

Baus and Lovett Reply: In the preceding Comment [1], Rowlinson argues that our definition [2] of the stress tensor leads to a vanishing surface tension. In our follow-up paper [3] we prove explicitly that this is not the case and that our definition leads, in the case of the planar liquid-vapor interface, to the celebrated Irving-Kirkwood expression. In order to clarify the basic differences between our views [2,3] and the more traditional views expressed in the Comment [1], we would like to emphasize the following four points.

(1) *The stress tensor.*—The origin of the ambiguity in the existing stress tensors is due to the fact that when this object is viewed as a point function or field its complete mathematical definition requires a specification of both its divergence and its curl. While the traditional works only consider the former we have also specified the latter through St. Venant's double-curl condition [2]. This, however, cannot "raise other difficulties" as stated in the Comment, because the underlying thermodynamics is determined completely by the divergence of the stress tensor [3].

(2) *The external constraints.*—The very notion of a stress tensor is an unnecessarily complicated object whose physical utility for the description of equilibrium fluids is not obvious to us. We have advocated instead that it should be possible to describe all the operationally meaningful quantities in terms of the mechanical forces conjugate to small deformations of the system by computing the resulting work of deformation as in our Eq. (4) [2]. It should be noticed, however, that such a computation of the work of deformation performed against the external forces which hold the system together requires one to start from a finite system in the presence of these external constraints, and to leave the thermodynamic limit of an infinite system for the end of the calculation. It is thus clearly impossible to, as done in the Comment, determine directly the stress tensor of the infinite system by removing the external forces from Eqs. (2), (7), and (11) of the Comment on the basis that they are "arbitrarily small." Indeed, from our Eq. (4) [2] it follows that their global effect can never be smaller than the work of deformation one is looking for.

(3) *The surface tension.*—How then should one proceed to find the surface tension? One would, in our view, start from the standard thermodynamic statement that the work of deformation, or equivalently the free-energy change (δF) due to this deformation, can be separated into contributions resulting from the deformation of each of the system's geometric characteristics, with (minus) the pressure (p) as the thermodynamic force conjugate to the volume change (δV), a surface tension (γ) conjugate to each areal change (δA), and a line tension (τ) conjugate to each linear change (δL), say, $\delta F = -p\delta V + \gamma\delta A + \tau\delta L$. Next, we compute a microscopic (statistical mechanical) expression for the mechanical force, $\delta F/\delta l$, conjugate to a displacement by δl of one of the boundaries by using our Eq. (4) [2]. Finally, we relate the

mechanical and thermodynamic forces by combining both approaches as

$$\frac{\delta F}{\delta l} = -p \frac{\delta V}{\delta l} + \gamma \frac{\delta A}{\delta l} + \tau \frac{\delta L}{\delta l} \quad (1)$$

and consider various displacements until an expression for the quantity sought, say, γ , can be obtained from (1).

(4) *The geometry of the container.*—The solution of (1) with respect to the thermodynamic forces depends strongly on the geometry of the container. For a rectangular box of sides L_x , L_y , and L_z this is easy since for an interface perpendicular to the z axis (i.e., for $A = L_x L_y$), Eq. (1) yields

$$\frac{\delta F}{\delta L_x} = -p L_y L_z + \gamma L_y, \quad \frac{\delta F}{\delta L_z} = -p L_x L_y \quad (2)$$

or

$$\gamma = \frac{1}{L_x L_y} \left[L_x \frac{\delta F}{\delta L_x} - L_z \frac{\delta F}{\delta L_z} \right], \quad (3)$$

where the contribution to (2) and (3) of any line tension in (1) is of order τ/L_a and can hence be neglected in the thermodynamic limit $L_a \rightarrow \infty$, $a = x, y, z$, where (3) will recover the standard Irving-Kirkwood result [3]. For a spherical box of radius R (as considered in the second part of the Comment) the situation is clearly more complicated since (i) the deformation by δR of the box size leads only to a single mechanical force, Eq. (1), so that the elimination of the pressure term cannot be performed as in Eq. (3), and (ii) the changes in δV and δA are no longer independent but constrained by Laplace's relation $\delta A/\delta V = 2/R$. This difficulty is well known and its resolution requires the introduction of Gibbs's surface of tension. The location of this surface can, however, not be found from the knowledge of the mechanical force ($\delta F/\delta R$) only, but requires moreover an investigation of the spatial distribution of the forces in order to find where the forces are acting.

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[1] J. S. Rowlinson, preceding Comment, Phys. Rev. Lett. **67**, 406 (1991).

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

[3] M. Baus and R. Lovett, Phys. Rev. A (to be published).