closely related but more general than the linearized hydrodynamic equations. For $j = n$, Eq. (2.7) simply reduces to the continuity equation

$$\delta\dot{n}(\mathbf{x}, t) + \nabla_\beta[\rho(\mathbf{x})u_\beta(\mathbf{x}, t)] = 0 \ , \qquad (2.18)$$

where a summation over repeated Cartesian component labels ($\beta = x, y, z$) is implied. For $j = g_\alpha$, Eq. (2.7) can be written with the aid of Eq. (2.17) as

$$\rho(\mathbf{x})\dot{u}_\alpha(\mathbf{x}, t) + v_0^2\rho(\mathbf{x})\nabla_\alpha \int d\mathbf{x}' \, K_{nn}(\mathbf{x}, \mathbf{x}')\delta n(\mathbf{x}', t) + \frac{1}{(mv_0)^2}\int \frac{d\omega}{2\pi} e^{-i\omega t} \int d\mathbf{x}' \langle \dot{\hat{g}}_\alpha(\mathbf{x})\psi(\omega)\dot{\hat{\mathbf{g}}}_\beta(\mathbf{x}') \rangle_0 u_\beta(\mathbf{x}', \omega)$$
$$+ \frac{1}{m}\int \frac{d\omega}{2\pi} e^{-i\omega t} \int d\mathbf{x}' \langle \dot{\hat{g}}_\alpha(\mathbf{x})[-\delta\hat{e}_n(\mathbf{x}') + \psi(\omega)\delta\dot{\hat{e}}_n(\mathbf{x}')] \rangle_0 \rho(\mathbf{x}')\theta(\mathbf{x}', \omega) = \frac{1}{m}\langle \psi(t)\dot{\hat{g}}_\alpha(\mathbf{x}) \rangle_0 \qquad (2.19)$$

and for $j = e_n$, Eq. (2.7) can be similarly transformed into

$$\rho(\mathbf{x})\dot{\epsilon}(\mathbf{x}, t) + \int \frac{d\omega}{2\pi} e^{-i\omega t} \int d\mathbf{x}' \langle \delta\dot{\hat{e}}_n(\mathbf{x})\psi(\omega)\delta\dot{\hat{e}}_n(\mathbf{x}') \rangle_0 \rho(\mathbf{x}')\theta(\mathbf{x}', \omega)$$
$$+ \frac{1}{mv_0^2}\int \frac{d\omega}{2\pi} e^{-i\omega t} \int d\mathbf{x}' \langle [\delta\hat{e}_n(\mathbf{x}) + \delta\dot{\hat{e}}_n(\mathbf{x})\psi(\omega)]\dot{\hat{g}}_\beta(\mathbf{x}') \rangle_0 u_\beta(\mathbf{x}', \omega) = \langle \psi(t)\delta\dot{\hat{e}}_n(\mathbf{x}) \rangle_0 \ , \qquad (2.20)$$

where, for later convenience, we have introduced in Eqs. (2.19) and (2.20) a one-sided Fourier transform, e.g.,

$$\psi(t) = \int \frac{d\omega}{2\pi} \psi(\omega) \, e^{-i\omega t} \ , \qquad (2.21a)$$

$$\psi(\omega) = \int_0^\infty dt \, \psi(t) \, e^{i\omega t} \ , \qquad (2.21b)$$

and similarly for $\theta(\mathbf{x}, \omega)$ and $\mathbf{u}(\mathbf{x}, \omega)$. Equations (2.18)–(2.20) are still exact and merely represent a formal rewriting of the macroscopic conservation equations, i.e., of the nonequilibrium average of the microscopic conservation Eqs. (2.4). Their structure and notation is however already fairly similar to that of the linearized hydrodynamic equations and for this reason Eqs. (2.18)–(2.20) are usually referred to as "generalized" hydrodynamic equations. They constitute a convenient starting point for a first-principle derivation of the "ordinary" hydrodynamic equations which form an approximation to the exact Eqs. (2.18)–(2.20), as will be discussed in the next section. When the equilibrium state of the fluid is uniform and isotropic, such as is the case for a one-phase system, a spatial Fourier transform of Eqs. (2.18)–(2.20) reduces them to those encountered in the literature.[3,5,15]

III. HYDRODYNAMIC EQUATIONS FOR NONUNIFORM FLUIDS

The formal manipulations of Eqs. (2.4) which resulted in Eqs. (2.18)–(2.20) merely amount to isolating those parts of the macroscopic stress tensor $\sigma(\mathbf{x}, t) = \langle\hat{\sigma}(\mathbf{x}, t)\rangle$ and macroscopic energy current density $\mathbf{J}(\mathbf{x}, t) = \langle\hat{\mathbf{J}}(\mathbf{x}, t)\rangle$, which are linear in the hydrodynamic variables $\delta n(\mathbf{x}, t)$, $\mathbf{u}(\mathbf{x}, t)$, and $\theta(\mathbf{x}, t)$. In order to obtain the linearized hydrodynamic equations themselves, Eqs. (2.18)–(2.20) have still to be transformed into equations which are (1) closed, (2) local in time, and (3) local in space. Below we discuss the three basic approximations involved in reducing Eqs. (2.18)–(2.20) to the linearized hydrodynamic equations of a nonuniform fluid. The detailed *a priori* justification of these approximations is, even for a uniform fluid,[2-4] a very difficult problem which will not be considered in any detail here. The *a posteriori* justification of these approximations rests entirely on the widespread successful use which has been made of the hydrodynamic equations for more than a century.[1]

A. Transient terms

The first approximation will consist in the neglect of the source term appearing in the right-hand side of Eqs. (2.19) and (2.20). These terms are seen to evolve according to the evolution operator projected onto the space orthogonal to the conserved densities, i.e., $\psi(t)$ [notice that since $\delta\hat{n}$ is itself conserved, there is no source term in Eq. (2.18)]. This orthogonal space consists of products of conserved densities and of the remaining nonconserved variables. In the framework of linearized hydrodynamics the products of conserved densities are small in amplitude while the nonconserved densities evolve on a fast time scale resulting in quickly vanishing contributions. Hence, within a linearized theory, these source terms can be neglected after a transient time much shorter than the time scale on which the hydrodynamic variables are expected to evolve.

B. Long-time limit

As a second approximation we replace Eqs. (2.19) and (2.20) by equations which are local in time, i.e., which relate the time rate of change of the hydrodynamic variables to their value at the same time just as in the continuity Eq. (2.18). To this end we approximate $\psi(\omega)$ in the memory functions appearing in the left-hand side of Eqs. (2.19) and (2.20) by its low frequency limit $\psi(\omega) \simeq \psi(\omega=0)$. For example, in Eq. (2.19) we write

$$\int\frac{d\omega}{2\pi}e^{-i\omega t}\langle\dot{\hat{g}}_\alpha(\mathbf{x})\psi(\omega)\dot{\hat{g}}_\beta(\mathbf{x}')\rangle_0 u_\beta(\mathbf{x}', \omega)$$

$$=\int\frac{d\omega}{2\pi}e^{-i\omega t}[\langle\dot{\hat{g}}_\alpha(\mathbf{x})\psi(\omega=0)\dot{\hat{g}}_\beta(\mathbf{x}')\rangle_0 + 0(\omega)]u_\beta(\mathbf{x}', \omega)$$

$$\simeq\langle\dot{\hat{g}}_\alpha(\mathbf{x})\psi(\omega=0)\dot{\hat{g}}_\beta(\mathbf{x}')\rangle_0 u_\beta(\mathbf{x}', t)\ . \tag{3.1}$$

The order-ω correction term neglected in the second member of Eq. (3.1) corresponds to a correction of the order of the correlation time (of the rapid equilibrium fluctuations described by the memory function) over the time scale of observation of the hydrodynamic variables. Since the hydrodynamic variables are expected to correspond to the slowest possible motions, last term in Eq. (3.1) represents the dominant term of a long-time asymptotic expansion of the first term of Eq. (3.1). In this sense can we replace Eqs. (2.19) and (2.20) in the long-time limit by equations which are local in time and which contain only the zero-frequency memory functions.

C. Small-gradient expansion

The final approximation consists then in replacing Eqs. (2.19) and (2.20) by equations which are local in space, i.e., which relate the time rate of change of the hydrodynamic variables to their value (and that of their first few spatial derivatives) at the same space point {just as in the continuity [Eq. (2.18)]}. This can be achieved by spatial Taylor expansion of the nonlocal terms around their local value. Notice hereby that the time derivatives contained in the memory functions will introduce via Eqs. (2.4) a number of spatial gradients leading to the appearance not only of the hydrodynamical variables but also of their spatial derivatives. For example, we rewrite a specific term of Eq. (2.19) with the aid of Eq. (2.4b) as

$$\int d\mathbf{x}'\langle\dot{\hat{g}}_\alpha(\mathbf{x})\psi(\omega)\dot{\hat{g}}_{\alpha'}(\mathbf{x}')\rangle_0 u_{\alpha'}(\mathbf{x}', \omega)=\int d\mathbf{x}'\, u_{\alpha'}(\mathbf{x}', \omega)[\nabla_\beta\nabla'_{\beta'}\langle\hat{\sigma}_{\beta\alpha}(\mathbf{x})\psi(\omega)\hat{\sigma}_{\beta'\alpha'}(\mathbf{x}')\rangle_0]$$

$$=-\nabla_\beta\left[\int d\mathbf{x}'\langle\hat{\sigma}_{\beta\alpha}(\mathbf{x})\psi(\omega)\hat{\sigma}_{\beta'\alpha'}(\mathbf{x}')\rangle_0\nabla'_{\beta'}u_{\alpha'}(\mathbf{x}', \omega)\right]=-\nabla_\beta\left\{\int d\mathbf{x}'\langle\hat{\sigma}_{\beta\alpha}(\mathbf{x})\psi(\omega)\hat{\sigma}_{\beta'\alpha'}(\mathbf{x}')\rangle_0[\nabla_{\beta'}u_{\alpha'}(\mathbf{x}, \omega)+\cdots]\right\}, \tag{3.2a}$$

where we have integrated by parts over $\mathbf{x}'$ ($\nabla'=\partial/\partial\mathbf{x}'$) and expanded $\nabla'\mathbf{u}(\mathbf{x}', \omega)$ around its value at $\mathbf{x}'=\mathbf{x}$. Such an expansion is meaningful only when the spatial gradients are small and when the spatial correlations described by the memory functions, viz. $\langle\hat{\sigma}_{\beta\alpha}(\mathbf{x})\psi(\omega) \times\hat{\sigma}_{\beta'\alpha'}(\mathbf{x}')\rangle_0$ are short ranged. The latter assumption can be violated close to the critical point but we will always exclude this case from our considerations. In the small gradient expansion described in Eq. (3.2a) the evolution equations (2.19) and (2.20) will thus become local in space. Under the same assumption of short ranged correlations the relation (2.17) between the internal energy density $\epsilon(\mathbf{x}, t)$ and the temperature field $\theta(\mathbf{x}, t)$ can be approximately localized as

$$\rho(\mathbf{x})\epsilon(\mathbf{x}, t) = \int d\mathbf{x}'\, G_{e_n e_n}(\mathbf{x}, \mathbf{x}')\rho(\mathbf{x}')[\theta(\mathbf{x}, t) + \cdots] \simeq \rho(\mathbf{x})c_V(\mathbf{x})\theta(\mathbf{x}, t) \; , \tag{3.2b}$$

where $\rho(\mathbf{x})c_V(\mathbf{x}) = \int d\mathbf{x}'\, G_{e_n e_n}(\mathbf{x}, \mathbf{x}')\rho(\mathbf{x}')$ defines a local specific heat at constant volume multiplied by $k_B T^2$, which we have denoted simply as $c_V(\mathbf{x})$. Except for the fact that it leads to well-known phenomenological results, the convergence of the above small-gradient expansions is difficult to justify *a priori*.

D. Hydrodynamic equations

We now combine the three basic approximations stated above and write down the *linearized* hydrodynamic equations which result from Eqs. (2.18)–(2.20) in the long-time small-gradient limit. The continuity Eq. (2.18) remains unchanged and will be used hereafter only to eliminate $\delta n(\mathbf{x}, t)$ in favor of $\mathbf{u}(\mathbf{x}, t)$. To this end we time differentiate Eq. (2.19) and eliminate $\delta\dot{n}$ with the aid of Eq. (2.18). Under the above approximations we obtain

$$m\rho(\mathbf{x})\ddot{u}_\alpha(\mathbf{x}, t) = \rho(\mathbf{x})\nabla_\alpha[a(\mathbf{x})\nabla_\beta u_\beta(\mathbf{x}, t)] + \nabla_\beta[\eta_{\alpha\beta\alpha'\beta'}(\mathbf{x})\nabla_{\alpha'}\dot{u}_{\beta'}(\mathbf{x}, t)] - \nabla_\beta[b_{\alpha\beta}(\mathbf{x})\dot{\theta}(\mathbf{x}, t)] + \gamma_\alpha(\mathbf{x}, t) \; , \tag{3.3}$$

while Eq. (2.20) becomes

$$\rho(\mathbf{x})\dot{\epsilon}(\mathbf{x}, t) = h_{\alpha\beta}(\mathbf{x})\nabla_\alpha u_\beta(\mathbf{x}, t) + \nabla_\alpha[\kappa_{\alpha\beta}(\mathbf{x})\nabla_\beta\theta(\mathbf{x}, t)] + \mu(\mathbf{x}, t) \; . \tag{3.4}$$

Except for the γ_α and μ terms, Eqs. (3.3) and (3.4) are closed and local equations for the hydrodynamic variables $u_\alpha(\mathbf{x}, t)$ and $\theta(\mathbf{x}, t)$ [or $\epsilon(\mathbf{x}, t)$ locally related to $\theta(\mathbf{x}, t)$ by Eq. (3.2b)]. Equations (3.3) and (3.4) involve a number of thermodynamic and transport coefficients which, under the present approximations, are nonuniform (i.e., functions of $\mathbf{x}$) and anisotropic (i.e., they are not scalar quantities). The transport coefficients consist of the local viscosity tensor

$$\eta_{\alpha\beta\alpha'\beta'}(\mathbf{x}) = \frac{1}{mv_0^2}\int d\mathbf{x}' \times \langle\hat{\sigma}_{\alpha\beta}(\mathbf{x})\psi(\omega = 0)\hat{\sigma}_{\alpha'\beta'}(\mathbf{x}')\rangle_0 \tag{3.5}$$

and the local heat conductivity tensor

$$\kappa_{\alpha\beta}(\mathbf{x}) = \int d\mathbf{x}'\langle\hat{J}_\alpha(\mathbf{x})\psi(\omega = 0)\hat{J}_\beta(\mathbf{x}')\rangle_0\rho(\mathbf{x}') \; , \tag{3.6}$$

where $\hat{\sigma}_{\alpha\beta}$ and $\hat{J}_\alpha$ are defined by Eqs. (2.4b) and (2.4c). The thermodynamic coefficients consist of the local inverse compressibility

$$a(\mathbf{x}) = mv_0^2\int d\mathbf{x}'\, K_{nn}(\mathbf{x}, \mathbf{x}')\rho(\mathbf{x}') \tag{3.7}$$

and of the local tensors

$$b_{\alpha\beta}(\mathbf{x}) = \int d\mathbf{x}'\langle\hat{\sigma}_{\alpha\beta}(\mathbf{x}) \times [\delta\hat{e}_n(\mathbf{x}') - \psi(\omega = 0)\delta\hat{e}_n(\mathbf{x}')]\rangle_0\rho(\mathbf{x}') \tag{3.8}$$

and

$$h_{\alpha\beta}(\mathbf{x}) = \frac{1}{mv_0^2}\int d\mathbf{x}'\langle[\delta\hat{e}_n(\mathbf{x}) + \delta\dot{\hat{e}}_n(\mathbf{x})\psi(\omega = 0)]\hat{\sigma}_{\alpha\beta}(\mathbf{x}')\rangle_0 \; , \tag{3.9}$$

which in uniform fluids can be related to the temperature derivative of the pressure and to the thermal expansion coefficient. The two remaining terms γ_α and μ are related to the lack of translational invariance of the equilibrium properties and hence are specific to nonuniform systems:

$$\gamma_\alpha(\mathbf{x}, t) = mv_0^2\rho(\mathbf{x})\nabla_\alpha\int d\mathbf{x}'\, K_{nn}(\mathbf{x}, \mathbf{x}')u_\beta(\mathbf{x}', t)\nabla'_\beta\rho(\mathbf{x}') \; , \tag{3.10}$$

$$\mu(\mathbf{x}, t) = \nabla_\beta\int d\mathbf{x}'\langle\hat{J}_\beta(\mathbf{x})\psi(\omega = 0) \times \hat{J}_{\beta'}(\mathbf{x}')\rangle_0\theta(\mathbf{x}', t)\nabla'_{\beta'}\rho(\mathbf{x}') \; . \tag{3.11}$$

As seen from Eqs. (3.10) and (3.11), γ_α and μ, although local in time are not yet local in space. This is because these terms involve the gradients of the equilibrium profile, which in contradistinction to the gradients of the hydrodynamic variables are not considered as small. These terms will be localized in next section after we have introduced some simplifying assumptions concerning the equilibrium properties of the system.

IV. SYMMETRY RELATIONS FOR A SYSTEM WITH A PLANAR EQUILIBRIUM INTERFACE

The hydrodynamic equations obtained in the previous section are still quite complicated. Considerable simplifications will occur if we consider a nonuniform anisotropic fluid consisting of a two-phase system composed of a liquid bulk phase separated from a vapor bulk phase by a thin *planar* interfacial layer. The weak gravitational field required to bring about the planar interface will not be considered explicitly here and we assume that the geometry of the unperturbed equilibrium situation is given and stable with respect to the small nonequilibrium deviations of the hydrodynamic variables.

The equilibrium two-phase liquid–vapor system is characterized then by a translational invariance which is broken only in the direction perpendicular to the equilibrium interface. Taking this direction along the z axis this implies that all one-point functions will depend on $\mathbf{x} = (x, y, z)$ only through z, the distance to the interface. For example, the equilibrium density profile $\rho(\mathbf{x})$ will read now $\rho(\mathbf{x}) \equiv \rho(z)$. With respect to the rotational invariance we assume that the equilibrium two-phase system remains invariant for all rotations around the z axis. This partial breakdown of the rotational invariance implies then that all two-point functions, e.g., $K_{nn}(\mathbf{x}, \mathbf{x}')$, do depend on $\mathbf{x}$ and $\mathbf{x}'$ only through z, z' and $r = |\mathbf{r}|$, the two-dimensional distance parallel to the planar interface $|\mathbf{r}| = [(x - x')^2 + (y - y')^2]^{1/2}$, i.e., $K_{nn}(\mathbf{x}, \mathbf{x}') \equiv K_{nn}(r; z, z')$. With the present geometry all second-rank tensors $\kappa_{\alpha\beta}$, $b_{\alpha\beta}$, and $h_{\alpha\beta}$ defined by Eqs. (3.6), (3.8), and (3.9) will exhibit cylindrical symmetry. For example, the local heat conductivity tensor $\kappa_{\alpha\beta}(\mathbf{x})$ can now be written as

$$\kappa_{\alpha\beta}(\mathbf{x}) = \delta_{\alpha z}\delta_{\beta z}\kappa_N(z) + (\delta_{\alpha x}\delta_{\beta x} + \delta_{\alpha y}\delta_{\beta y})\kappa_T(z) \ , \tag{4.1}$$

where $\delta_{\alpha\beta}$ denotes the Kronecker delta. As seen from Eq. (4.1) all second rank tensors involve now only two independent functions, e.g., $\kappa_{\alpha\beta}$ involves a normal (N) and tangential (T) conductivity, respectively, $\kappa_N(z)$ and $\kappa_T(z)$. With respect to the fourth-rank viscosity tensor $\eta_{\alpha\beta\alpha'\beta'}$, the situation is more complicated but it will suffice here to consider only the combinations $\eta_{\alpha\beta\alpha'\beta'}\nabla_{\alpha'}u_{\beta'}$, which appear in Eq. (3.3). Introducing the rate of deformation tensor

$$s_{\alpha\beta}(\mathbf{x}, t) = \tfrac{1}{2}[\nabla_\alpha u_\beta(\mathbf{x}, t) + \nabla_\beta u_\alpha(\mathbf{x}, t)] \ , \tag{4.2}$$

we can write in the presence of cylindrical symmetry

$$\begin{aligned}\eta_{\alpha\beta\alpha'\beta'}(\mathbf{x})\nabla_{\alpha'}u_{\beta'}(\mathbf{x}, t) = {}& \delta_{\alpha\beta}\{\xi_N(z)s_{zz}(\mathbf{x}, t) + \xi_T(z)[s_{xx}(\mathbf{x}, t) + s_{yy}(\mathbf{x}, t)]\} + \delta_{\alpha z}\delta_{\beta z}2\eta_N(z)[s_{zz}(\mathbf{x}, t) - \tfrac{1}{3}s_0(\mathbf{x}, t)] \\ & + \delta_{\alpha x}\delta_{\beta x}2\eta_T(z)[s_{xx}(\mathbf{x}, t) - \tfrac{1}{3}s_0(\mathbf{x}, t)] + \delta_{\alpha y}\delta_{\beta y}2\eta_T(z)[s_{yy}(\mathbf{x}, t) - \tfrac{1}{3}s_0(\mathbf{x}, t)] + (\delta_{\alpha x}\delta_{\beta y} + \delta_{\alpha y}\delta_{\beta x})2\eta_T(z)s_{xy}(\mathbf{x}, t) \\ & + (\delta_{\alpha z}\delta_{\beta x} + \delta_{\alpha x}\delta_{\beta z})2\eta_{NT}(z)s_{xz}(\mathbf{x}, t) + (\delta_{\alpha z}\delta_{\beta y} + \delta_{\alpha y}\delta_{\beta z})2\eta_{NT}(z)s_{yz}(\mathbf{x}, t) \ ,\end{aligned} \tag{4.3}$$

where $s_0 = \sum_\alpha s_{\alpha\alpha} = \nabla \cdot \mathbf{u}$ is the trace of $s_{\alpha\beta}(\mathbf{x}, t)$. Hence, the viscous response involves only five independent viscosities[12]; a normal and a tangential dilatational viscosity, respectively, $\xi_N(z)$ and $\xi_T(z)$, a normal and a tangential shear viscosity, respectively, $\eta_N(z)$ and $\eta_T(z)$, and a mixed normal-tangential shear viscosity $\eta_{NT}(z)$. The number of thermodynamic and transport coefficients required to describe even this simple two-phase system is still considerably larger than in the case of a pure bulk phase. All these "coefficients" are moreover still functions of z.

In order to complete the hydrodynamic description of the liquid–vapor system we still have to make explicit the form taken by the specifically nonuniform contributions $\gamma_\alpha(\mathbf{x}, t)$ and $\mu(\mathbf{x}, t)$ of Eqs. (3.10) and (3.11), in the case of a planar equilibrium interface. From Eq. (3.10) and the localization procedure of Eq. (3.2) we can write in the present geometry

$$\begin{aligned}&\int d\mathbf{x}' K_{nn}(\mathbf{x}, \mathbf{x}')u_\beta(\mathbf{x}', t)\nabla'_\beta\rho(\mathbf{x}') \\ &\quad = \int dz' \int d\mathbf{r} K_{nn}(r; z, z')\rho'(z')[u_z(\mathbf{x}, t) + \cdots] \ ,\end{aligned} \tag{4.4}$$

where $\mathbf{r} = (x' - x, y' - y)$ is the two-dimensional vector introduced above ($r = |\mathbf{r}|$) and $\rho'(z) = \nabla_z\rho(z)$. The lowest-order term in the Taylor expansion in the right-hand side of Eq. (4.4) is seen to vanish by virtue of the equation defining the equilibrium density profile[7–10]:

$$\int dz' \int d\mathbf{r} K_{nn}(r; z, z')\rho'(z') = 0 \ , \tag{4.5}$$

while the first-order terms vanish because of the symmetry properties of $K_{nn}(r; z, z')$. To the lowest nontrivial order in the gradients we have hence in the present geometry

$$\begin{aligned}\gamma_\alpha(\mathbf{x}, t) = {}& \rho(z)\nabla_\alpha[\alpha_T(z)(\nabla_x^2 + \nabla_y^2)u_z(\mathbf{x}, t)] \\ & + \rho(z)\nabla_\alpha[\alpha_N(z)\nabla_z^2 u_z(\mathbf{x}, t)] \ ,\end{aligned} \tag{4.6}$$

where

$$\alpha_T(z) = \frac{mv_0^2}{4}\int dz' \int d\mathbf{r}\, r^2 K_{nn}(r; z, z')\rho'(z') \ , \tag{4.7a}$$

$$\alpha_N(z) = \frac{mv_0^2}{2}\int dz' \int d\mathbf{r}\, (z' - z)^2 K_{nn}(r; z, z')\rho'(z') \ . \tag{4.7b}$$

Similarly, to lowest order in the gradients we have for $\mu(\mathbf{x}, t)$ of Eq. (3.11)

$$\mu(\mathbf{x}, t) = \nabla_z[\beta_N(z)\theta(\mathbf{x}, t)] \ , \tag{4.8}$$

with

$$\beta_N(z) = \int d\mathbf{x}' \langle \hat{J}_z(\mathbf{x})\psi(\omega = 0)\hat{J}_z(\mathbf{x}')\rangle_0 \rho'(z') \ , \tag{4.9}$$

where $\hat{J}_z$ is the normal microscopic energy current density defined by Eq. (2.4c).

In conclusion, the linearized hydrodynamic equations of a liquid–vapor system with a planar equilibrium interface involve, the equilibrium density profile $\rho(z)$, five thermodynamic coefficients [$a(z)$, $b_N(z)$, $b_T(z)$, $h_N(z)$, $h_T(z)$], seven transport coefficients [$\kappa_N(z)$, $\kappa_T(z)$, $\xi_N(z)$, $\xi_T(z)$, $\eta_N(z)$, $\eta_T(z)$, $\eta_{NT}(z)$] and three interfacial properties [$\alpha_N(z)$, $\alpha_T(z)$, $\beta_N(z)$], in total, 16 coefficients.

V. LIMITING CASE OF A THIN INTERFACIAL LAYER

The situation reached at this stage although much simpler than the original description is still far too complicated to be compared with the phenomenological treatment of interfacial hydrodynamics. The hydrodynamic equations we have obtained are partial differential equations for the macroscopic variables $\mathbf{u}(\mathbf{x}, t)$ and $\theta(\mathbf{x}, t)$, which are local in time and in space but which contain variable coefficients such as $\rho(z)$, etc. The variations of these coefficients describe the continuous transition from one bulk phase to the other via the interfacial layer. Under normal circumstances, i.e., for temperatures well below the critical temperature, the interfacial layer is only a few atomic diameters thick[7–10] and there is no need to retain such a small scale information in a theory of the macroscopic hydrodynamic motions. The interface is however also not a geometric surface across which the various coefficients are discontinuous as assumed in the phenomenological theories. Here we will follow the Gibbs method of surface thermodynamics,[17] and consider a diffuse interface which on a macroscopic scale is microscopically thin and well localized around a geometric dividing surface. For the geometric Gibbs dividing surface of the planar equilibrium interface we take the x–y plane, $z = 0$, so that z denotes the distance of the point $\mathbf{x} = (x, y, z)$ to the interface. A more precise, physically unambiguous, definition of the plane $z=0$ will be introduced below. We then divide our equilibrium two-phase system into three regions. If ϵ denotes the thickness of the interface, we localize the vapor phase in the $z \geqslant \epsilon$ half-space and the liquid phase in the $z \leqslant -\epsilon$ half-space, while the region $|z| < \epsilon$ constitutes the interfacial layer. We now assume that ϵ can be chosen such that for $|z| \geqslant \epsilon$ the (liquid or vapor) bulk phases are uniform and isotropic while the translational and rotational invariance is broken only in the thin interfacial layer $|z| < \epsilon$. Strictly speaking, such an ϵ does not exist since for $|z| \gtrsim \epsilon$, $\rho(z)$ will always slightly differ from $\rho_+(\rho_-)$, the asymptotic density of the vapor (liquid) phase $[\rho_\pm = \lim_{z\to\pm\infty}\rho(z)]$. We can however define the "thin interface" as one for which the relative deviation of $\rho(z)$ from its asymptotic value $\rho_\pm$ does not exceed say a few percent, when $\pm z > \epsilon$. In this case the bulk phases will be (not exactly but) to a very good approximation uniform and isotropic. In the interfacial layer $|z| < \epsilon$, $\rho(z)$ will change by orders of magnitude and this region clearly remains nonuniform and anisotropic even while constituting only a thin layer.

Henceforth, we will consider that all coefficients appearing in the hydrodynamic equations, say $a(z)$, quickly tend to their asymptotic bulk values $a_\pm = \lim_{z\to\pm\infty} a(z)$ when $|z|$ exceeds ϵ and we will replace $a(z)$ by $a_\pm$ when $\pm z \geqslant \epsilon$. In the interface region $|z| < \epsilon$, $a(z)$ undergoes a quick variation from it vapor-phase value a_+ to its liquid-phase value a_-. The details of this small-scale variation can be eliminated from the macroscopic theory by constructing a Gibbs surface excess value in analogy with the equilibrium theory.[17] To this end, we introduce for each local coefficient, say $a(z)$, a discontinuous reference value, say $a_G(z)$, corresponding to a situation where the interface is approximated by a geometric surface, the Gibbs dividing surface, which we localize at $z=0$:

$$a_G(z) = a_+\theta_+(z) + a_-\theta_-(z) \ , \tag{5.1}$$

where $\theta_+(z) = 1-\theta_-(z) = \theta(z)$ is Heaviside's step function $\theta(z)=1$, for $z>0$ and zero otherwise. The excess value $\delta_G a(z) = a(z) - a_G(z)$ quickly vanishes with $|z|$ and can be characterized by its "surface" excess value $\bar{a}$:

$$\bar{a} = \int_{-\infty}^{\infty} dz[a(z) - a_G(z)] \ . \tag{5.2}$$

In the theory to be constructed below coefficients like $a(z)$ will be characterized in the bulk phases by their bulk value $a_\pm$ and in the interface region by their surface excess value $\bar{a}$. The microscopic variations of functions like $a(z)$ will thus be eliminated from the theory in favor of the three constants $a_\pm$ and $\bar{a}$.

With respect to the tensorial quantities, e.g., $\kappa_{\alpha\beta}(z)$, we assume similarly that the cylindrical symmetry characteristic of the interface region $|z| < \epsilon$ quickly degenerates into the full spherical symmetry characteristic of the bulk phases when $|z|$ exceeds ϵ. In other words, when $\pm z \geqslant \epsilon$, both $\kappa_N(z)$ and $\kappa_T(z)$ quickly tend to a common value $\kappa_\pm$, which is the heat conductivity of the $\pm$ bulk phase while the anisotropy $\kappa_N(z) - \kappa_T(z)$ is nonvanishing only in the interface region $|z| < \epsilon$. Hence, in the bulk phases ($\pm z \geqslant \epsilon$) we have as usual $\kappa_{\alpha\beta}(z) = \kappa_\pm\delta_{\alpha\beta}$, whereas the anisotropic interface region ($|z| < \epsilon$) will be characterized by the surface excess values of $\kappa_N(z)$ and $\kappa_T(z)$:

$$\bar{\kappa}_N = \int_{-\infty}^{\infty} dz[\kappa_N(z) - \kappa_+\theta_+(z) - \kappa_-\theta_-(z)] \ , \tag{5.3a}$$

$$\bar{\kappa}_T = \int_{-\infty}^{\infty} dz[\kappa_T(z) - \kappa_+\theta_+(z) - \kappa_-\theta_-(z)] \ , \tag{5.3b}$$

which will be designed shortly as the normal and tangential surface heat conductivities, respectively, $\bar{\kappa}_N$ and $\bar{\kappa}_T$.

In conclusion, in the bulk phases we have $\rho(z) = \rho_\pm$, $a(z) = a_\pm$, $b_N(z) = b_T(z) = b_\pm$, $h_N(z) = h_T(z) = h_\pm$, $\kappa_N(z) = \kappa_T(z) = \kappa_\pm$, $\xi_N(z) = \xi_T(z) = \xi_\pm$, $\eta_N(z) = \eta_T(z) = \eta_{NT}(z) = \eta_\pm$ for $\pm z \geqslant \epsilon$, whereas the interface region ($|z| < \epsilon$) will be characterized by the surface quantities $\bar{\rho}$, $\bar{a}$, $\bar{b}_N$, $\bar{b}_T$, $\bar{h}_N$, $\bar{h}_T$, $\bar{\kappa}_N$, $\bar{\kappa}_T$, $\bar{\xi}_N$, $\bar{\xi}_T$, $\bar{\eta}_N$, $\bar{\eta}_T$, $\bar{\eta}_{NT}$ defined in analogy with Eqs. (5.2) and (5.3).

We now consider the simplifications of the hydrodynamic equations (3.3) and (3.4) for the case of a liquid–vapor system with a planar equilibrium interface which is sufficiently "thin" so that a suitable ϵ value can be defined and the above considerations will apply. Notice finally that the surface excess values introduced above are defined with respect to the dividing surface of the equilibrium interface. This is natural only in a linearized theory where the introduction of a nonequilibrium dividing surface would lead to nonlinear correction terms. These surface excess values do not depend on ϵ itself but on the choice of the Gibbs dividing surface ($z=0$). Below we will find it convenient to physically localize this surface in an unambiguous way be requiring the surface excess density $\bar{\rho}$ to vanish. This is precisely the zero adsorption condition also used in the equilibrium theory.[17]

VI. HYDRODYNAMIC EQUATIONS OF THE BULK PHASES

The exact evolution equations for the conserved densities [Eqs. (2.18)–(2.20)] can be approximated after a transient time and for linearized deviations around a two-phase equilibrium state, in the limit of long times and small gradients by the hydrodynamic equations (2.18), (3.3) and (3.4). In the case of a planar equilibrium interface these equations can be simplified considerably for points $\mathbf{x}$ such that the distance to the interface, i.e., $|z|$, is large enough for all thermodynamic and transport coefficients to become again rotationally and translationally invariant, e.g., for these coefficients to become constants independent of $|z|$. Away from the critical point the planar interface can be considered to be well localized and sufficiently thin so that the above simplifications can be expected to occur as soon as $|z| \geqslant \epsilon$, where ϵ denotes the "thickness" of the interfacial layer. Putting $z = \pm\epsilon$ entirely in the bulk phases, we then also expect the above hydrodynamic equations (3.3) and (3.4) to reduce exactly to the ordinary linearized hydrodynamic equations of each bulk phase for all points for which $|z| \geqslant \epsilon$. In order to see whether this is indeed the case we still have to analyze the two interface terms $\gamma_\alpha(\mathbf{x},t)$ and $\mu(\mathbf{x},t)$, appearing in

Eqs. (3.3) and (3.4). From Eqs. (4.6)–(4.9) it is seen that both γ_α and μ involve equilibrium correlation functions like $K_{mn}(\mathbf{x}, \mathbf{x}')$ multiplied by $\rho'(z')$ and with $\mathbf{x}'$ integrated on the whole space. When $\mathbf{x}$ belongs to a bulk phase (i.e., when $|z| > \epsilon$) and if these equilibrium correlations are short ranged then the $\mathbf{x}'$ integral will be effectively restricted to $\mathbf{x}'$ points belonging to the same bulk phase as $\mathbf{x}$. But when $\mathbf{x}'$ belongs to a bulk phase these contributions vanish. Therefore, provided all equilibrium correlations are short ranged, i.e., provided we stay well away from the critical point, the bulk phases can be decoupled from the interface. As the study of the interface region in next section will reveal, this however does not imply that the two bulk phases evolve independently from each other but that the contact between the bulk phases via the interface is established only locally at the edges of the interfacial layer.

Under the above assumptions the hydrodynamic equations (2.18), (3.3) and (3.4) can be simplified considerably in the bulk phases as we now indicate. For $\pm z > \epsilon$, Eq. (2.18) reduces to the continuity equation[1] of the ± phase:

$$\delta\dot{n}(\mathbf{x}, t) + \rho_\pm \nabla_\beta u_\beta(\mathbf{x}, t) = 0 \; ; \quad \pm z > \epsilon \; , \tag{6.1}$$

where ρ_+ is the density of the vapor phase ($z > \epsilon$) and ρ_- the density of the liquid phase ($z < -\epsilon$). In view of the above discussion Eq. (3.3) can be reduced in the bulk phases to the form

$$\begin{aligned} m\rho_\pm \ddot{u}_\alpha(\mathbf{x}, t) &= \rho_\pm a_\pm \nabla_\alpha \nabla_\beta u_\beta(\mathbf{x}, t) - b_\pm \nabla_\alpha \dot{\theta}(\mathbf{x}, t) \\ &\quad + (\xi_\pm + \tfrac{1}{3}\eta_\pm)\nabla_\alpha \nabla_\beta \dot{u}_\beta(\mathbf{x}, t) + \eta_\pm \nabla_\beta \nabla_\beta \dot{u}_\alpha(\mathbf{x}, t) \; ; \quad \pm z > \epsilon \; , \end{aligned} \tag{6.2}$$

or removing one time derivative with the aid of Eq. (6.1), Eq. (6.2) can be also written in the standard Navier–Stokes form[1]

$$m\rho_\pm \mathring{u}_\alpha(\mathbf{x}, t) + \nabla_\beta \Pi^\pm_{\beta\alpha}(\mathbf{x}, t) = 0 \; ; \quad \pm z > \epsilon \; , \tag{6.3}$$

with a macroscopic stress tensor $\Pi^\pm_{\alpha\beta}$:

$$\begin{aligned} \Pi^\pm_{\alpha\beta}(\mathbf{x}, t) &= \delta p_\pm(\mathbf{x}, t)\delta_{\alpha\beta} - (\xi_\pm - \tfrac{2}{3}\eta_\pm)\delta_{\alpha\beta}\nabla_\gamma u_\gamma(\mathbf{x}, t) \\ &\quad - \eta_\pm[\nabla_\beta u_\alpha(\mathbf{x}, t) + \nabla_\alpha u_\beta(\mathbf{x}, t)] \end{aligned} \tag{6.4}$$

and a local pressure change $\delta p_\pm$:

$$\delta p_\pm(\mathbf{x}, t) = a_\pm \delta n(\mathbf{x}, t) + b_\pm \theta(\mathbf{x}, t) \; , \tag{6.5}$$

due to a density change ($a_\pm = \partial p/\partial \rho_\pm |_T$) and to a temperature change ($b_\pm = \partial p/\partial T|_{\rho_\pm}$), while as usual $\xi_\pm$, $\eta_\pm$ denote respectively, the "bulk" or dilatational viscosity and the shear viscosity of the ± bulk phase. Similarly Eq. (3.4) becomes

$$\begin{aligned} \rho_\pm \mathring{\epsilon}(\mathbf{x}, t) &= h_\pm \nabla_\beta u_\beta(\mathbf{x}, t) \\ &\quad + \kappa_\pm \nabla_\beta \nabla_\beta \theta(\mathbf{x}, t) \; ; \quad \pm z > \epsilon \; , \end{aligned} \tag{6.6}$$

or equivalently in the standard Fourier-law form[1]

$$\rho_\pm T\dot{s}(\mathbf{x}, t) + \nabla_\beta J^\pm_\beta(\mathbf{x}, t) = 0 \; ; \quad \pm z > \epsilon \; , \tag{6.7}$$

where $s(\mathbf{x}, t)$ is the entropy density

$$\rho_\pm Ts(\mathbf{x}, t) = \rho_\pm \epsilon(\mathbf{x}, t) + (h_\pm/\rho_\pm)\delta n(\mathbf{x}, t) \; , \tag{6.8}$$

and $J^\pm_\beta$ the macroscopic heat current

$$J^\pm_\beta(\mathbf{x}, t) = -\kappa_\pm \nabla_\beta \theta(\mathbf{x}, t) \tag{6.9}$$

of the ± bulk phase ($\pm z > \epsilon$).

VII. INTERFACIAL HYDRODYNAMICS

In the interfacial region ($|z| < \epsilon$) Eqs. (3.3) and (3.4) retain their full complexity: all coefficients [e.g., $a(z)$] depend explicitly on z, all tensors [e.g., $\kappa_{\alpha\beta}(z)$] exhibit the cylindrical anisotropy of the interfacial layer while the specifically interface terms [e.g., $\gamma_\alpha(\mathbf{x}, t)$] involve now long-range correlations typical of the equilibrium interface. All these complexities occur however only on a microscopic scale of the order of the interface thickness ϵ (a few atomic radii) and it is clearly artificial to retain such details in a theory of the large scale macroscopic variations of concern to hydrodynamics. Therefore, we now use the smallness of ϵ in order to simplify the hydrodynamic equations in the interface region. We will show under what conditions these equations can be reduced to much simpler equations involving only surface excess properties such as surface transport coefficients and surface excess thermodynamic properties. To dominant order in ϵ we will then be able to establish contact with the phenomenological treatment[1,4,11] of interfacial hydrodynamics.

A. Procedure

We now integrate Eqs. (3.3) and (3.4) over the interface from $z = -\epsilon$ to $z = \epsilon$, where, as above, the points $z = \pm\epsilon$ are located in the bulk phases. Taking into account the discussion of Secs. IV and V we obtain from Eq. (3.3):

$$\begin{aligned} m\int_{-\epsilon}^{\epsilon} dz\, \rho(z)\ddot{u}_\alpha(\mathbf{x}, t) &= \int_{-\epsilon}^{\epsilon} dz\, \rho(z)\nabla_\alpha a(z)[\nabla_z u_z(\mathbf{x}, t) + \boldsymbol{\nabla}_s \cdot \mathbf{u}(\mathbf{x}, t)] - \int_{-\epsilon}^{\epsilon} dz\, \nabla_\alpha[\delta_{\alpha z} b_N(z) + (1 - \delta_{\alpha z})b_T(z)]\dot{\theta}(\mathbf{x}, t) \\ &\quad + \int_{-\epsilon}^{\epsilon} dz\, \rho(z)\nabla_\alpha[\alpha_N(z)\nabla_z^2 u_z(\mathbf{x}, t) + \alpha_T(z)\boldsymbol{\nabla}_s^2 u_z(\mathbf{x}, t)] + \int_{-\epsilon}^{\epsilon} dz\, \nabla_\alpha\{\xi_N(z)\mathring{s}_{zz}(\mathbf{x}, t) + \xi_T(z)[\dot{s}_{xx}(\mathbf{x}, t) + \dot{s}_{yy}(\mathbf{x}, t)]\} \\ &\quad + 2\int_{-\epsilon}^{\epsilon} dz\, \delta_{\alpha z}(\nabla_z\{\eta_N(z)[\mathring{s}_{zz}(\mathbf{x}, t) - \tfrac{1}{3}\mathring{s}_0(\mathbf{x}, t)]\} + \sum_{\beta = x, y} \nabla_\beta[\eta_{NT}(z)\dot{s}_{\beta z}(\mathbf{x}, t)]) \\ &\quad + 2\int_{-\epsilon}^{\epsilon} dz (1 - \delta_{\alpha z})\left\{\nabla_z[\eta_{NT}(z)\dot{s}_{z\alpha}(\mathbf{x}, t)] - \tfrac{1}{3}\nabla_\alpha[\eta_T(z)\mathring{s}_0(\mathbf{x}, t)] + \sum_{\beta = x, y} \nabla_\beta[\eta_T(z)\dot{s}_{\beta\alpha}(\mathbf{x}, t)]\right\} , \end{aligned} \tag{7.1}$$

where, exceptionally, the summation convention over repeated Cartesian labels has not been applied while the notation of Eq. (4.2) has been used together with $s_0(\mathbf{x}, t) = \sum_\alpha s_{\alpha\alpha}(\mathbf{x}, t)$. Equation (3.4) yields similarly

$$\int_{-\epsilon}^{\epsilon} dz\, \rho(z)\mathring{\epsilon}(\mathbf{x},t) = \int_{-\epsilon}^{\epsilon} dz [h_N(z)\nabla_z u_z(\mathbf{x},t) + h_T(z)\boldsymbol{\nabla}_s\cdot \mathbf{u}(\mathbf{x},t)] + \int_{-\epsilon}^{\epsilon} dz\, \{\nabla_z[\kappa_N(z)\nabla_z\theta(\mathbf{x},t)] + \kappa_T(z)\boldsymbol{\nabla}_s^2\theta(\mathbf{x},t)\} + \int_{-\epsilon}^{\epsilon} dz\, \nabla_z[\beta_N(z)\theta(\mathbf{x},t)] , \tag{7.2}$$

where both in Eq. (7.1) and in Eq. (7.2) $\boldsymbol{\nabla}_s$ denotes the two-dimensional surface gradient $\boldsymbol{\nabla}_s = \{\nabla_x, \nabla_y\}$. We now assume that the velocity field $u_\alpha(\mathbf{x}, t)$ and the temperature field $\theta(\mathbf{x}, t)$ are smooth functions of $\mathbf{x}$ even for z values belonging to the interface region. The reason for this being that these variables denote hydrodynamic perturbations over a uniform equilibrium profile. Indeed, in the equilibrium state the velocity field is zero everywhere and the temperature field is constant everywhere and equal to the equilibrium temperature T. This is not so for the density $n(\mathbf{x}, t)$, which has an equilibrium profile $\rho(z)$, which exhibits strong gradients in the interface region. In order to avoid possible strong gradients in the density perturbation $\delta n(\mathbf{x}, t)$, we have eliminated $\delta n(\mathbf{x}, t)$ from the remaining hydrodynamic equations with the aid of the continuity equation (2.18). Similarly, since the equilibrium profile of the internal energy is nonuniform we eliminate $\epsilon(\mathbf{x}, t)$ from Eq. (7.2) in favor of $\theta(\mathbf{x}, t)$ with the aid of Eq. (3.2b), i.e., $\epsilon(\mathbf{x}, t) = c_V(z)\theta(\mathbf{x}, t)$. In order to proceed we now reexpress the left-hand side of Eqs. (7.1) and (7.2) in terms of surface quantities. Since, $u_\alpha(\mathbf{x}, t)$ is a smooth variable while ϵ is small we take $u_\alpha(\mathbf{x}, t)$ out of the integral and evaluate it at the geometrical surface around which the equilibrium interface is localized. We take this surface to be the $z = 0$ plane and introduce surface excess values with respect to this plane [cf. Eqs. (5.1) and (5.2)]. For instance, we write explicitly

$$\int_{-\epsilon}^{\epsilon} dz\, \rho(z)u_\alpha(\mathbf{x},t) \simeq u_\alpha(x,y,z=0;t)\int_{-\epsilon}^{\epsilon} dz\,\rho(z) \simeq \bar{\rho}u_\alpha^s(\mathbf{x},t) , \tag{7.3}$$

where we have used the smoothness of $u_\alpha(\mathbf{x}, t)$ in order to extract its value at the equilibrium surface $z = 0$, which we indicate by a superscript s as $u_\alpha^s(\mathbf{x}, t) \equiv u_\alpha(x, y, z = 0; t)$, from the integral, next we add and subtract the Gibbs reference value of Eq. (5.1); $\int_{-\epsilon}^{\epsilon} dz\, \rho(z) = \int_{-\epsilon}^{\epsilon} dz[\rho(z) - \rho_G(z)] + \epsilon(\rho_+ + \rho_-)$ for a thin interface $\int_{-\epsilon}^{\epsilon} dz\, [\rho(z) - \rho_G(z)]$ can then be approximated by the surface excess density $\bar{\rho}$ [cf. Eq. (5.2)] and the order-ϵ term can be neglected when both $\bar{\rho}$ and $(\rho_+ + \rho_-)$ are finite. The left-hand side of Eqs. (7.1) and (7.2) can thus be written to dominate order in ϵ as $\bar{\rho}\ddot{u}_\alpha^s(\mathbf{x}, t)$ and $\overline{\rho c_V}\dot{\theta}^s(\mathbf{x}, t)$. The question now is whether we can also express the right-hand side of Eqs. (7.1) and (7.2) in terms of surface properties? The answer is yes and we illustrate this now with the aid of a few typical terms. The novelty introduced by the right-hand side of Eqs. (7.1) and (7.2) is that these now also involve the gradients of the hydrodynamic variables. We therefore will assume that the tangential gradients of the hydrodynamic variables, e.g., $\nabla_x\theta(\mathbf{x}, t)$, remain smooth functions of z but that this is not necessarily the case for the normal gradients of the hydrodynamic variable, e.g., $\nabla_z\theta(\mathbf{x}, t)$, which can be expected to change rapidly. The latter gradients will therefore always be first integrated by parts with respect to z. As a first example, consider the heat diffusivity term of Eq. (7.2):

$$\int_{-\epsilon}^{\epsilon} dz\, \{\nabla_z[\kappa_N(z)\nabla_z\theta(\mathbf{x},t)] + \kappa_T(z)\boldsymbol{\nabla}_s^2\theta(\mathbf{x},t)\} = [\kappa_N\nabla_z\theta]_-^+ + \bar{\kappa}_T\boldsymbol{\nabla}_s^2\theta^s + O(\epsilon) , \tag{7.4}$$

The first term in the right-hand side of Eq. (7.4) represents the "jump" in the normal heat current $(-\kappa_N\nabla_z\theta)$:

$$[\kappa_N\nabla_z\theta]_-^+ = \kappa_N(z=\epsilon)(\nabla_z\theta)_{z=\epsilon} - \kappa_N(z=-\epsilon)(\nabla_z\theta)_{z=-\epsilon} \simeq \kappa_+(\nabla_z\theta)_+ - \kappa_-(\nabla_z\theta)_- , \tag{7.5}$$

where we took into account that at $z = \pm\epsilon$, $\kappa_N(z)$ takes on its bulk value $\kappa_\pm$, whereas $(\nabla_z\theta)_\pm$ denotes the value of $\nabla_z\theta$ at $z = \pm\epsilon$, an expression which remains meaningful even in the limit of vanishing ϵ, where $\nabla_z\theta$ becomes discontinuous at $z = \pm 0$, these limiting values being still denoted as $(\nabla_z\theta)_\pm$. The second term in the right-hand side of Eq. (7.4) has been obtained in a manner similar to Eq. (7.3) and is seen to involve a surface heat conductivity $\bar{\kappa}_T$ [Eq. (5.3)] and the surface Laplacian $(\boldsymbol{\nabla}_s^2 = \nabla_x^2 + \nabla_y^2)$ of the surface temperature field $[\theta^s(\mathbf{x}, t) \equiv \theta(x, y, z = 0; t)]$. As second example, we consider the following term appearing in Eq. (7.2):

$$\int_{-\epsilon}^{\epsilon} dz\, h_N(z)\nabla_z u_z(\mathbf{x},t) = \int_{-\epsilon}^{\epsilon} dz\, \nabla_z[h_N(z)u_z(\mathbf{x},t)] - \int_{-\epsilon}^{\epsilon} dz\, u_z(\mathbf{x},t)\nabla_z h_N(z) \simeq [h_N u_z]_-^+ - u_z^s[h_N]_-^+ \simeq O(\epsilon) , \tag{7.6}$$

where we took into account that $u_z(\mathbf{x}, t)$ is a smooth function of z while $\nabla_z u_z(\mathbf{x}, t)$ is not.

B. Results

Continuing this procedure we obtain from Eq. (7.2):

$$\overline{\rho c_V}\dot{\theta}^s = \bar{h}_T\boldsymbol{\nabla}_s\circ\mathbf{u}^s + [\kappa_N\nabla_z\theta]_-^+ + \bar{\kappa}_T\boldsymbol{\nabla}_s^2\theta^s + [\beta_N\theta]_-^+ + O(\epsilon) , \tag{7.7}$$

while the normal component $(\alpha = z)$ of Eq. (7.1) yields

$$m\bar{\rho}\ddot{u}_z^s = [(\xi_N + \tfrac{4}{3}\eta_N)\nabla_z\dot{u}_z]_-^+ + [(\xi_T - \tfrac{2}{3}\eta_N)\boldsymbol{\nabla}_s\cdot\mathring{\mathbf{u}}]_-^+ + \bar{\eta}_{NT}\boldsymbol{\nabla}_s^2\mathring{u}_z^s - [b_N\dot{\theta}]_-^+ + [\rho a\boldsymbol{\nabla}\cdot\mathbf{u}]_-^+ + [(\rho\alpha_N\nabla_z^2u_z + \rho\alpha_T\nabla^2u_z)]_-^+ - \overline{\rho'\alpha_T}\boldsymbol{\nabla}_s^2u_z^s - \overline{\rho'a}\boldsymbol{\nabla}_s\circ\mathbf{u}^s + O(\epsilon) \tag{7.8}$$

and finally the tangential components $(\alpha = x, y)$ of Eq. (7.1)

$$m\bar{\rho}\ddot{u}_\alpha^s = [\eta_{NT}(\nabla_z\dot{u}_\alpha + \nabla_\alpha\dot{u}_z)]_-^+ + [\rho\alpha_N\nabla_\alpha\nabla_z u_z]_-^+ + (\bar{\xi}_T - \tfrac{2}{3}\bar{\eta}_T)\nabla_\alpha\boldsymbol{\nabla}_s\circ\mathring{\mathbf{u}}^s + \bar{\eta}_T(\boldsymbol{\nabla}_s^2\mathring{u}_\alpha^s + \nabla_\alpha\boldsymbol{\nabla}_s\circ\mathring{\mathbf{u}}^s) - \bar{b}_T\nabla_\alpha\dot{\theta}^s + \overline{\rho a}\nabla_\alpha\boldsymbol{\nabla}_s\circ\mathbf{u}^s + \overline{\rho\alpha}_T\nabla_\alpha\boldsymbol{\nabla}_s^2u_z^s + O(\epsilon) ; \quad \alpha = x, y , \tag{7.9}$$

where $\boldsymbol{\nabla}_s\cdot\mathbf{u}^s$ denotes the value of the surface divergence $(\boldsymbol{\nabla}_s\circ\mathbf{u} = \nabla_x u_x + \nabla_y u_y)$ evaluated at the surface $z = 0$. Taking into account that in the bulk phases we have $\xi_N(z = \pm\epsilon) = \xi_T(z = \pm\epsilon) = \xi_\pm$, etc., Eqs. (7.7) and (7.8) can be simplified into

$$\overline{\rho c_V}\mathring{\theta}^s = \bar{h}_T \nabla_s \cdot \mathbf{u}^s + \bar{\kappa}_T \nabla_s^2 \theta^s + [\kappa \nabla_z \theta]_-^+ + [\beta_N \theta]_-^+ , \qquad (7.10)$$

$$m\bar{\rho}\ddot{u}_z^s = \bar{\eta}_{NT} \nabla_s^2 \mathring{u}_z^s - [\dot{\Pi}_{zz}]_-^+ + [\rho\alpha_N \nabla_z^2 u_z + \rho\alpha_T \nabla_s^2 u_z]_-^+ - \overline{\rho'\alpha}_T \nabla_s^2 u_z^s , \qquad (7.11)$$

$$m\bar{\rho}\ddot{u}_\alpha^s = (\bar{\xi}_T - \tfrac{2}{3}\bar{\eta}_T)\nabla_\alpha \nabla_s \cdot \dot{\mathbf{u}}^s + \bar{\eta}_T(\nabla_s^2 \dot{u}_\alpha^s + \nabla_\alpha \nabla_s \cdot \dot{\mathbf{u}}^s) - \bar{b}_T \nabla_\alpha \mathring{\theta}^s + \overline{\rho a}\, \nabla_\alpha \nabla_s \cdot \mathbf{u}^s + \overline{\rho\alpha}_T \nabla_\alpha \nabla_s^2 u_z^s - [\dot{\Pi}_{z\alpha}]_-^+ + [\rho\alpha_N \nabla_\alpha \nabla_z u_z]_-^+ ; \quad \alpha = x, y , \qquad (7.12)$$

where all $O(\epsilon)$ terms have been dropped; $[\dot{\Pi}_{\alpha\beta}]_-^+$ denotes the jump in the time derivative of the linearized macroscopic stress tensor

$$[\mathring{\Pi}_{\alpha\beta}]_-^+ = \{[-\rho a \nabla \cdot \mathbf{u} + b\mathring{\theta} - (\xi - \tfrac{2}{3}\eta)\nabla \cdot \mathring{\mathbf{u}}]\delta_{\alpha\beta} - \eta(\nabla_\alpha \mathring{u}_\beta + \nabla_\beta \mathring{u}_\alpha)\}_-^+ , \qquad (7.13)$$

the $\overline{\rho' a}$ term of Eq. (7.8) has been dropped since

$$\overline{\rho' a} = m v_0^2 \int_{-\infty}^{\infty} dz\, \rho'(z) \int d\mathbf{x}'\, K_{nn}(\mathbf{x}, \mathbf{x}')\rho(z') \equiv 0 \qquad (7.14)$$

vanishes identically by virtue of the equilibrium profile equation (4.5) while finally $\overline{\rho'\alpha}_T$:

$$\overline{\rho'\alpha}_T = \frac{m v_0^2}{4} \int_{-\infty}^{\infty} dz\, \rho'(z) \int d\mathbf{x}' \times [(x-x')^2 + (y-y')^2] K_{nn}(\mathbf{x}, \mathbf{x}')\rho'(z') \qquad (7.15)$$
$$= -\sigma ,$$

can be identified as minus the surface tension σ of the liquid–vapor interface.[7–9]

C. Final equations

We now gather all results and write them down in a form which greatly facilitates the understanding of the physical meaning of the various terms. Using the temperature field $\theta(\mathbf{x}, t)$ and velocity field $\mathbf{u}(\mathbf{x}, t)$ as fundamental variables we rewrite Eq. (6.6) with the aid of Eq. (3.2b), in the limit of vanishing interface thickness ($\epsilon \to 0$), in each bulk phase as

$$\rho_\pm c_V^\pm \dot{\theta}(\mathbf{x}, t) + \nabla \cdot \mathbf{J}_\theta^\pm(\mathbf{x}, t) = 0 ; \quad \pm z > 0 , \qquad (7.16)$$

where $\mathbf{J}_\theta^\pm(\mathbf{x}, t)$ is the energy current of the ± phase

$$\mathbf{J}_\theta^\pm(\mathbf{x}, t) = -h_\pm \mathbf{u}(\mathbf{x}, t) - \kappa_\pm \nabla\theta(\mathbf{x}, t) ; \quad \pm z > 0 , \qquad (7.17)$$

whereas at the Gibbs dividing surface ($z = 0$) of the interface, Eq. (7.10) will be written as

$$\overline{\rho c_V}\mathring{\theta}(\mathbf{x}, t) + \nabla_s \cdot \mathbf{J}_\theta^s(\mathbf{x}, t) = -[\mathbf{n} \cdot \mathbf{J}]_-^+ + [I_\theta]_-^+ ; \quad z = 0 , \qquad (7.18)$$

where $\mathbf{J}_\theta^s$ is a surface energy current

$$\mathbf{J}_\theta^s(\mathbf{x}, t) = -\bar{h}_T \mathbf{u}(\mathbf{x}, t) - \bar{\kappa}_T \nabla_s \theta(\mathbf{x}, t) ; \quad z = 0 , \qquad (7.19)$$

which is analogous to $\mathbf{J}_\theta^\pm(\mathbf{x}, t)$ of Eq. (7.17), except that the bulk properties $h_\pm$, $\kappa_\pm$ have been replaced by surface excess properties $\bar{h}_T$, $\bar{\kappa}_T$ and the gradients $[\nabla = (\nabla_x, \nabla_y, \nabla_z)]$ by surface gradients $[\nabla_s = (\nabla_x, \nabla_y)]$. While the left-hand side of Eq. (7.18) is the surface equivalent of the bulk Eq. (7.16) its right-hand side does not vanish like in the bulk but contains the jumps $\{[a]_-^+ = a(z = +0) - a(z = -0)\}$ of a bulk quantity and of an interfacial quantity. The latter bulk quantity is the normal heat current (here and below $\mathbf{n}$ will denote the normal to the planar equilibrium interface, i.e., $\mathbf{n} = \mathbf{1}_z$) $\mathbf{n} \cdot \mathbf{J} = J_z = -\kappa_N \nabla_z \theta$:

$$-[\mathbf{n} \cdot \mathbf{J}]_-^+ = \kappa_+[\nabla_z \theta(\mathbf{x}, t)]_{z=+0} - \kappa_-[\nabla_z \theta(\mathbf{x}, t)]_{z=-0} , \qquad (7.20)$$

while the interface property is $I_\theta(\mathbf{x}, t) = \beta_N(z)\theta(\mathbf{x}, t)$ so that $[I_\theta]_-^+$ of Eq. (7.18) can be written as

$$[I_\theta]_-^+ = (\beta_N^+ - \beta_N^-)\theta(x, y, 0; t) \qquad (7.21)$$

because of the continuity of $\theta(\mathbf{x}, t)$ at $z = 0$ ($[\theta]_-^+ = 0$). Similarly Eq. (6.3) can be rewritten as

$$m\rho_\pm \ddot{\mathbf{u}}(\mathbf{x}, t) + \nabla \cdot \dot{\Pi}^\pm(\mathbf{x}, t) = 0 ; \quad \pm z > 0 , \qquad (7.22)$$

where $\dot{\Pi}^\pm(\mathbf{x}, t)$ is the time derivative of the macroscopic stress tensor of the ± bulk phase

$$\mathring{\Pi}_{\alpha\beta}^\pm(\mathbf{x}, t) = [-\rho_\pm a_\pm \nabla \cdot \mathbf{u}(\mathbf{x}, t) + b_\pm \dot{\theta}(\mathbf{x}, t) - (\xi_\pm - \tfrac{2}{3}\eta_\pm)\nabla \cdot \mathring{\mathbf{u}}(\mathbf{x}, t)]\delta_{\alpha\beta} - \eta_\pm[\nabla_\alpha \dot{u}_\beta(\mathbf{x}, t) + \nabla_\beta \mathring{u}_\alpha(\mathbf{x}, t)] ; \quad \pm z > 0 , \qquad (7.23)$$

whereas Eq. (7.12) can be rewritten as the surface equivalent of Eq. (7.22) for the tangential velocity field u_α ($\alpha = x, y$):

$$m\bar{\rho}\ddot{u}_\alpha(\mathbf{x}, t) + \nabla_\beta^s \mathring{\Pi}_{\beta\alpha}^s(\mathbf{x}, t) = -[\dot{\Pi}_{z\alpha}]_-^+ + [I_\alpha]_-^+ + \sigma_\alpha ; \quad \alpha = (x, y) ; \quad z = 0 , \qquad (7.24)$$

where we have put $\nabla_\alpha^s = (\nabla_s)_\alpha$ and again the left-hand side of Eq. (7.24) resembles the left-hand side of the bulk Eq. (7.22) with the bulk densities $\rho_\pm$ replaced by the surface excess density $\bar{\rho}$, the three-dimensional vectors and gradients $(\mathbf{u}, \nabla, \ldots)$ replaced by two-dimensional ones $(u_\alpha, \nabla_s, \ldots)$ and similarly the bulk pressure tensor $\Pi_{\alpha\beta}^\pm$ of Eq. (7.23) replaced by a two by two surface pressure tensor $\Pi_{\alpha\beta}^s$ whose time derivative reads

$$\mathring{\Pi}_{\alpha\beta}^s(\mathbf{x}, t) = [-\overline{\rho a}\nabla_s \cdot \mathbf{u}(\mathbf{x}, t) + \bar{b}_T \mathring{\theta}(\mathbf{x}, t) - (\bar{\xi}_T - \tfrac{2}{3}\bar{\eta}_T)\nabla_s \cdot \mathring{\mathbf{u}}(\mathbf{x}, t)]\delta_{\alpha\beta} - \bar{\eta}_T[\nabla_\alpha \dot{u}_\beta(\mathbf{x}, t) + \nabla_\beta \mathring{u}_\alpha(\mathbf{x}, t)]; \quad (\alpha, \beta) = (x, y) ; \quad z = 0 , \qquad (7.25)$$

whereas the right-hand side of Eq. (7.24) does not vanish but contains the jump in the time derivative of the tangential bulk stresses $[\dot{\Pi}_{z\alpha}]_-^+$ defined already in Eq. (7.13), the jump in interface properties $[I_\alpha]_-^+$ with

$$I_\alpha(\mathbf{x}, t) = \rho(z)\alpha_N(z)\nabla_\alpha \nabla_z u_z(\mathbf{x}, t) ; \quad \alpha = x, y , \qquad (7.26)$$

and finally the interface property

$$\sigma_\alpha(\mathbf{x}, t) = \overline{\rho\alpha}_T \nabla_\alpha \nabla_s^2 u_z(\mathbf{x}, t) ; \quad \alpha = x, y ; \quad z = 0 . \qquad (7.27)$$

Finally, Eq. (7.11) for the normal velocity field u_z can be written in a form similar to Eq. (7.24):

$$m\bar{\rho}\ddot{u}_z(\mathbf{x}, t) + \nabla_\beta^s \dot{\Pi}'_{\beta z}(\mathbf{x}, t) = -[\mathring{\Pi}_{zz}]_-^+ + [I_z]_-^+ + \sigma_z ; \quad z = 0 , \qquad (7.28)$$

where $\dot{\Pi}'_{\alpha z}$ is the time derivative of a tangential—normal surface shear stress

$$\dot{\Pi}'_{\alpha z}(\mathbf{x}, t) = -\bar{\eta}_{NT} \nabla_\alpha \dot{u}_z(\mathbf{x}, t) ; \quad \alpha = x, y ; \quad z = 0 , \qquad (7.29)$$

while $[\mathring{\Pi}_{zz}]_-^+$ results from the jump in the normal bulk stresses [cf. Eq. (7.13)], $[I_z]_-^+$ represents the jump in the interfacial properties I_z:

$$I_z(\mathbf{x}, t) = \rho(z)\alpha_N(z)\nabla_z^2 u_z(\mathbf{x}, t) + \rho(z)\alpha_T(z)\nabla_s^2 u_z(\mathbf{x}, t) , \qquad (7.30)$$

and σ_z is the interfacial property

$$\sigma_z(\mathbf{x}, t) = \sigma \nabla_s^2 u_z(\mathbf{x}, t) \; ; \quad z = 0 \, , \tag{7.31}$$

where $\sigma = -\overline{\rho' \alpha_T}$ is the surface tension defined by Eq. (7.15).

VIII. DISCUSSION AND RELATION TO THE PHENOMENOLOGICAL THEORIES

Our final equations consist of Eqs. (7.16) and (7.22) for the bulk phases and Eqs. (7.18), (7.24), and (7.28) for the interface or surface phase of the liquid–vapor system. They have been obtained under the assumption that the system remains close to equilibrium so that nonlinear terms can be neglected. The equilibrium situation considered is assumed to exhibit cylindrical symmetry around a planar interface. The dynamics of the two-phase monoatomic fluid is described in the long-time long-wavelength hydrodynamic limit where the macroscopic variables change sufficiently slowly in space and in time so that a local description becomes possible. In the limit of vanishing interface thickness the system splits into two bulk phases coupled to a surface phase which reflects the special interfacial properties. In the bulk phases the dynamic equations reduce to the ordinary hydrodynamic equations consisting of the linearized Navier–Stokes equation for the velocity field and the linearized Fourier equation for the temperature field, with thermodynamic and transport properties relevant to each bulk phase. In the interface the dynamic equations reduce to linearized hydrodynamic equations for a two-dimensional surface phase described by the Gibb's surface excess values of the thermodynamic and transport properties of the inhomogeneous fluid within their right-hand side three types of source terms. An additional surface hydrodynamic equation for the normal velocity field describes the motion of the interface itself. The three types of source terms which appear in the surface hydrodynamic equations consist of (1) jumps in the normal bulk heat current and the normal and tangential bulk stresses which establish the necessary connection between the surface phase and the adjacent bulk phases, (2) jumps in the typical interface properties I_θ and I [Eqs. (7.21), (7.26), and (7.29)], and (3) the surface excess values of the interface properties described by σ [Eqs. (7.27) and (7.30)]. All coefficients appearing in these equations are defined in terms of statistical mechanical averages over the distribution functions of the nonuniform fluid. These distribution functions can, in principle, be obtained from the equilibrium statistical mechanics of nonuniform fluids once the atomic interactions have been specified. The present theory of interfacial hydrodynamics in thus a *microscopic* theory in the sense that we did start from Newton's equations for a given potential but not in the sense that all of the underlying approximations can be precisely justified. With respect to this last point very little is known, at present, even for the case of bulk hydrodynamics.

We now compare our results with the existing phenomenological theories. The dynamics of the liquid–vapor interface was recently studied by Turski and Langer[14] on the basis of a set of hydrodynamic equations for a nonuniform fluid derived from the van der Waals–Cahn–Hilliard free energy functional. Except for the explicit van der Waals approximations their starting equations are comparable to our Eqs. (2.18), (3.3) and (3.4). These authors have moreover neglected the viscous contributions $[\eta_{\alpha\beta\alpha'\beta'}(\mathbf{x})]$ to Eq. (3.3) and approximated the local heat conductivity tensor $\kappa_{\alpha\beta}(\mathbf{x})$ by a constant (i.e., in their notations $\kappa_{\alpha\beta}(\mathbf{x}) = \lambda\delta_{\alpha\beta}$). Comparing their Eqs. (2.5)–(2.7) with our Eqs. (3.3) and (3.4) we see that their method amounts to further neglect the specific interface term $\mu(\mathbf{x}, t)$ of Eq. (3.4) and to approximate $b_{\alpha\beta}(\mathbf{x})$ and $h_{\alpha\beta}(\mathbf{x})$ of Eqs. (3.3) and (3.4) by diagonal matrices corresponding to the bulk values but evaluated at the local density $\rho = \rho(\mathbf{x})$ (e.g., $b_{\alpha\beta}(\mathbf{x}) = \delta_{\alpha\beta}(\partial P/\partial T)|_{\rho=\rho(\mathbf{x})}$).

The study of the interface between two immiscible fluids on the basis of the methods of nonequilibrium thermodynamics by Bedeaux, Albano, and Mazur[13] is in turn closely related to our Eqs. (7.18), (7.24), and (7.28). These authors have studied the macroscopic conservation laws by writing the conserved densities and their conjugated current densities as the sum of two bulk contributions, one of each bulk phase, to which, they add a separate contribution for the surface phase which is singular and located on a moving geometric dividing surface. Within this context these authors have considered the nonlinear case and it is only after linearizing their results that we can compare them with those obtained here. Their Eq. (3.47) has exactly the same structure as our Eq. (7.18) if (1) we identify their surface internal energy density with $\overline{\rho c_V}\theta^s(\mathbf{x}, t)$, (2) identify their surface energy current density with $\mathbf{J}_\theta^s$ of Eq. (7.19), and (3) neglect the jump of I_θ in Eq. (7.18). Notice that the $[I_\theta]_-^+$ term [cf. Eqs. (7.21) and (4.9)] contains a spatial correlation of the microscopic normal heat current between a point at the edge of the bulk phase ($z = \pm\epsilon$) and a point inside the interface [i.e., for z' such that $\rho'(z') \neq 0$] and reflects the fact that the interface is not a geometric surface but a transition layer. It is hence clear that such a term can not appear in a theory where the interface is treated *a priori* as a geometric surface. In practice such crossed bulk-interface correlations could however turn out to be small. The main advantage of the present theory over the irreversible thermodynamics treatment stems from the fact that we provide explicit statistical mechanical expressions for the various surface quantities entering Eq. (7.18). Notice hereby that the surface heat conductivity of Eq. (7.18) is defined as a surface excess value with respect to the unperturbed equilibrium dividing surface ($z = 0$) since deviations therefrom will lead to nonlinear corrections to Eq. (7.19). Consider now the relation between the surface Navier–Stokes Eqs. (7.24) and (7.28), and their Eq. (3.37). Here the situation is slightly more complicated. First of all, the above authors[11] consider essentially the simplifying case where there is no singular surface mass density. In our treatment, for the reasons explained above, we have eliminated the mass density in favor of the velocity field by taking the time derivative of the Navier–Stokes equation and using the (linearized) continuity Eq. (2.18). That it was reasonable to do this can be seen from the fact that the $[I_\alpha]_-^+$ and $[I_z]_-^+$ contributes to Eqs. (7.24) and

(7.28) can not be written *a priori* as time derivatives and hence unless these contributions can be neglected we can not remove the additional time derivative from Eqs. (7.24) and (7.28). After the elimination of $\delta n(\mathbf{x}, t)$, the only mass density which remains in our equations is the equilibrium mass density $m\rho(\mathbf{x})$ or in the case of the surface equations the surface excess density $m\overline{\rho}$. Now it is customary from the equilibrium theory to physically localize the Gibbs dividing surface by the condition of zero adsorption $\overline{\rho}=0$. It is clearly necessary to specify the meaning of the mathematical equation for the Gibbs dividing surface $(z=0)$ by a physical condition like $\overline{\rho}=0$ but there is no *a priori* reason why we should make the same choice as in the equilibrium theory, we could take for instance $\overline{\kappa}_T=0$ or $\overline{\rho c_V}=0$, etc. It is however convenient to use the same condition of zero adsorption as in the equilibrium theory $\overline{\rho}=0$, while this is presumably also the easiest choice from the experimental point of view. If we make this choice $(\overline{\rho}=0)$ then the surface Navier–Stokes Eqs. (7.24) and (7.28) are no longer equations of motion but become *boundary conditions* relating the jump in the bulk stresses $[\mathbf{n}\cdot\Pi]_-^+$ to the surface stresses $\nabla_s\cdot(\Pi^s+\Pi')$ and the surface properties σ and $[\mathbf{I}]_-^+$. These equations can now be compared with Eq. (3.37) of Ref. 11. First we have to neglect the $[\mathbf{I}]_-^+$ terms from our equations since, for the same reasons as discussed above in the case of $[I_\theta]_-^+$, no such terms can appear in a theory where the interface is treated *a priori* as singular. Once this term is neglected the additional time derivative can be removed from the remaining terms of Eqs. (7.24) and (7.28). (The resulting integration constants can always be put equal to zero by a proper choice of the initial perturbations.) Let us now introduce the instantaneous local normal elevation of the equilibrium dividing surface $\xi(x,y;t)$ through[18]

$$\dot{\xi}(x,y;t)=u_z(x,y,0;t)\ , \tag{8.1}$$

so that the instantaneous local *mean* curvature $c(x,y;t)$ (which is usually written in terms of the principal radii of curvature R_1 and R_2 as $c=R_1^{-1}+R_2^{-1}$) becomes

$$c(x,y;t)=\nabla_s^2\,\xi(x,y;t)\ , \tag{8.2}$$

which is correct only for the case of small curvatures[18] such as those produced by the small nonequilibrium perturbations considered here. The σ terms of Eqs. (7.24) and (7.28) can now be written as time derivatives and added as specific interface contributions to the surface stress tensor $\Pi_{\alpha\beta}^s$ of Eq. (7.25). Indeed from Eqs. (7.22), (8.1), and (8.2) we obtain

$$\sigma_\alpha(\mathbf{x},t)=\overline{\rho\alpha}_T\nabla_\alpha\dot{c}(x,y;t)$$

$$=-\nabla_\beta^s\dot{\Pi}_{\beta\alpha}''(\mathbf{x},t)\ ;\quad \alpha=x,y\ , \tag{8.3a}$$

$$\Pi_{\alpha\beta}''(\mathbf{x},t)=-\delta_{\alpha\beta}\overline{\rho\alpha}_Tc(x,y;t)\ ;\quad (\alpha,\beta)=(x,y)\ , \tag{8.3b}$$

where $\Pi_{\alpha\beta}''$ denotes now an additional interfacial contribution to the surface stress tensor $(\Pi_{\alpha\beta}^s+\Pi_{\alpha\beta}'')$. Similarly, from Eqs. (7.30), (8.1) and (8.2) we obtain

$$\sigma_z(\mathbf{x},t)=\sigma\dot{c}(x,y;t)$$

$$=-\nabla_\beta^s\dot{\Pi}_{\beta z}''(\mathbf{x},t)\ ;\quad \sigma=-\overline{\rho'\alpha}_T\ , \tag{8.4a}$$

$$\Pi_{\alpha z}''(\mathbf{x},t)=-\sigma\nabla_\alpha\xi(x,y;t)\ ;\quad \alpha=x,y\ , \tag{8.4b}$$

$$-\nabla_\beta^s\Pi_{\beta z}''(\mathbf{x},t)=\sigma c(x,y;t)=p_s(x,y;t)\ , \tag{8.4c}$$

where $\Pi_{\alpha z}''$ $(\alpha=x,y)$ is an additional tangential-normal surface stress tensor whose surface divergence equals minus the surface pressure $p_s=\sigma c$ and which is to be added to $\Pi_{\alpha z}'$ of Eq. (7.28). The content of Eq. (7.24) can now be reduced to that of Eq. (3.37) of Ref. 11 if we take $\overline{\rho}=0$ and neglect the $[I_\alpha]_-^+$ and σ_α terms leading to $\nabla_\beta^s\Pi_{\beta\alpha}^s=-[\Pi_{z\alpha}]_-^+$, which is identical to their result except that here $\Pi_{\alpha\beta}^s$ and $\Pi_{\alpha\beta}$ have been explicitly defined by Eqs. (7.25) and (7.13). Similarly, taking $\overline{\rho}=0$ and dropping the $[I_z]_-^+$ and $\Pi_{\alpha z}'$ terms reduces Eq. (7.28), via Eq. (8.4), to $p_s=[\Pi_{zz}]_-^+$, which is equivalent to their Eq. (3.41) except that here all quantities, including the surface tension σ of Eq. (8.4), have been defined explicitly in terms of the underlying atomic model. The phenomenological theory of Ref. 11 is thus clearly an approximation to the present one.

Another interesting limiting case of Eqs. (7.24) and (7.28) consists in taking $\overline{\rho}=0$, neglecting the $[\mathbf{I}]_-^+$ terms and using Eqs. (8.3) and (8.4) leading to

$$\nabla_s\cdot(\Pi^s+\Pi'+\Pi'')=-[\mathbf{n}\cdot\Pi]_-^+\ , \tag{8.5}$$

expressing the balance between the jump in bulk stresses (Π) and the surface divergence of a surface stress tensor composed of the surface excess values of the local bulk stresses (Π^s) and of genuine interfacial stresses (Π',Π''). If we assume moreover the genuine interfacial properties to dominate over the surface excess values of the local bulk properties (i.e., neglect Π^s), Eq. (8.5) can be written as a modified Laplace formula

$$[\Pi_{z\alpha}]_-^+=\overline{\rho\alpha}_T\nabla_\alpha c(x,y;t)\ ;\quad \alpha=x,y\ , \tag{8.6a}$$

$$[\Pi_{zz}]_-^+=-\overline{\rho'\alpha}_Tc(x,y;t)+\overline{\eta}_{NT}\dot{c}(x,y;t)\ , \tag{8.6b}$$

where a gradient of the local inverse curvature $c(x,y;t)$ is seen from Eq. (8.6a) to be able to balance a jump in the tangential bulk stresses while Eq. (8.6b) shows that a nonvanishing rate of change of the local curvature $(\dot{c}\neq 0)$ can balance a jump in normal stresses even for vanishingly small surface tensions $(\sigma=-\overline{\rho'\alpha}_T\simeq 0)$. Finally, the widespread use of the phenomenological theory of Levich[4,1] can be seen from Eqs. (7.18), (7.24), and (7.28) to rest on the choice $\overline{\rho}=0$ and on the neglect of the $[I_\theta]_-^+$ and $[\mathbf{I}]_-^+$ terms together with *all* the surface excess values *except* the surface tension. In this case Eq. (7.18) tells us simply that the jump in the normal heat current vanishes:

$$[J_z]_-^+=0\ , \tag{8.7}$$

Eq. (7.24) that the jump in the tangential stresses vanishes:

$$[\Pi_{z\alpha}]_-^+=0\ ;\quad \alpha=x,y\ , \tag{8.8}$$

while Eq. (7.27) reduces to Laplace's formula

$$[\Pi_{zz}]_-^+=p_s\ , \tag{8.9}$$

stating that the jump in the normal stresses is balanced by a surface pressure $p_s=\sigma c$, which equals the surface tension (σ) times the inverse local curvature $[c=c(x,y;t)]$. These Eqs. (8.7)–(8.9) together with the continuity at the interface of the hydrodynamic variables

$$[\theta]_-^+=0\ ,\quad [\mathbf{u}]_-^+=0\ , \tag{8.10}$$

and of their tangential gradients

$$[\nabla_s\theta]_-^+=0\ ;\ \ [\nabla_s\mathbf{u}]_-^+=0 \qquad (8.11)$$

constitute the classic equations of phenomenological interfacial hydrodynamics.[1,4]

IX. CONCLUSIONS

Combining the statistical mechanical approach to the linearized hydrodynamic equations of dense fluids (Mori–Zwanzig method) with the ideas of surface thermodynamics (Gibb's method) we have shown under what assumptions the macroscopic conservation equations of a nonuniform fluid (liquid–vapor system) can be reduced to the classic equations of interfacial hydrodynamics (ordinary hydrodynamic equation for each bulk phase plus a set of given boundary conditions at the interface). These approximations involve the standard hydrodynamical limit (restriction to low-frequency and long-wavelength phenomena) for the nonequilibrium perturbations of those hydrodynamical variables which have a uniform equilibrium profile (the velocity and temperature fields) together with approximations specific to the dynamics of the interfacial layer. In order to establish contact with the phenomenological theories we have neglected all terms which are explicitly proportional to the thickness of the interfacial layer. In this way we have obtained a surface Fourier equation and surface Navier–Stokes equations for the surface values of the hydrodynamical variables which together with the bulk Fourier equation and bulk Navier–Stokes equation for the bulk values of the hydrodynamical variables constitute a complete description of the hydrodynamics of a two-phase liquid–vapor system for equilibrium temperatures which are sufficiently far from the critical temperature so that the interfacial layer can be assimilated *a posteriori* (but not *a priori*) to a geometric surface.[19] The surface Fourier and Navier–Stokes equations obtained in this way resemble the corresponding bulk equations except that the hydrodynamic variable and their gradients are restricted to the surface while the bulk thermodynamic and transport coefficients are replaced by the corresponding Gibbs surface excess values. The right-hand side of these surface hydrodynamic equations do not vanish but contain the necessary coupling of the surface values of the hydrodynamical variables to their bulk values through the jumps in the normal current densities associated with the hydrodynamic variables as well as through a number of specific interfacial terms describing the viscoelastic nonequilibrium deformation of the equilibrium interface in relation to the structure of the underlying interfacial layer.

When all surface excess values and all interfacial properties except the surface tension are neglected these surface hydrodynamical equations reduce to boundary conditions which are equivalent to those of classical interfacial hydrodynamics. This classical theory rests thus on very stringent approximations to the interfacial dynamics.

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