Stress-strain relations in nonuniform equilibrium fluids

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The local stress tensor is defined as the field thermodynamically conjugate to the local strain tensor. Any free-energy change resulting from a strain can then be expressed either in terms of the stresses or in terms of the equivalent single-particle external force field. Using this equivalence, one obtains a well-defined expression for the local stress tensor in terms of this force field. On this basis we obtain unambiguous expressions for the surface tension and for the location of the surface of tension of a planar interface.

I. INTRODUCTION

Statistical-mechanical expressions for the surface tension of a planar liquid-vapor interface based on an explicit calculation of the mechanical stresses in an interface were introduced some 40 years ago by Kirkwood and Buff.[1] A formulation in terms of the stress tensor of Irving and Kirkwood[2] was subsequently provided by Buff.[3] The Irving and Kirkwood stress tensor involves a line integral over a path connecting a pair of molecules,[2] and it was recognized[2,4] that, in a nonuniform fluid, the result was path dependent. The recent reformulation of this stress tensor by Schofield and Henderson[5] emphasized that any path was consistent with the original formulation and that the surface tension calculated from this expression was in fact path independent. In contrast, however, the corresponding expression for the location of the surface of tension remained path dependent,[5] and the resulting failure to obtain a well-defined expression was taken then as symptomatic of a general defect in this type of description of interfacial properties.[6]

In the present investigation we will show that these problems originate from restricting all the considerations to the hydrostatic force balance equation which yields only an incomplete specification of the stress tensor. No such difficulties will appear if we *redefine* the local stress tensor as the field which is thermodynamically conjugate to the local strain tensor. As a result all free-energy changes which result from a strain will be well defined. We will show that, in particular, this is the case also for the position of the surface of tension of a planar interface.

In Sec. II we will discuss in detail the relation between the strain tensor and the displacement field while in Sec. III we will do the same for the stress tensor and the external force field. In Sec. IV we will compute a few free-energy changes (corresponding to the pressure, the surface tension, and the location of the surface of tension) for a fluid at two-phase coexistence with a planar interface. Our conclusions will then be gathered in the final section, Sec. IV.

II. THE DISPLACEMENT FIELD AND THE STRAIN TENSOR

In the classical theory of elasticity[7] the *deformation* of a continuous medium is described in terms of a *displacement* field $\mathbf{u}(\mathbf{r})$ which describes the way in which the matter at $\mathbf{r}$ has been displaced to a new position $\mathbf{r}'=\mathbf{r}+\mathbf{u}(\mathbf{r})$. Mathematically such a deformation can be described by a *local* change of coordinates, and for *small* deformations, i.e., when all calculations are carried out to first order in $\mathbf{u}$ only, this change of coordinates can always be inverted as

$$\mathbf{r}'=\mathbf{r}+\mathbf{u}(\mathbf{r}) \quad \mathbf{r}=\mathbf{r}'-\mathbf{u}(\mathbf{r}') , \tag{2.1}$$

at least for a single valued $\mathbf{u}(\mathbf{r})$. The Jacobian of this coordinate transformation corresponds to the determinant of the *distortion* tensor $\overleftrightarrow{d}(\mathbf{r})$:

$$\overleftrightarrow{d}(\mathbf{r})=\nabla\mathbf{u}(\mathbf{r}) , \tag{2.2}$$

where we have used a dyadic notation and $\nabla=\partial/\partial\mathbf{r}$. The physical content of (2.2) can be made explicit by separating $\overleftrightarrow{d}$ into a symmetric $[\overleftrightarrow{d}_{\rm sym}=\frac{1}{2}(\overleftrightarrow{d}+\overleftrightarrow{d}^{\dagger})]$ and an antisymmetric $[\overleftrightarrow{d}_{\rm antisym}=\frac{1}{2}(\overleftrightarrow{d}-\overleftrightarrow{d}^{\dagger})]$ part [with $\overleftrightarrow{d}^{\dagger}$ denoting the transpose of $\overleftrightarrow{d}$]. The symmetric part of (2.2) defines then the *strain* tensor field or local strain tensor $\overleftrightarrow{\epsilon}(\mathbf{r})$:

$$\overleftrightarrow{\epsilon}(\mathbf{r})=\tfrac{1}{2}\{\nabla\mathbf{u}(\mathbf{r})+[\nabla\mathbf{u}(\mathbf{r})]^{\dagger}\} , \tag{2.3}$$

while the antisymmetric part of (2.2) defines the local *rotation* tensor $\overleftrightarrow{\omega}(\mathbf{r})$:

$$\overleftrightarrow{\omega}(\mathbf{r})=\tfrac{1}{2}\{\nabla\mathbf{u}(\mathbf{r})-[\nabla\mathbf{u}(\mathbf{r})]^{\dagger}\} , \tag{2.4}$$

which can also be related to the (axial) rotation vector $\mathbf{R}(\mathbf{r})$:

$$\overleftrightarrow{\omega}(\mathbf{r})=-\mathbf{R}(\mathbf{r})\times\overleftrightarrow{1}, \quad \mathbf{R}(\mathbf{r})=\tfrac{1}{2}\nabla\times\mathbf{u}(\mathbf{r}) , \tag{2.5}$$

where $\overleftrightarrow{1}$ denotes the unit tensor. The geometric interpretation of (2.1)–(2.5) can now be made obvious by considering a small neighborhood $\delta\mathbf{r}$ of $\mathbf{r}$ and Taylor-expanding $\mathbf{u}(\mathbf{r}+\delta\mathbf{r})$ around $\mathbf{u}(\mathbf{r})$ as

$$\mathbf{u}(\mathbf{r}+\delta\mathbf{r})=\mathbf{u}(\mathbf{r})+\delta\mathbf{r}\cdot\overleftrightarrow{\mathrm{d}}(\mathbf{r})$$
$$=\mathbf{u}(\mathbf{r})+\mathbf{R}(\mathbf{r})\times\delta\mathbf{r}+\overleftrightarrow{\epsilon}(\mathbf{r})\cdot\delta\mathbf{r}\ , \tag{2.6}$$

which shows clearly how a deformation in the neighborhood of $\mathbf{r}$ can always be decomposed into a translation, a rotation, and a strain. From the physical point of view it is often useful to distinguish those coordinate transformations (2.1) which correspond to a *global* translation or a *global* rotation of the system as a whole. In order to distinguish such global displacements from the genuine local deformations of interest to us it is necessary and sufficient to assume that during the deformation described by (2.1) there is *at least* one point of the system whose vicinity remains fixed in space. If we denote such a "fixed point" by $\mathbf{r}_0$ then the conditions characterizing a *local* deformation are

$$\mathbf{u}(\mathbf{r}_0)=0\ ,\quad \mathbf{R}(\mathbf{r}_0)=0\ , \tag{2.7}$$

since according to (2.6) the vicinity of $\mathbf{r}_0$ will undergo neither a translation nor a rotation, and hence the system will remain fixed in space during the deformation described by (2.1) and (2.7). Notice, however, that while the vicinity of $\mathbf{r}_0$ remains fixed as far as its position and orientation in space are concerned it still can undergo a strain deformation [provided $\overleftrightarrow{\epsilon}(\mathbf{r}_0)\neq 0$]. The strain appears thus as the irreducible part of any local deformation. This then raises the question of whether the strain also completely determines the deformation. The answer is clearly not trivial since a general symmetric tensor such as $\overleftrightarrow{\epsilon}(\mathbf{r})$ has six independent components which could easily overdetermine the three components of the displacement field $\mathbf{u}(\mathbf{r})$. The clue to the answer stems from the observation that (2.3) defines $\mathbf{u}(\mathbf{r})$ to be some sort of vector potential for the tensor field $\overleftrightarrow{\epsilon}(\mathbf{r})$, a situation quite analogous to that prevailing between the electric field and its scalar potential in electrostatics where the relation is known to be unique (up to a constant). To see this more clearly, let us write

$$\mathbf{u}(\mathbf{r}_2)-\mathbf{u}(\mathbf{r}_1)=\int_{C_{12}}d\mathbf{u}(\boldsymbol{l})=\int_{C_{12}}d\boldsymbol{l}\cdot\nabla\mathbf{u}(\boldsymbol{l})\ , \tag{2.8}$$

where $\nabla=\partial/\partial\boldsymbol{l}$ and the line integral extends over an arbitrary path C_{12} from $\mathbf{r}_1$ to $\mathbf{r}_2$. Using $\overleftrightarrow{\mathrm{d}}(\mathbf{r})=\overleftrightarrow{\epsilon}(\mathbf{r})+\overleftrightarrow{\omega}(\mathbf{r})$ and (2.5) we obtain

$$\mathbf{u}(\mathbf{r}_2)-\mathbf{u}(\mathbf{r}_1)=\int_{C_{12}}\overleftrightarrow{\epsilon}(\boldsymbol{l})\cdot d\boldsymbol{l}+\int_{C_{12}}\mathbf{R}(\boldsymbol{l})\times d\boldsymbol{l}\ . \tag{2.9}$$

The second term in the right-hand side (rhs) of (2.9), which originates from the local rotations, can be expressed in terms of the strain by using

$$\mathbf{R}\times d\boldsymbol{l}=\mathbf{R}\times d(\boldsymbol{l}-\mathbf{a})$$
$$=d[\mathbf{R}\times(\boldsymbol{l}-\mathbf{a})]-(d\mathbf{R})\times(\boldsymbol{l}-\mathbf{a})\ , \tag{2.10}$$

where $\mathbf{a}$ is an arbitrary constant vector to be specified below. The second term in the rhs of (2.10) can now be transformed by using

$$d\mathbf{R}=\tfrac{1}{2}\nabla\times(d\mathbf{u})$$
$$=\tfrac{1}{2}\nabla\times(d\boldsymbol{l}\cdot\nabla\mathbf{u})$$
$$=\nabla\times(\overleftrightarrow{\epsilon}\cdot d\boldsymbol{l}) \tag{2.11}$$

so that, gathering the results, we obtain

$$\mathbf{u}(\mathbf{r}_2)-\mathbf{u}(\mathbf{r}_1)$$
$$=\mathbf{R}(\mathbf{r}_2)\times(\mathbf{r}_2-\mathbf{a})-\mathbf{R}(\mathbf{r}_1)\times(\mathbf{r}_1-\mathbf{a})$$
$$+\int_{C_{12}}\{\overleftrightarrow{\epsilon}(\boldsymbol{l})+(\boldsymbol{l}-\mathbf{a})\times[\nabla\times\overleftrightarrow{\epsilon}(\boldsymbol{l})]\}\cdot d\boldsymbol{l}\ , \tag{2.12}$$

while taking $\mathbf{a}=\mathbf{r}_2$ and relabeling the variables $(\mathbf{r}_1,\mathbf{r}_2)\to(\mathbf{r}_0,\mathbf{r})$ we finally obtain

$$\mathbf{u}(\mathbf{r})=\mathbf{u}(\mathbf{r}_0)+\mathbf{R}(\mathbf{r}_0)\times(\mathbf{r}-\mathbf{r}_0)$$
$$+\int_{C_0}\{\overleftrightarrow{\epsilon}(\boldsymbol{l})+(\boldsymbol{l}-\mathbf{r})\times[\nabla\times\overleftrightarrow{\epsilon}(\boldsymbol{l})]\}\cdot d\boldsymbol{l}\ , \tag{2.13a}$$

where C_0 is an arbitrary path from the arbitrary point $\mathbf{r}_0$ to $\mathbf{r}$. Taking $\mathbf{r}_0$ to be a fixed point we obtain from (2.13a) and (2.7) the equivalent relation for a *local* deformation:

$$\mathbf{u}(\mathbf{r})=\int_{C(\mathbf{r}_0,\mathbf{r})}\{\overleftrightarrow{\epsilon}(\boldsymbol{l})+(\boldsymbol{l}-\mathbf{r})\times[\nabla\times\overleftrightarrow{\epsilon}(\boldsymbol{l})]\}\cdot d\boldsymbol{l}\ , \tag{2.13b}$$

where $C(\mathbf{r}_0,\mathbf{r})$ is now an arbitrary path from the *fixed point* $\mathbf{r}_0$ to the point of observation $\mathbf{r}$. As is obvious from (2.8), the expression (2.13) is path independent for any $\overleftrightarrow{\epsilon}(\mathbf{r})$ of the form (2.3). This can also be shown directly by considering the difference between two arbitrary contours which amounts to evaluating the line integral of (2.13) around a closed contour, which can then be transformed into a surface integral as

$$\oint\{\overleftrightarrow{\epsilon}(\boldsymbol{l})+(\boldsymbol{l}-\mathbf{r})\times[\nabla\times\overleftrightarrow{\epsilon}(\boldsymbol{l})]\}\cdot d\boldsymbol{l}$$
$$=\int\int d\mathbf{S}_1\cdot[\mathrm{inc}\,\overleftrightarrow{\epsilon}(\boldsymbol{l})]\times(\boldsymbol{l}-\mathbf{r})\ , \tag{2.14}$$

where $\mathrm{inc}\,\overleftrightarrow{\epsilon}(\mathbf{r})$ is defined by the following double curl operation on $\overleftrightarrow{\epsilon}(\mathbf{r})$ (or any other tensor field):

$$\mathrm{inc}\,\overleftrightarrow{\epsilon}(\mathbf{r})\equiv\nabla\times[\nabla\times\overleftrightarrow{\epsilon}(\mathbf{r})]^{\dagger}\ . \tag{2.15}$$

But from (2.3) it follows that

$$[\nabla\times\overleftrightarrow{\epsilon}(\mathbf{r})]^{\dagger}=\tfrac{1}{2}\nabla\nabla\times\mathbf{u}(\mathbf{r}) \tag{2.16}$$

and hence, using (2.15) and (2.16), we have

$$\mathrm{inc}\,\overleftrightarrow{\epsilon}(\mathbf{r})=0 \tag{2.17}$$

so that the rhs of (2.14) vanishes identically and hence (2.13) is indeed path independent for any $\overleftrightarrow{\epsilon}(\mathbf{r})$ of the form (2.3).

Historically, the relation (2.13) is known[8] as the Kirchhoff-Cesaro-Volterra relation.[9] It allows one to calculate the displacement field from a knowledge of the strain tensor, up to a global translation $[u(\mathbf{r}_0)]$ and a global rotation $[\mathbf{R}(\mathbf{r}_0)]$. The latter displacements can be viewed as the integration "constants" resulting from solving (2.3) with respect to $\mathbf{u}(\mathbf{r})$ for a given $\overleftrightarrow{\epsilon}(\mathbf{r})$. In the physically interesting case of deformations with a fixed point these "constants" vanish [see (2.7)] which, in the partial differential equation language, corresponds to tak-

ing the solution of the homogeneous equation corresponding to (2.3) to vanish. Taking this into account, (2.3) and (2.13) establish a unique relation between $\mathbf{u}(\mathbf{r})$ and $\overleftrightarrow{\epsilon}(\mathbf{r})$. This relationship is similar to the well-known relation between the electrostatic potential and the line integral of the electric field (in which case one usually takes the "fixed point" to be at infinity where the electrostatic potential vanishes). In the same way as not every vector field is an electrostatic field, not any symmetric tensor field will be a strain field. For this to be the case the vector field has to be curl-free and the tensor field has to be inc-free, i.e., it has to satisfy (2.17). Historically, this condition is ascribed to Saint-Venant.[10] In the partial differential equation language it corresponds to the integrability condition for (2.3) viewed as an equation for $\mathbf{u}(\mathbf{r})$. The double curl operation (2.15) was termed "incompatibility" (inc) by Saint-Venant because it measures the extent to which a given symmetric tensor field is incompatible with a physically realizable strain field. For a real strain field the incompatibility vanishes, i.e., the strain field must satisfy (2.17). The relation (2.17) can also be viewed as stating that out of the six components of $\overleftrightarrow{\epsilon}(\mathbf{r})$, only three can be varied independently, or in other words a physical strain tensor field $\overleftrightarrow{\epsilon}(\mathbf{r})$ always derives from a vector field, namely $\mathbf{u}(\mathbf{r})$. The easiest way to see this is to transform (2.17) into Fourier space as

$$\mathbf{k}\times\overleftrightarrow{\epsilon}(\mathbf{k})\times\mathbf{k}=\mathbf{0} , \tag{2.18}$$

where $\overleftrightarrow{\epsilon}(\mathbf{k})$ is the Fourier transform of $\overleftrightarrow{\epsilon}(\mathbf{r})$. From (2.18) it follows then that all the transverse (with respect to $\mathbf{k}$) components of $\overleftrightarrow{\epsilon}(\mathbf{k})$ have to vanish, leaving only the longitudinal-longitudinal and the two longitudinal-transverse components of $\overleftrightarrow{\epsilon}(\mathbf{k})$ as possible degrees of freedom. In the electrostatic analog the equivalent statement would be that the transverse components of the electric field have to vanish, leaving one with a purely longitudinal field, i.e., there is only one field component. The same conclusion can also be reached from a closer examination of (2.17) in ordinary space (in the electrostatic case the conclusion follows in real space from the observation that the electric field is curl-free).

The above discussion of the relations between the vectorial $[\mathbf{u}(\mathbf{r})]$ and the equivalent tensorial $[\overleftrightarrow{\epsilon}(\mathbf{r})]$ description of a given deformation will now be exploited to find the corresponding relations between the vectorial (the external forces) and the tensorial (the stresses) description of the *causes* of this deformation.

III. THE EXTERNAL FORCE FIELD AND THE STRESS TENSOR

In the modern density-functional theory of nonuniform equilibrium fluids[11] the basic variable is the average *local* number density $\rho(\mathbf{r})$. In terms of this variable such a system will look like a continuous medium and all the considerations of Sec. II are thus equally applicable to nonuniform fluids such as a two-phase liquid-vapor system or a fluid-wall system. For instance, a small deformation, $\mathbf{r}\to\mathbf{r}+\delta\mathbf{u}(\mathbf{r})$, will induce a small density change, $\rho(\mathbf{r})\to\rho(\mathbf{r})+\delta\rho(\mathbf{r})$, given by[5]

$$\delta\rho(\mathbf{r})=-\nabla\cdot[\rho(\mathbf{r})\delta\mathbf{u}(\mathbf{r})] , \tag{3.1}$$

where the prefix δ is used to emphasize the smallness of these changes. The field which is thermodynamically conjugated to $\rho(\mathbf{r})$ is the external single-particle potential $\phi(\mathbf{r})$, or more precisely, $\mu-\phi(\mathbf{r})$, where μ is the chemical potential. This external potential is assumed to contain, among other things, all the information about the physical boundaries of the fluid and of the different phases. As a consequence one can consider the $\mathbf{r}$ space to be formally infinite, all boundary conditions being taken care of by $\phi(\mathbf{r})$, even if the physical system is in fact finite. The thermodynamic description of this system can then be formulated[11] either in terms of the grand potential $\Omega=\Omega(T;[\mu-\phi])$ or in terms of the (Helmholtz) free energy $F=F(T;[\rho])$, where T denotes the temperature, μ the chemical potential, and the square brackets indicate a *functional* dependence on either $\mu-\phi(\mathbf{r})$ or $\rho(\mathbf{r})$. The two thermodynamic potentials Ω and F are related by a functional Legendre transformation:

$$F(T;[\rho])=\Omega(T;[\mu-\phi]) - \int d\mathbf{r}\{\mu-\phi(\mathbf{r})\}\frac{\delta\Omega}{\delta\{\mu-\phi(\mathbf{r})\}} , \tag{3.2}$$

while the two field variables $\rho(\mathbf{r})$ and $\mu-\phi(\mathbf{r})$ can be eliminated one in favor of the other by using one of the conjugate relations[11]

$$\rho(\mathbf{r})=-\frac{\delta\Omega[\mu-\phi]}{\delta\{\mu-\phi(\mathbf{r})\}}, \quad \mu-\phi(\mathbf{r})=\frac{\delta F[\rho]}{\delta\rho(\mathbf{r})} . \tag{3.3}$$

Since the relation between $\rho(\mathbf{r})$ and $\mu-\phi(\mathbf{r})$ is known to be invertible the solution of (3.3) will be unambiguous (for simplicity we omit henceforth the implicit T dependence). Within this density-functional approach the thermodynamics of a deformation can then be studied by considering the underlying density change. Using (3.3) we obtain for the reversible work, δF, corresponding to a small reversible deformation:

$$\delta F=\int d\mathbf{r}\{\mu-\phi(\mathbf{r})\}\delta\rho(\mathbf{r}) , \tag{3.4}$$

where $\mu-\phi(\mathbf{r})$ refers to the *undeformed* system and $\delta\rho(\mathbf{r})$ is related to the small displacement $\delta\mathbf{u}(\mathbf{r})$ by (3.1). In order to reinforce the relation between the density-functional expression (3.4) and the theory of elasticity of Sec. II we will rewrite (3.4) in either of the two equivalent forms:

$$\delta F=\int d\mathbf{r}\,\mathbf{f}(\mathbf{r})\cdot\delta\mathbf{u}(\mathbf{r}) \tag{3.5}$$

$$=\int d\mathbf{r}\,\overleftrightarrow{\sigma}(\mathbf{r}):\delta\overleftrightarrow{\epsilon}(\mathbf{r}) , \tag{3.6}$$

where $\delta\overleftrightarrow{\epsilon}(\mathbf{r})$ is the change in strain resulting from $\delta\mathbf{u}(\mathbf{r})$ [see (2.3)]:

$$\delta\overleftrightarrow{\epsilon}(\mathbf{r})=\tfrac{1}{2}\{\nabla\delta\mathbf{u}(\mathbf{r})+[\nabla\delta\mathbf{u}(\mathbf{r})]^{\dagger}\} , \tag{3.7}$$

$\mathbf{f}(\mathbf{r})$ is the external force *density* corresponding to the external potential $\phi(\mathbf{r})$ acting on the undeformed system of density $\rho(\mathbf{r})$:

$$\mathbf{f}(\mathbf{r})=-\rho(\mathbf{r})\nabla\phi(\mathbf{r}) , \tag{3.8}$$

while the strain-stress relation (3.6) *defines* the local stress tensor $\vec{\sigma}(\mathbf{r})$ of the undeformed system.

The relation between (3.4) and (3.5), which obviously represents the work done by the external forces against the deformation $\delta\mathbf{u}(\mathbf{r})$, can easily be obtained by using (3.1) in (3.4) and integrating by parts. In doing so one encounters the following surface term:

$$\int\int d\mathbf{S}\cdot\{[\mu-\phi(\mathbf{r})]\rho(\mathbf{r})\delta\mathbf{u}(\mathbf{r})\} , \tag{3.9}$$

which vanishes because for any system confined by $\phi(\mathbf{r})$ to a finite volume the density $\rho(\mathbf{r})$ will vanish outside the system's physical boundaries. The passage from the scalar description (3.4) to the vectorial description (3.5) is thus always possible. Notice, however, that the converse is not true since (3.4) is more general than (3.5). Indeed (3.4) is valid for *any* density change, not just those changes resulting from a pure strain deformation of the system [see (3.1)]. The passage, now, from the vectorial description (3.5) to the tensorial description of (3.6) is clearly less trivial. Whereas the reversible work relation (3.5) indicates that the forces ($\mathbf{f}$) and the displacements ($\mathbf{u}$) are thermodynamically conjugate variables (or fields), the stress-strain relation (3.6) *defines* the stress tensor ($\vec{\sigma}$) as the variable (field) conjugate to the strain tensor ($\vec{\epsilon}$). Since, from Sec. II, we know the exact relation between the displacement field [$\mathbf{u}(\mathbf{r})$] and the local strain tensor [$\vec{\epsilon}(\mathbf{r})$] we can now use this relationship in order to deduce from (3.5) and (3.6) the corresponding relation between the force field ($\mathbf{f}$) and the local stress tensor ($\vec{\sigma}$). The present approach to the stress tensor definition is thus purely thermodynamic. Before considering this relation in detail we establish its connection with the traditional hydrostatic approach. To this end we first observe that since in (3.6) $\delta\vec{\epsilon}(\mathbf{r})$ is by definition [see (3.7)] a symmetric tensor, $\vec{\sigma}(\mathbf{r})$ has to be likewise a symmetric tensor. Using then (3.7) into (3.6) and integrating by parts we obtain

$$\delta F=-\int d\mathbf{r}[\nabla\cdot\vec{\sigma}(\mathbf{r})]\cdot\delta\mathbf{u}(\mathbf{r}) \tag{3.10}$$

if the surface term vanishes, i.e., if $\vec{\sigma}(\mathbf{r})$ vanishes outside the finite physical system. The equivalence of (3.10) with (3.5) for any $\delta\mathbf{u}(\mathbf{r})$ implies then that we have

$$\nabla\cdot\vec{\sigma}(\mathbf{r})=-\mathbf{f}(\mathbf{r}) , \tag{3.11}$$

which is the well-known (hydrostatic) force balance equation at the basis of the earlier treatments[6,7] (notice also that the pressure tensor is minus the stress tensor). The thermodynamic definition of $\vec{\sigma}(\mathbf{r})$ based on (3.5) and (3.6) thus contains the mechanical definition based on (3.11). Next, we observe from (3.6) that since $\delta\vec{\epsilon}(\mathbf{r})$ satisfies $\mathrm{inc}\,\delta\vec{\epsilon}(\mathbf{r})=0$ [see (2.17)], $\vec{\sigma}(\mathbf{r})$ is defined by (3.6) only up to a tensorial gauge field of the form $\mathrm{inc}\,\vec{a}(\mathbf{r})$ where $\vec{a}(\mathbf{r})$ is an arbitrary symmetric tensor field which vanishes outside the physical system. Indeed, integrating twice by parts we obtain, for the contribution of $\mathrm{inc}\,\vec{a}(\mathbf{r})$ to (3.6),

$$\int d\mathbf{r}[\mathrm{inc}\,\vec{a}(\mathbf{r})]:\delta\vec{\epsilon}(\mathbf{r})=\int d\mathbf{r}\,\vec{a}(\mathbf{r}):[\mathrm{inc}\,\delta\vec{\epsilon}(\mathbf{r})]=0 , \tag{3.12}$$

so that any stress tensor of the form $\mathrm{inc}\,\vec{a}(\mathbf{r})$ performs no work. The same conclusion follows from (3.11) since the corresponding homogeneous equation

$$\nabla\cdot\vec{\sigma}_0(\mathbf{r})=0 \tag{3.13}$$

has the general solution $\vec{\sigma}_0(\mathbf{r})=\mathrm{inc}\,\vec{a}(\mathbf{r})$ for a symmetric tensor $\vec{\sigma}_0(\mathbf{r})$. The general solution of our problem can thus always be written

$$\vec{\sigma}(\mathbf{r})=\vec{\sigma}_0(\mathbf{r})+\vec{\sigma}_1(\mathbf{r}) , \tag{3.14}$$

where $\vec{\sigma}_0(\mathbf{r})$ denotes an arbitrary gauge field and $\vec{\sigma}_1(\mathbf{r})$ a particular solution of our problem. This gauge invariance of $\vec{\sigma}(\mathbf{r})$ can be restricted somewhat by observing that with the same boundary conditions for $\vec{\sigma}(\mathbf{r})$ as above we must have

$$\int d\mathbf{r}[\mathrm{inc}\,\vec{\sigma}(\mathbf{r})]:\delta\vec{\epsilon}(\mathbf{r})=\int d\mathbf{r}\,\vec{\sigma}(\mathbf{r}):[\mathrm{inc}\,\delta\vec{\epsilon}(\mathbf{r})]=0 \tag{3.15}$$

for any $\delta\vec{\epsilon}(\mathbf{r})$ and hence in the context of (3.6) we may require that $\vec{\sigma}(\mathbf{r})$ satisfies the stronger condition:

$$\mathrm{inc}\,\vec{\sigma}(\mathbf{r})=0 \tag{3.16}$$

so that both $\vec{\sigma}(\mathbf{r})$ and $\vec{\epsilon}(\mathbf{r})$ will belong to the same (inc-free) functional space. Both symmetric tensor fields will have then only three independent components (see the discussion at the end of Sec. II), a property which follows also from the requirement of the equivalence between the tensorial description (3.6) and its vectorial counterpart (3.5). Indeed, from (3.16) it follows that $\vec{\sigma}(\mathbf{r})$ can always be written as $\{\nabla\mathbf{v}(\mathbf{r})\}_{\mathrm{sym}}$ with $\mathbf{v}(\mathbf{r})$ being some sort of vector potential for $\vec{\sigma}(\mathbf{r})$. Using this form of $\vec{\sigma}(\mathbf{r})$ in (3.11) then shows that $\nabla\cdot\mathbf{v}(\mathbf{r})$ is the potential for $\nabla\cdot\mathbf{f}(\mathbf{r})$ while $\frac{1}{2}\nabla\times\mathbf{v}(\mathbf{r})$ is the potential for $\nabla\times\mathbf{f}(\mathbf{r})$. To proceed we will thus first look for a particular solution $\vec{\sigma}_1(\mathbf{r})$ and next (partially) fix the gauge field $\vec{\sigma}_0(\mathbf{r})$ in (3.14) so that (3.16) be satisfied. The remaining gauge invariance then concerns the contributions $\vec{\sigma}_0(\mathbf{r})=\mathrm{inc}\,\vec{a}(\mathbf{r})$ satisfying

$$\mathrm{inc}\{\mathrm{inc}\,\vec{a}(\mathbf{r})\}=0 , \tag{3.17}$$

where $\vec{a}(\mathbf{r})$ is a symmetric tensor vanishing outside the system. This gauge invariance is inherent to the tensorial description but is physically irrelevant since the resulting gauge field performs no work.

We first consider the particular solution $\vec{\sigma}_1(\mathbf{r})$. Using (2.13) in (3.5) we obtain

$$\delta F=\delta\mathbf{u}(\mathbf{r}_0)\cdot\left[\int d\mathbf{r}\,\mathbf{f}(\mathbf{r})\right]+\mathbf{R}(\mathbf{r}_0)\cdot\left[\int d\mathbf{r}(\mathbf{r}-\mathbf{r}_0)\times\mathbf{f}(\mathbf{r})\right]+\int d\mathbf{r}\,\mathbf{f}(\mathbf{r})\cdot\int_{C(\mathbf{r}_0,\mathbf{r})}\{\delta\vec{\epsilon}(\boldsymbol{l})+(\boldsymbol{l}-\mathbf{r})\times[\nabla\times\delta\vec{\epsilon}(\boldsymbol{l})]\}\cdot d\boldsymbol{l} . \tag{3.18}$$

The first two terms in the rhs of (3.18) will vanish if $\mathbf{r}_0$ is a fixed point, i.e., if the deformation is local [see (2.7)], or equivalently if the external force density produces no global acceleration [$\int d\mathbf{r}\,\mathbf{f}(\mathbf{r})=0$] nor a global torque [$\int d\mathbf{r}\,\mathbf{r}\times\mathbf{f}(\mathbf{r})=0$]. This is consistent with our boundary conditions for $\vec{\sigma}(\mathbf{r})$ since from (3.11) it also follows that

$$-\int d\mathbf{r}\,\nabla\cdot\vec{\sigma}(\mathbf{r})=\int d\mathbf{r}\,\mathbf{f}(\mathbf{r})=0\ , \tag{3.19}$$

$$\int d\mathbf{r}\,\nabla\cdot[\vec{\sigma}(\mathbf{r})\times\mathbf{r}]=\int d\mathbf{r}\,\mathbf{r}\times\mathbf{f}(\mathbf{r})=\mathbf{0}\ , \tag{3.20}$$

because $\vec{\sigma}(\mathbf{r})$ vanishes outside the system. Assuming then that the system remains globally at rest we obtain, after integrating the third term of (3.18) by parts,

$$\delta F=\int d\mathbf{r}\int_{C(\mathbf{r}_0,\mathbf{r})}\{\mathbf{f}(\mathbf{r})+[\mathbf{f}(\mathbf{r})\times(\boldsymbol{l}-\mathbf{r})]\times\nabla_{\boldsymbol{l}}\}\cdot\delta\vec{\epsilon}(\boldsymbol{l})\cdot d\boldsymbol{l}\ , \tag{3.21}$$

which comparing with (3.6) yields

$$\vec{\sigma}_1(\mathbf{r})=\left\{\int d\mathbf{r}_1\int_{C(\mathbf{r}_0,\mathbf{r}_1)}d\boldsymbol{l}\{\mathbf{f}(\mathbf{r}_1)+[\mathbf{f}(\mathbf{r}_1)\times(\boldsymbol{l}-\mathbf{r}_1)]\times\nabla_{\boldsymbol{l}}\}\delta(\mathbf{r}-\boldsymbol{l})\right\}_{\rm sym}\ , \tag{3.22}$$

where $\{\vec{t}\}_{\rm sym}$ is a shorthand notation for the symmetric part of the tensor $\vec{t}$, e.g., $\{\vec{t}\}_{\rm sym}=\frac{1}{2}(\vec{t}+\vec{t}^{\dagger})$. Notice also that the same result can be obtained from [see (3.6)]

$$\vec{\sigma}_1(\mathbf{r})=\frac{\delta F}{\delta\vec{\epsilon}(\mathbf{r})} \tag{3.23}$$

and computing the functional derivative of the free energy directly from (3.18) or (3.21) by using the following identity for symmetric tensor fields:

$$\frac{\delta\epsilon_{ij}(\mathbf{r})}{\delta\epsilon_{kl}(\mathbf{r}')}=\tfrac{1}{2}(\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk})\delta(\mathbf{r}-\mathbf{r}')\ , \tag{3.24}$$

where, for clarity, we have used the indicial notation $\vec{\epsilon}=\{\epsilon_{ij}\}$. The present definition (3.23) of the stress tensor as a (functional) derivative of the free energy with respect to the strain tensor is a straightforward extension to nonuniform fluids of the standard definition,[7] usually ascribed to Thomson,[12] prevailing for uniform continuous media.

We now determine (partially) the gauge $\vec{\sigma}_0(\mathbf{r})$ so as to satisfy (3.16). Because of (3.14) this is equivalent to

$$\mathrm{inc}\,\vec{\sigma}_0(\mathbf{r})=-\mathrm{inc}\,\vec{\sigma}_1(\mathbf{r})\ , \tag{3.25}$$

where $\vec{\sigma}_1(\mathbf{r})$ is given by (3.22). This equation for $\vec{\sigma}_0$ is most easily solved in Fourier-transform space [see (2.18)]. Writing $\vec{\sigma}_0(\mathbf{r})=\mathrm{inc}\,\vec{a}(\mathbf{r})$, we obtain from (3.24)

$$\mathbf{k}\times[\mathbf{k}\times\vec{a}(\mathbf{k})\times\mathbf{k}]\times\mathbf{k}=\mathbf{k}\times\vec{\sigma}_1(\mathbf{k})\times\mathbf{k}\ , \tag{3.26}$$

and using the identity

$$\hat{\mathbf{k}}\times\{\hat{\mathbf{k}}\times[\hat{\mathbf{k}}\times\vec{a}(\mathbf{k})\times\hat{\mathbf{k}}]\times\hat{\mathbf{k}}\}\times\hat{\mathbf{k}}=\hat{\mathbf{k}}\times\vec{a}(\mathbf{k})\times\hat{\mathbf{k}}\ ,$$

where $\hat{\mathbf{k}}=\mathbf{k}/|\mathbf{k}|$, we obtain from (3.26) and $\vec{\sigma}_0(\mathbf{k})=-\mathbf{k}\times\vec{a}(\mathbf{k})\times\mathbf{k}$

$$\vec{\sigma}_0(\mathbf{k})=-\hat{\mathbf{k}}\times[\hat{\mathbf{k}}\times\vec{\sigma}_1(\mathbf{k})\times\hat{\mathbf{k}}]\times\hat{\mathbf{k}}\ , \tag{3.27}$$

which is the desired solution of (3.25). Taking the inverse Fourier transform of (3.27) we obtain finally

$$\vec{\sigma}_0(\mathbf{r})=-\int d\mathbf{r}_1\frac{1}{4\pi|\mathbf{r}-\mathbf{r}_1|}\mathrm{inc}\left[\int d\mathbf{r}_2\frac{1}{4\pi|\mathbf{r}_1-\mathbf{r}_2|}\mathrm{inc}\,\vec{\sigma}_1(\mathbf{r}_2)\right]\ , \tag{3.28}$$

where $\vec{\sigma}_1(\mathbf{r})$ is given by (3.22). The complete stress tensor $\vec{\sigma}(\mathbf{r})=\vec{\sigma}_0(\mathbf{r})+\vec{\sigma}_1(\mathbf{r})$ satisfying (3.16) will thus be given by the sum of $\vec{\sigma}_0(\mathbf{r})$ of (3.28) and of $\vec{\sigma}_1(\mathbf{r})$ of (3.22), with the understanding that only $\vec{\sigma}_1(\mathbf{r})$ is responsible for doing the work described by (3.6) while $\vec{\sigma}_0(\mathbf{r})$ does not contribute to (3.6).

In Sec. II we have already shown that the line integral in (3.18) is independent of the path $C(\mathbf{r}_0,\mathbf{r})$ from $\mathbf{r}_0$ to $\mathbf{r}$ while for $\mathbf{r}_0$ one can choose any fixed point of the local deformation. One can show similarly that (3.21) and also $\vec{\sigma}(\mathbf{r})$, i.e., the sum of (3.22) and (3.28) but not each term separately, are independent of the chosen contour. To this end one again considers the difference between two arbitrary contours and transforms the closed contour integral into a surface integral of the curl of the integrand. Some lengthy but straightforward algebra shows that this curl vanishes both for (3.21) and $\vec{\sigma}(\mathbf{r})$, because of, respectively, (2.17) and (3.16). For (3.21) the result is also obvious from the fact that (3.21) and (3.6) are equivalent to (3.5) while the latter equation has no contour dependence.

We have now completed the study of the relation between the vectorial description (3.5) in terms of the forces and the displacement fields and the equivalent tensorial description (3.6) in terms of the stress and strain fields. The resulting relation between the forces and the stresses [see (3.22)] is thus seen to closely parallel the corresponding relation [see (2.13)] between the displacement and the strain.[13] In conclusion, the stress tensor, defined as the tensor field thermodynamically conjugate to the strain tensor [see (3.6) and (3.23)], has the following properties: (1) it is symmetric, (2) it satisfies the force balance equation (3.1), (3) it is inc-free [see (3.16)] so that there are only three independent components, (4) it is independent of the path used to compute it, and (5) it leads to path-independent free-energy changes (3.6) or (3.21).

IV. FREE-ENERGY CHANGES IN TERMS OF THE DISTRIBUTION FUNCTIONS

One of the most common applications of the Irving and Kirkwood stress tensor in nonuniform equilibrium

fluids[6] has been the derivation of an expression for the surface tension of a planar liquid-vapor interface in terms of the one- and two-particle distribution functions, respectively, $\rho(\mathbf{r})$ and $\rho_2(\mathbf{r},\mathbf{r}')$, for a system with pairwise additive interactions. We now reconsider this problem in the light of Sec. III. To this end we first have to eliminate from the expressions of Sec. III the external force density $\mathbf{f}(\mathbf{r})$ in terms of the distribution functions. From the lowest-order Born-Green-Yvon hierarchy equation[6] we obtain the desired relation in the form

$$\mathbf{f}(\mathbf{r})=k_BT\nabla\rho(\mathbf{r})+\int d\mathbf{r}'\rho_2(\mathbf{r},\mathbf{r}')\nabla V(|\mathbf{r}-\mathbf{r}'|)\ , \tag{4.1}$$

where $V(|\mathbf{r}|)$ is the pair potential. We will thus substitute, everywhere in the expressions of Sec. III, $\mathbf{f}(\mathbf{r})$ by the rhs of (4.1). Notice also that corresponding expressions in terms of the direct correlation function,[6] $C(\mathbf{r},\mathbf{r}')$, can be obtained by using instead of (4.1) the relation[6]

$$\mathbf{f}(\mathbf{r})=k_BT\nabla\rho(\mathbf{r})-k_BT\rho(\mathbf{r})\int d\mathbf{r}'C(\mathbf{r},\mathbf{r}')\nabla'\rho(\mathbf{r}')\ .$$

This is planned to be shown in more detail elsewhere;[14] here we will concentrate on (4.1).

A. Pressure

We first consider the pressure. As is well known, the thermodynamic definition of the pressure p

$$p=-\frac{\delta F}{\delta V} \tag{4.2}$$

relates it to the free-energy change δF produced by an isotropic strain leading to a volume change δV. A constant isotropic strain corresponds to $\overleftrightarrow{\epsilon}(\mathbf{r})=\overleftrightarrow{1}$ (the unit tensor; notice that inc $\overleftrightarrow{1}=0$). Returning to (3.6) we write henceforth $\delta\overleftrightarrow{\epsilon}(\mathbf{r})=\lambda\overleftrightarrow{\epsilon}(\mathbf{r})$, with λ a small parameter to be determined. From the general results of Sec. II or from a trivial integration of (3.7) one finds that the displacement $\delta\mathbf{u}(\mathbf{r})=\lambda\mathbf{u}(\mathbf{r})$ corresponding to $\delta\overleftrightarrow{\epsilon}(\mathbf{r})=\lambda\overleftrightarrow{1}$ is $\delta\mathbf{u}(\mathbf{r})=\lambda\mathbf{r}$. This deformation $[\mathbf{r}\to(1+\lambda)\mathbf{r}]$ corresponds thus to an overall dilatation ($\lambda>0$) or compression ($\lambda<0$). Its fixed point is $\mathbf{r}=\mathbf{0}$ [notice that here $\mathbf{R}(\mathbf{r})=\frac{1}{2}\nabla\times\mathbf{u}(\mathbf{r})=\mathbf{0}$]. The relative volume change is given by[7] $\nabla\cdot\delta\mathbf{u}=3\lambda=\delta V/V$, or $\lambda=\delta V/3V$ with V the system's volume and δV its infinitesimal change. Having determined the deformation we compute the resulting free-energy change δF from (3.5) and (3.6) while (4.2) yields

$$p=-\frac{1}{3V}\int d\mathbf{r}\,\mathbf{r}\cdot\mathbf{f}(\mathbf{r}) \tag{4.3}$$

$$=-\frac{1}{3V}\int d\mathbf{r}\,\mathrm{Tr}\,\overleftrightarrow{\sigma}(\mathbf{r})\ , \tag{4.4}$$

whereas using (4.1) in (4.3) we obtain

$$p=k_BT\int\frac{d\mathbf{r}}{V}\rho(\mathbf{r})-\frac{1}{6V}\int d\mathbf{r}\int d\mathbf{r}'\rho_2(\mathbf{r},\mathbf{r}')(\mathbf{r}-\mathbf{r}')\cdot\nabla_{\mathbf{r}-\mathbf{r}'}V(|\mathbf{r}-\mathbf{r}'|)\ , \tag{4.5}$$

which can equally well be obtained by using (4.1) in (4.4) and following the more complicated route via (3.22) and (3.21). To obtain (4.5) we have assumed that (1) the surface term originating from integrating by parts in (4.3) the contribution of the first term in the rhs of (4.1) vanishes:

$$\int d\mathbf{r}\,\nabla\cdot[\mathbf{r}\rho(\mathbf{r})]=0\ , \tag{4.6a}$$

which is correct since $\rho(\mathbf{r})$ vanishes outside the finite system, and (2) we have symmetrized ($\mathbf{r}\leftrightarrow\mathbf{r}'$) the contribution to (4.3) of the second term in the rhs of (4.1). Notice also that Eq. (4.6a) is a particular case of the more general property

$$\int d\mathbf{r}\,\delta\rho(\mathbf{r})\equiv-\int d\mathbf{r}\,\nabla\cdot[\rho(\mathbf{r})\delta\mathbf{u}(\mathbf{r})]=0\ , \tag{4.6b}$$

which results from the fact that the local density change (3.1) is performed at a constant number of particles. The present procedure establishes thus the equivalence of the expressions of the pressure in terms of the virial of the external forces (4.3), the trace of the stress tensor (4.4), and the distribution function expression (4.5).

B. Surface tension

From the thermodynamic definition of the surface tension γ

$$\gamma=\frac{\delta F}{\delta A} \tag{4.7}$$

it follows that we have to look for a strain which will produce a change δA in the area A of the interface and compute the corresponding free-energy change δF. Taking a constant traceless strain so as to produce no volume change, we can take $\delta\epsilon_{xx}(\mathbf{r})=-\delta\epsilon_{zz}(\mathbf{r})=\lambda$ and $\delta\epsilon_{ij}(\mathbf{r})$ zero otherwise, for an interface parallel to the x-y plane. The corresponding displacement field in the Cartesian coordinates $\mathbf{r}=(x,y,z)$ is now $\delta\mathbf{u}(\mathbf{r})=\lambda(x,0,-z)$. We again have inc $\delta\overleftrightarrow{\epsilon}(\mathbf{r})=0$, $\mathbf{R}(\mathbf{r})=\mathbf{0}$, and $\mathbf{r}=\mathbf{0}$ as fixed point. Taking $\lambda=\delta A/A$ we obtain then for γ from (4.7) and (3.5) and (3.6)

$$\gamma=\frac{1}{A}\int d\mathbf{r}[xf_x(\mathbf{r})-zf_z(\mathbf{r})] \tag{4.8}$$

$$=\frac{1}{A}\int d\mathbf{r}[\sigma_{xx}(\mathbf{r})-\sigma_{zz}(\mathbf{r})]\ , \tag{4.9}$$

while using (4.1) in (4.8) yields

$$\gamma=\frac{1}{A}\int d\mathbf{r}\int d\mathbf{r}'\rho_2(\mathbf{r},\mathbf{r}')(x\nabla_x-z\nabla_z)V(|\mathbf{r}-\mathbf{r}'|)\ , \tag{4.10}$$

a result which can equally well be obtained from (4.1), (4.9) and (3.22) or (3.21). To obtain (4.10) we have dropped the surface term

$$\int d\mathbf{r}\{\nabla_x[x\rho(\mathbf{r})]-\nabla_z[z\rho(\mathbf{r})]\} \tag{4.11}$$

on account of the fact that $\rho(\mathbf{r})$ vanishes outside V [see also (4.6b)]. Symmetrizing ($\mathbf{r}\to\mathbf{r}'$) the rhs of (4.10) and

using $\nabla_x V(r)=(x/r)V'(r)$, with $r=|\mathbf{r}|$ and $V'(r)=dV(r)/dr$, one obtains from (4.10)

$$\gamma=\frac{1}{2A}\int d\mathbf{r}\int d\mathbf{r}'\rho_2(\mathbf{r},\mathbf{r}')\left[\frac{(x-x')^2-(z-z')^2}{|\mathbf{r}-\mathbf{r}'|}\right]\times V'(|\mathbf{r}-\mathbf{r}'|)\ , \tag{4.12}$$

which is a standard expression for the surface tension in terms of the pair distribution function. In the limit of an infinite system the A factor of (4.12) can be removed as usual by assuming $\rho_2(\mathbf{r},\mathbf{r}')$ to be translationally invariant parallel to the interface. In this limit one can thus recover the standard Kirkwood and Buff expression[1] from (4.12).

C. Surface of tension

The location z_s of the surface of tension of the planar interface considered above is defined in terms of the first moment of the integrand of (4.9) as

$$z_s\gamma=\frac{1}{A}\int d\mathbf{r}\, z[\sigma_{xx}(\mathbf{r})-\sigma_{zz}(\mathbf{r})]\ , \tag{4.13}$$

where γ is given by (4.9). In order to find the distribution function expression corresponding to z_s we proceed as above and first determine the strain leading to (4.13). This time we must have $\delta\epsilon_{xx}(\mathbf{r})=\lambda z=-\delta\epsilon_{zz}(\mathbf{r})$ and $\delta\epsilon_{ij}(\mathbf{r})$ zero otherwise, with $\lambda=\delta A/z_s A$. The corresponding displacement field is $\delta\mathbf{u}(\mathbf{r})=\lambda(xz,0,-(x^2+z^2)/2)$. We again have $\mathrm{inc}\,\delta\vec{\epsilon}=0$, $\nabla\cdot\delta\mathbf{u}=0$ and $\mathbf{r}=\mathbf{0}$ as fixed point (notice, however, that this time $\nabla\times\delta\mathbf{u}\neq\mathbf{0}$ for $\mathbf{r}\neq\mathbf{0}$). According to (3.5) and (3.6) the equation (3.5) corresponding to (4.13) is now

$$z_s\gamma=\frac{1}{A}\int d\mathbf{r}\left[xzf_x(\mathbf{r})-\frac{(x^2+z^2)}{2}f_z(\mathbf{r})\right]\ , \tag{4.14}$$

while using (4.1) in (4.14) yields

$$z_s\gamma=\frac{1}{A}\int d\mathbf{r}\int d\mathbf{r}'\rho_2(\mathbf{r},\mathbf{r}')\left[xz\nabla_x-\frac{(x^2+z^2)}{2}\nabla_z\right]\times V(|\mathbf{r}-\mathbf{r}'|)\ , \tag{4.15}$$

which can also be obtained directly from (4.13) using (4.1) and (3.22) or (3.21). To obtain (4.15) we have neglected the surface term

$$\int d\mathbf{r}\left[\nabla_x[xz\rho(\mathbf{r})]-\nabla_z\left[\frac{(x^2+z^2)}{2}\rho(\mathbf{r})\right]\right] \tag{4.16}$$

for the same reason as above [see (4.6b)]. Symmetrizing (4.15) and introducing the coordinates $(\mathbf{r}-\mathbf{r}',(\mathbf{r}+\mathbf{r}')/2)$ one obtains from (4.15)

$$z_s\gamma=\frac{1}{2A}\int d\mathbf{r}'\int d\mathbf{r}\rho_2(\mathbf{r},\mathbf{r}')\frac{(z+z')}{2}\times\left[\frac{(x-x')^2-(z-z')^2}{|\mathbf{r}-\mathbf{r}'|}\right]\times V'(|\mathbf{r}-\mathbf{r}'|)\ , \tag{4.17}$$

which should be divided by γ of (4.12) in order to obtain z_s. Again, one can remove the A dependence of (4.17) by going to the limit of an infinite system with translational invariance parallel to the interface. The discussion of such a limiting procedure is outside the scope of the present investigation but will be considered in more detail elsewhere.[14]

Before closing this section let us also observe that one often inquires[6] for the higher-order moments of the interfacial stress profile:

$$I=\frac{1}{A}\int d\mathbf{r}\, g(z)[\sigma_{xx}(\mathbf{r})-\sigma_{zz}(\mathbf{r})]\ , \tag{4.18}$$

with, say, $g(z)\sim z^n$ $(n>1)$. In relation with (3.6) this corresponds to $\delta\epsilon_{xx}(\mathbf{r})=-\delta\epsilon_{zz}(\mathbf{r})=\lambda g(z)$ and $\delta\epsilon_{ij}(\mathbf{r})=0$ otherwise. Integrating the corresponding equation for $\delta\mathbf{u}(\mathbf{r})$ one finds, however, that this is possible only when $g'(z)$ is a constant, i.e., when $g(z)$ is a linear function of z, $g(z)=c_1+c_2 z$, so that only the first two moments (i.e., γ and $z_s\gamma$) correspond to a physically realizable strain deformation. Notice that this is all that is required by thermodynamics. If higher moments are required *per se* then this will be possible only if one also adds shear components to (4.18), i.e., when $\delta\epsilon_{xz}\neq 0$. Although one expects that for a fluid the corresponding shear stresses $[\sigma_{xz}(\mathbf{r})]$ will eventually vanish in the bulk phases of an infinite system, it is less obvious to show that their contribution to (4.18) will also disappear in the thermodynamic limit. It is therefore prudent to conclude that although the surface tension and the surface of tension of a planar interface always correspond to a well-defined strain deformation, the calculation of the higher-order moments of the interfacial stress profile may pose some more delicate problems which will not be considered here any further.

V. CONCLUSIONS

We have defined[13] the stress tensor of a nonuniform equilibrium fluid as the (field) variable thermodynamically conjugate to the local strain tensor. The unique relation (for a system globally at rest) which exists between the displacement field and the strain tensor was then used to induce a similar relation between the force field and the stress tensor. This leads to a stress tensor which is uniquely defined in terms of the force field and which is symmetric, path independent, and satisfies the usual force balance equation. Any free-energy change resulting from a strain can then be computed either from the stress tensor or from the forces. Some simple examples which illustrate the general procedure have been given. They include the surface tension and the surface of tension of a fluid with a planar interface. The more difficult case of the curved interfaces is planned to be considered later.

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