Symmetry of the Pressure Tensor in a Nonuniform Fluid

For many years it has been recognized that there is an ambiguity in the existing definition of the stress (or its negative, the pressure) in an inhomogeneous fluid at equilibrium. Baus and Lovett [1] have recently proposed to resolve this ambiguity by imposing St. Venant's condition of "compatibility" on the form of the tensor.

Previous definitions of the pressure at a point $\mathbf{r}$ have involved only the state of the fluid in a space around $\mathbf{r}$ whose linear dimensions are of the order of the range of the intermolecular forces. The proposal of Baus and Lovett breaches this restriction but this may not be a conclusive argument against it. The constraints imposed by symmetry may be more serious and are the subject of this Comment.

Let us consider first a flat interface in the x-y plane between a liquid and its vapor. Symmetry requires that the pressure tensor in both homogeneous phases reduces to a scalar p and that near the interface it has the diagonal form

$$\mathbf{p}(\mathbf{r})=p_T(z)[\mathbf{e}_x\mathbf{e}_x+\mathbf{e}_y\mathbf{e}_y]+p_N(z)[\mathbf{e}_z\mathbf{e}_z], \tag{1}$$

where p_N and p_T are the normal and transverse components, and $\mathbf{e}_x$ is a unit vector in the x direction. The tensor also satisfies the condition for mechanical equilibrium,

$$\nabla\cdot\mathbf{p}(\mathbf{r})+\rho(\mathbf{r})\nabla v(\mathbf{r})=0, \tag{2}$$

where $\rho(\mathbf{r})$ and $v(\mathbf{r})$ are the density and external potential at $\mathbf{r}$. We can take $v(\mathbf{r})$ to be arbitrarily small; it is needed only to keep the interface macroscopically flat. Baus and Lovett require that $\mathbf{p}$ also satisfies St. Venant's condition,

$$\nabla\times[\nabla\times\mathbf{p}(\mathbf{r})]^{\dagger}=0, \tag{3}$$

where the dagger denotes the transpose of the tensor.

Equation (2) tells us that $p_N(z)$ is constant, and so equal to the scalar pressure $p^l=p^g$ in both phases. Equation (3) requires that $d^2p_T(z)/dz^2$ is zero for all z, which, with the boundary conditions

$$p_T(z\to\infty)=p^g=p_T(z\to-\infty)=p^l, \tag{4}$$

requires that $p_T(z)$ is also a constant. The natural conclusion is that the surface tension,

$$\gamma=\int_{-\infty}^{\infty}dz\,[p_N(z)-p_T(z)], \tag{5}$$

is zero. Baus and Lovett's expression does not, however, lead to a vanishing surface tension since there are contributions to the free energy from the boundaries that have been ignored in this simple analysis.

Let us therefore consider a system in which the interface has no boundary, namely, a spherical drop of an almost involatile liquid at the center of a spherical vessel large compared with the size of the drop. Again we can choose the external potential to be arbitrarily weak; it is needed only to keep the drop away from the walls. The symmetry of the system requires that $\mathbf{p}(\mathbf{r})$ has the form

$$\mathbf{p}(\mathbf{r})=p_N(r)[\mathbf{e}_r\mathbf{e}_r]+p_T(r)[\mathbf{e}_\theta\mathbf{e}_\theta+\mathbf{e}_\varphi\mathbf{e}_\varphi], \tag{6}$$

where p_N and p_T are again the normal and transverse components which are functions only of r, the distance from the center of the drop. The unit tensors are now in a spherical coordinate system (r,θ,φ).

Equation (2), with $v(\mathbf{r})=0$, now requires that

$$\frac{dp_N(r)}{dr}+\frac{2}{r}[p_N(r)-p_T(r)]=0, \tag{7}$$

and St. Venant's condition requires that

$$\frac{2}{r}F(r)\mathbf{1}+\left(\frac{1}{r^2}F'(r)-\frac{1}{r^3}F(r)\right)\mathsf{I}=0, \tag{8}$$

where $\mathbf{1}$ is the unit tensor and I a moment of inertia tensor,

$$\mathsf{I}=r^2\mathbf{1}-\mathbf{rr}, \tag{9}$$

and

$$F(r)=\frac{dp_T(r)}{dr}-\frac{1}{r}[p_N(r)-p_T(r)]. \tag{10}$$

The two conditions (7) and (8) require that $F(r)=0$ and that

$$\frac{d}{dr}[p_N(r)+2p_T(r)]=0. \tag{11}$$

But we know that

$$p_N(r)+2p_T(r)=\begin{cases}3p^l & \text{for } r\ll R,\\ 3p^g\simeq 0 & \text{for } r\gg R,\end{cases} \tag{12}$$

where R is the radius of the drop. Laplace's equation requires that the difference between p^l and p^g is $2\gamma/R$, so, again, we have a vanishing surface tension. It seems to be unphysical to require a contribution from the boundary in this case since there is no matter there and the pressure tensor is zero for $r\gg R$. The tensor of Baus and Lovett leads, presumably, to a nonzero value of γ and so violates one or more of the assumptions made in the argument above, probably $\mathbf{p}=0$ at the distant boundary. It is clearly of interest to know which assumption is unnecessary, and how the dilemma is to be resolved.

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[1] M. Baus and R. Lovett, Phys. Rev. Lett. **65**, 1781 (1990).