Generalization of the Stress Tensor to Nonuniform Fluids and Solids and Its Relation to Saint-Venant's Strain Compatibility Conditions

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Combining some results from the classical theory of elasticity with the modern functional derivative approach to nonuniform systems, we obtain a well-defined stress tensor for nonuniform equilibrium fluids and solids. This stress tensor is symmetric and satisfies the force balance equation, so it provides an unambiguous route to quantities such as the surface free energy. The ambiguities associated with earlier stress-tensor definitions are traced back to their failure to take account of Saint-Venant's strain compatibility conditions.

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Stress-strain relations are used in a wide variety of physical problems.[1,2] While the strain tensor of a nonuniform system can be easily defined,[1] this is not the case for the stress tensor.[2] Indeed, as noted in the recent monograph of Rowlinson and Widom,[2] there still "...appears to be no unique definition of this quantity." Although the very notion of a stress tensor of a nonuniform fluid was introduced some forty years ago by Kirkwood and co-workers,[3,4] it has been known for some time[2] that their definition[4] is incomplete in that it depends on a line integral whose value is contour dependent. This is quite disturbing from a practical point of view since, as emphasized by Schofield and Henderson,[5] this ambiguity extends to the notion of a "surface of tension" which Gibbs introduced in defining the surface tension of a liquid drop[2] (or a curved interface), although the physical consequences of the surface tension of drops are currently observable in, e.g., nucleation phenomena. In the present Letter we provide an unambiguous definition of the stress tensor by combining some results from the classical theory of elasticity[6] with the more modern functional derivative techniques familiar from the theory of nonuniform fluids.[7] Although intrinsically more complicated than the earlier proposals,[3-5,8] the present definition is equally amenable to explicit calculations of observable quantities such as the surface tension and the surface of tension. Finally, the failure of the previous attempts to construct a well-defined stress tensor is explained as arising from the fact that they all overlooked the important role played in this construction by Saint-Venant's strain compatibility conditions.[9]

Following the general ideas of the classical theory of elasticity,[1,6] we use a displacement field $\mathbf{u}(\mathbf{r})$ to describe a small *deformation* of the original system resulting from locally translating any point $\mathbf{r}$ into $\mathbf{r}+\mathbf{u}(\mathbf{r})$. This deformation will also slightly distort the system, an effect which can be characterized by the *distorsion* tensor $\overleftrightarrow{d}(\mathbf{r})=\nabla\mathbf{u}(\mathbf{r})$, in dyadic notation. The latter can always be resolved into a local *rotation* $\overleftrightarrow{\omega}(\mathbf{r})=\frac{1}{2}[\overleftrightarrow{d}(\mathbf{r})-\overleftrightarrow{d}^{\dagger}(\mathbf{r})]$, originating from the antisymmetric part of $\overleftrightarrow{d}$, and a local *strain* $\overleftrightarrow{\epsilon}(\mathbf{r})=\frac{1}{2}[\overleftrightarrow{d}(\mathbf{r})+\overleftrightarrow{d}^{\dagger}(\mathbf{r})]$, due to the symmetric part of $\overleftrightarrow{d}$, with $\overleftrightarrow{d}^{\dagger}$ denoting the transpose of the tensor $\overleftrightarrow{d}$. Whereas the strain tensor $\overleftrightarrow{\epsilon}(\mathbf{r})$ can obviously be obtained by differentiation from the displacement $\mathbf{u}(\mathbf{r})$, it is less often noted[6] that the converse is also true: Given a symmetric tensor field $\overleftrightarrow{\epsilon}(\mathbf{r})$ we can obtain the corresponding $\mathbf{u}(\mathbf{r})$ from the so-called Kirchhoff-Cesaro-Volterra relation,[10]

$$\mathbf{u}(\mathbf{r})=\int_{C(\mathbf{r}_0,\mathbf{r})}\{\overleftrightarrow{\epsilon}(\mathbf{l})+(\mathbf{l}-\mathbf{r})\times[\nabla_l\times\overleftrightarrow{\epsilon}(\mathbf{l})]\}\cdot d\mathbf{l}\,, \qquad (1)$$

where the line integral can be taken along any contour $C(\mathbf{r}_0,\mathbf{r})$ going from $\mathbf{r}_0$ to $\mathbf{r}$, with $\mathbf{r}_0$ being a *fixed point* of the deformation, the existence of which is guaranteed by the fact that during the deformation the system as a whole has undergone neither a *global* translation $[\mathbf{u}(\mathbf{r}_0)=0]$ nor a *global* rotation $[\nabla\times\mathbf{u}(\mathbf{r}_0)=0]$. As first noted by Saint-Venant,[9] the six components of $\overleftrightarrow{\epsilon}$ will not overdetermine the three components of $\mathbf{u}$ because for any symmetric tensor $\overleftrightarrow{\epsilon}$ which is compatible with a strain tensor, $\overleftrightarrow{\epsilon}$ has moreover to satisfy the following conditions, only three of which are independent, known as "Saint-Venant's strain compatibility conditions":

$$\mathrm{Inc}\overleftrightarrow{\epsilon}(\mathbf{r})\equiv\nabla\times[\nabla\times\overleftrightarrow{\epsilon}(\mathbf{r})]^{\dagger}=0\,, \qquad (2)$$

where Inc denotes the so-called incompatibility operator, so that (2) states that the incompatibility of $\overleftrightarrow{\epsilon}$, or $\mathrm{Inc}\overleftrightarrow{\epsilon}$, should vanish for any realizable strain tensor. The important point to note is that (2) also guarantees that the integrand of (1) is a total differential and hence that (1) yields a $\mathbf{u}(\mathbf{r})$ field which is independent of the particular contour $C(\mathbf{r}_0,\mathbf{r})$ chosen for its evaluation. Hence, for any (single-valued) $\mathbf{u}(\mathbf{r})$, Eqs. (1) and (2) establish a *unique* relation between $\overleftrightarrow{\epsilon}(\mathbf{r})$ and $\mathbf{u}(\mathbf{r})$ in any (simply connected) system.[6]

Suppose now that we would like to generalize the standard Thomson[11] definition of the stress tensor as being the derivative of the free energy with respect to the strain tensor[1] to a nonuniform system. This definition emphasizes from the outset the use of the stress tensor as an intermediary in work-related calculations, an emphasis which is only implicit in the earlier formulations.[3-5,8] Let us therefore denote by $F=F[\mathbf{u}]$ the Helmholtz free energy of the *deformed* system viewed as a functional[12] of $\mathbf{u}(\mathbf{r})$, which by virtue of (1) is itself a unique functional of $\overleftrightarrow{\epsilon}(\mathbf{r})$. Here it will be understood that the temperature, number of particles, and undeformed volume of the system are kept constant throughout and therefore these variables will not be indicated explicitly in what follows. Let us proceed now by computing the desired local *response* of the free energy to a local change in strain. At linear-response order, which is all that is needed in order to characterize the response of the undeformed system, this response $\overleftrightarrow{R}(\mathbf{r})$ can be obtained from

$$\overleftrightarrow{R}(\mathbf{r})=\frac{\delta F[\mathbf{u}]}{\delta\overleftrightarrow{\epsilon}(\mathbf{r})}\bigg|_{\mathbf{u}=0}=\frac{\delta W[\mathbf{u}]}{\delta\overleftrightarrow{\epsilon}(\mathbf{r})}\bigg|_{\mathbf{u}=0}, \tag{3}$$

where we took into account that this free-energy change can be identified[1] with the reversible work $W[\mathbf{u}]$ done by the displacement $\mathbf{u}(\mathbf{r})$ against the external forces:

$$W[\mathbf{u}]=\int dV\,\mathbf{u}(\mathbf{r})\cdot\mathbf{f}(\mathbf{r})\,, \tag{4}$$

where, to first order in $\mathbf{u}(\mathbf{r})$, $\mathbf{f}(\mathbf{r})$ can be taken to be the external force *density* associated[7] with the *undeformed* nonuniform system. In any explicit calculation of (3), the external force density $\mathbf{f}(\mathbf{r})$ of (4) has to be related to the internal forces by a statistical-mechanical relation such as the Born-Green-Yvon equation[2]

$$\mathbf{f}(\mathbf{r})=k_BT\nabla\rho_1(\mathbf{r})+\int dV'\rho_2(\mathbf{r},\mathbf{r}')\nabla\phi(|\mathbf{r}-\mathbf{r}'|)\,, \tag{5}$$

where $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r},\mathbf{r}')$ denote, respectively, the one- and two-body densities, $\phi(|\mathbf{r}|)$ the pair potential, and T the temperature, or by the equivalent relation in terms of the direct correlation function.[13] As will become clear, the details of this relationship are not genuine to the present problem, which is *macroscopic* in nature and hence independent of any particular property of the Hamiltonian or of any particular statistical-mechanical representation of $\mathbf{f}(\mathbf{r})$. Combining now (1) and (4) we obtain, after computing the functional derivative in (3),

$$\overleftrightarrow{R}(\mathbf{r}_1)=\left\{\int dV\int_{C(\mathbf{r}_0,\mathbf{r})}d\mathbf{l}\{\mathbf{f}(\mathbf{r})+[\mathbf{f}(\mathbf{r})\times(\mathbf{l}-\mathbf{r})]\times\nabla_l\}\delta(\mathbf{r}_1-\mathbf{l})\right\}_{\rm sym}, \tag{6}$$

where $\{\overleftrightarrow{t}\}_{\rm sym}$ is a shorthand notation for the symmetric part of $\overleftrightarrow{t}$, e.g., $\{\overleftrightarrow{t}\}_{\rm sym}=\frac{1}{2}(\overleftrightarrow{t}+\overleftrightarrow{t}^{\dagger})$. Notice that the symmetry of $\overleftrightarrow{R}$ follows directly from the symmetry of $\overleftrightarrow{\epsilon}$ via Eq. (3). This then would solve our problem were it not for Eq. (2). Indeed, Saint-Venant's condition (2) can be viewed as stating that only three of the six components of $\overleftrightarrow{\epsilon}$ can be varied independently whereas (6) has been obtained from (3) by assuming all six components of $\overleftrightarrow{\epsilon}$ to be independent. Allowing this violation of (2), makes Eq. (6) contour dependent.

To avoid this we now define the stress tensor $\overleftrightarrow{\sigma}(\mathbf{r})$ as being a new free-energy response which is constrained to satisfy Saint-Venant's condition, since only in this case will our operations on the free energy acquire a well-defined meaning. The restriction (2) is most easily applied in Fourier space since if $\overleftrightarrow{\epsilon}(\mathbf{k})=\int dV\,\overleftrightarrow{\epsilon}(\mathbf{r})\times\exp(i\mathbf{k}\cdot\mathbf{r})$, (2) simply becomes

$$\mathbf{k}\times\overleftrightarrow{\epsilon}(\mathbf{k})\times\mathbf{k}=0\,. \tag{7}$$

We can thus define $\overleftrightarrow{\sigma}(\mathbf{k})$ as the orthogonal complement of $\overleftrightarrow{R}(\mathbf{k})$ with respect to the "null space" defined by (7) ($\hat{\mathbf{k}}=\mathbf{k}/|\mathbf{k}|$):

$$\sigma(\mathbf{k})=\overleftrightarrow{R}(\mathbf{k})-\hat{\mathbf{k}}\times[\hat{\mathbf{k}}\times\overleftrightarrow{R}(\mathbf{k})\times\hat{\mathbf{k}}]\times\hat{\mathbf{k}} \tag{8}$$

so that $\mathbf{k}\times\overleftrightarrow{\sigma}(\mathbf{k})\times\mathbf{k}=0$ and $\overleftrightarrow{\sigma}(\mathbf{k})$ will have no nonzero components in Saint-Venant's null space. Returning now to the original $\mathbf{r}$ space we obtain by inverse Fourier transform of (8) the final definition of the stress tensor $\overleftrightarrow{\sigma}(\mathbf{r})$:

$$\overleftrightarrow{\sigma}(\mathbf{r})=\overleftrightarrow{R}(\mathbf{r})-\int dV_1\frac{1}{4\pi|\mathbf{r}-\mathbf{r}_1|}{\rm Inc}_1\int dV_2\frac{1}{4\pi|\mathbf{r}_1-\mathbf{r}_2|}{\rm Inc}_2\overleftrightarrow{R}(\mathbf{r}_2)\,, \tag{9}$$

where the indices 1 and 2 indicate on which variables ($\mathbf{r}_1$ or $\mathbf{r}_2$) Saint-Venant's Inc operator [see (2)] is acting. Notice moreover that when using (6) in (9) only the difference of the two terms will be well defined, not each term separately. It can now be shown[14] that the stress tensor defined by Eqs. (6) and (9) has the following properties. (i) It is symmetric: $\overleftrightarrow{\sigma}^{\dagger}(\mathbf{r})=\overleftrightarrow{\sigma}(\mathbf{r})$, a property which follows here directly from the symmetry of $\overleftrightarrow{\epsilon}(\mathbf{r})$ via Eqs. (3) and (8) or (9). Consequently, both the linear- and angular-momentum conservation laws can be treated on equal footing[1] in terms of this stress tensor. (ii) It satisfies the force balance equation: $\nabla\cdot\overleftrightarrow{\sigma}(\mathbf{r})\equiv\nabla\cdot\overleftrightarrow{R}(\mathbf{r})=-\mathbf{f}(\mathbf{r})$. Hence, body forces can always be resolved into surface stresses.[1] (iii) It satisfies a Saint-Venant-like condition: $\nabla\times(\nabla\times\overleftrightarrow{\sigma})^{\dagger}=0$. This condition garantees[14] that the difference on the right-hand side of (9) is independent of the contour used to compute Eq. (6). (iv) If ${\rm Inc}\,\delta\overleftrightarrow{\epsilon}(\mathbf{r})=0$, then the change in free energy resulting from this change in strain, $\delta\overleftrightarrow{\epsilon}(\mathbf{r})$, reads

$$\delta F=\int dV\,\overleftrightarrow{\sigma}(\mathbf{r}):\delta\overleftrightarrow{\epsilon}(\mathbf{r})=\int dV\,\overleftrightarrow{R}(\mathbf{r}):\delta\overleftrightarrow{\epsilon}(\mathbf{r})=\int dV\int_{C(\mathbf{r}_0,\mathbf{r})}\{\mathbf{f}(\mathbf{r})+[\mathbf{f}(\mathbf{r})\times(\mathbf{l}-\mathbf{r})]\times\nabla_l\}\cdot\delta\overleftrightarrow{\epsilon}(\mathbf{l})\cdot d\mathbf{l}\,, \tag{10}$$

where the line integral of (10) is contour independent.[14] The present unambiguous definition of a stress tensor produces thus a highly nonlocal object [see the second term in the right-hand side of (9)] which, just as the strain tensor, contains only three *independent* components. This, however, is sufficient in order to characterize the three components of $\mathbf{f}(\mathbf{r})$ or any external work-related quantity such as the surface tension or the surface of tension.[2] More detailed expressions will be given elsewhere.[14]

Finally, the difficulties with the earlier attempts[3-5,8] to construct a stress tensor for a nonuniform fluid can now be easily understood. First, the force balance equation, $\nabla\cdot\overleftrightarrow{\sigma}=-\mathbf{f}$, which is always taken as a starting point clearly underdetermines $\overleftrightarrow{\sigma}$ since there are only three equations to determine all the components of $\overleftrightarrow{\sigma}$. Second, any expression for the full $\overleftrightarrow{\sigma}$ which is "extracted" from the force balance equation but which does not satisfy Saint-Venant's condition, $\mathrm{Inc}\overleftrightarrow{\sigma}=0$, operates in the null space of the strain which leads to contour dependence.[15]

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[15]For instance, in the present setting the Schofield-Henderson expression of the stress tensor reads

$$\overleftrightarrow{\sigma}(\mathbf{r}_1)=\int dV\int_{C(\mathbf{r}_0,\mathbf{r})} d\mathbf{l}\,\mathbf{f}(\mathbf{r})\delta(\mathbf{r}_1-\mathbf{l}),$$

which is contour dependent (see Ref. 5).