Comment

Reply to "Comment on 'Calculation of Solid−Fluid Interfacial Free Energy with Consideration of Solid Deformation by Molecular Dynamics Simulations'"

Tianhao Wu and Abbas Firoozabadi*

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We appreciate Parambathu et al.'s interest[1] in our work.[2] As stated in our paper, we derive working expressions for calculating solid−fluid interfacial free energy based on the free-energy perturbation method with consideration of solid deformation.[2] For clarity, we start with the basic expression for the differential of Helmholtz free energy for a system consisting of bulk fluid, bulk deformable solid, and the interface between the two.

In a closed system with a general flat interface, including solid−fluid or fluid−fluid interfaces,

$$dF = -SdT + \gamma dA + V\sum_i\sum_j \sigma_{ij}d\epsilon_{ij} \tag{1}$$

where F is Helmholtz free energy, S is entropy, T is temperature, γ is interfacial free energy density, A is interfacial area, V is volume, σ_{ij} and ε_{ij} are components of the stress and strain tensor, respectively, and i and j are plane indices. Equation 1 (eq 8 in ref 2) is a key expression in the representation of Helmholtz free energy of a two-phase system composed of a solid−fluid system. It also represents a fluid−fluid system. The work for change in the interfacial area is represented by γdA. The third term, $\sum_i\sum_j \sigma_{ij}d\epsilon_{ij}$, represents the work of deformation of the two bulk phases.

Assume the system is under hydrostatic conditions, $\sum_i\sum_j \sigma_{ij}d\epsilon_{ij} = -pdV$. Then, eq 1 reduces to

$$dF = -SdT + \gamma dA - pdV \tag{2}$$

where p is pressure. The derivation is provided in the Supporting Information of ref 2.

For a fluid (f)−fluid (f) system at constant volume and constant temperature, the expression for the interfacial free energy density from eq 2 can be written as

$$\gamma_{ff} = \frac{1}{2}\left(\frac{\partial F}{\partial A}\right)_{T,V,N} \tag{3}$$

The factor 2 appears for two interfaces in a periodic system. Note that our derivations are limited to descriptions of a flat interface. A curved interface may require consideration of line tension.[3]

For a solid (s)−fluid (f) system with two interfaces, eq 1 leads to[2]

$$\gamma_{sf} = \frac{1}{2}\left(\frac{\partial F}{\partial A}\right)_{T,V,N} - \frac{L_{z,s}}{2}\left[\frac{1}{2}(\sigma_{xx}+\sigma_{yy}) - \sigma_{zz}\right] \tag{4}$$

where $L_{z,s}$ is the thickness of the solid phase. Other details and axis definitions are presented in ref 2. When $\Delta\sigma = (\sigma_{xx}+\sigma_{yy})/2 - \sigma_{zz} = 0$, eq 3 can be obtained from eq 4. Equation 4 is more general. When eq 3 is applied to a solid−fluid system, it is not guaranteed that the solid is stress-free. This is a key consideration, which has led some authors to report negative solid−fluid interfacial free energy density.

The perturbation method can be used to evaluate the solid (s)−fluid (f) interfacial free energy density:

$$\gamma_{sf} = -\frac{k_B T}{4\Delta A}\left[\ln\left\langle\exp\left(-\frac{\Delta U^+}{k_B T}\right)\right\rangle - \ln\left\langle\exp\left(-\frac{\Delta U^-}{k_B T}\right)\right\rangle\right] - \frac{L_{z,s}}{2}\left[\frac{1}{2}(\sigma_{xx}+\sigma_{yy}) - \sigma_{zz}\right] \tag{5}$$

where k_B is the Boltzmann constant and ΔU (see definition of terms not defined above in ref 2) is the change of potential energy due to the perturbation.

The test-area method has been used to compute γ_{ff} extensively and γ_{sf} in a limited number of publications. While the fluid−fluid interfacial free energy has been verified and computed successfully, the method of calculation of γ_{sf} has been reported to give a negative interfacial free energy density.[4]

Negative interfacial free energy is only one aspect of the potential problems in the conventional test-area method. Other potential problems have been discussed in our paper.
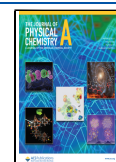
We have proposed working expressions for the calculation of the solid−fluid interfacial free energy with consideration of solid deformation, in which the effect has been quantified.

In this reply, we itemize the comments and concerns by Parambathu et al. Hopefully, it will shed further light on our proposed method.

1. DISCUSSION ABOUT THE DERIVATION OF EQUATION 2 FROM EQUATION 1

Parambathu et al. state that "*For a solid under hydrostatic compression, because of isotropy the nondiagonal elements of the strain tensor vanish. Hence, $\sigma_{ik} = -p\delta_{ik}$ and $\delta_{ik}du_{ik} = du_{ii} = dV$. Thus, $d\tilde{F} = -\tilde{S}\cdot dT - pdV$. In modern notation, eq 4 is Gibbs' eq 417.[2] (See also his eq 356.) For a general deformation, note the **absence** of the dA term, since the strain tensor already subsumes this effect. ... Further, eq 3 is also mathematically erroneous as it attempts to identify a separate response to dA when those area changes are already included in the strain tensor.*"

The statement that "*For a general deformation, note the **absence** of the dA term, since the strain tensor already subsumes this effect. ... Further, eq 3 is also mathematically erroneous as it attempts to identify a separate response to dA when those area changes are already included in the strain tensor*" is a huge misunderstanding of the thermodynamics of interfaces and the relationship between strain tensor and dA. The term $\sigma_{ik}du_{ik}$ represents the work of bulk-phase deformation, not the interface. The work for interface area change is described by γdA. The contribution of stretching of the interfacial area is not included in $\sigma_{ik}du_{ik}$. dA is not subsumed in du_{ik} for the term $\sigma_{ik}du_{ik}$. Mathematically, dA can be "expressed" by strain tensor as $dA \approx A \times (d\varepsilon_{xx} + d\varepsilon_{yy})$. But, it does not mean that any term containing strain tensor must "include" the effect about dA.

The derivation of eq 2 from eq 1 shows a clear guide to the understanding of this point. The work of the bulk phase $\sigma_{ik}du_{ik}$ is a general term for both solids and fluids. The takeaway from ref 5 is that $\sigma_{ik}du_{ik}$ for hydrostatic compression/expansion reduces to $-pdV$ ($\sigma_{ik}du_{ik} = -pdV$), which is denoted as $V\sum_i\sum_j \sigma_{ij}d\epsilon_{ij} = -pdV$ in the unified notation of ref 2. In fluids, hydrostatic compression/expansion is maintained. Then, eq 2 is obtained from eq 1. Note that the derivations by Landua et al.[5] relate to the bulk phase without the interface. A complete derivation in unified notation is presented in the Supporting Information of ref 2 (eqs S10−S16).

Overall, eq 1 describes the physics for solid−fluid and fluid−fluid systems. Equation 2 describes the physics in fluid−fluid systems and some special conditions in solid−fluid systems (e.g., hydrostatic and unstressed).

2. DISCUSSION ABOUT "AN INSEPARABLE PART OF THE PHYSICS"

Parambathu et al. state that "*Stated differently, dA can never be identified as an independent variation for a solid: any deflections of the area will always be coupled with changes in the bulk, and seeking to separate a bulk contribution is a futile endeavor. ... To summarize, for a solid (and by extension a solid in contact with a liquid), a change in the surface area will necessarily involve changes in the bulk energetics, as that is an inseparable part of the physics. Equation 3 is inconsistent with this physics.*"

"*An inseparable part of the physics*" does not mean an inseparable part of the "contribution". In other words, the change in surface area and the deformation of the bulk phases occur at the same time, which is a "coupling process". But,

their contributions can be measured and analyzed separately, which is also the contribution of our work. Otherwise, all the studies about interfacial behavior of solid−fluid systems would be "*a futile endeavor*". More generally, all the studies for analyzing the "coupling process" would be "*a futile endeavor*", too.

3. "A POSTERIORI CORRECTION" AND MISUNDERSTANDING ABOUT γ_{SL} VS $(\partial F/\partial A)_{N,V,T}$

Parambathu et al. state that "*Assuming the simulations are done with care, finding $\gamma_{sl} < 0$ from eqs 1 and 2 is complete and cogent information about the system is simulated: it just shows that if the constraint on the area is relaxed, the system will expand until such time a stable state, if it exists, is found. Sampling from such a state may be of uncertain value, but the results from equilibrium statistical mechanics needs no 'fixing'. ... The authors propose their a posteriori correction based on the following differential relation ....*"

We disagree. We do not apply "a posteriori correction". The source of the misunderstanding by Parambathu et al. may be from mixing up the concepts of γ_{sl} and $(\partial F/\partial A)_{N,V,T}$. From the simulations, we can obtain $(\partial F/\partial A)_{N,V,T}$ by the perturbation method. Indeed, it is straightforward to calculate $(\partial F/\partial A)_{N,V,T}$ and it can be negative, but it is not the motivation in ref 2. The challenge is how to calculate interfacial free energy density γ_{sl}. In fluid−fluid systems, $(\partial F/\partial A)_{N,V,T}$ is equal to the interfacial free energy density. In solid−fluid systems, it may not. We propose a working equation based on the relationship between γ_{sl} and $(\partial F/\partial A)_{N,V,T}$. It is expressed through eqs 3 and 4. In the conventional test-area method, it is assumed that $\gamma_{sl} = (\partial F/\partial A)_{N,V,T}$ for all conditions that may lead to significant deviation in solid−fluid systems. The statement that "*we refrain from giving this quantity any name for a system with a solid−liquid interface*" may be a consequence of this misunderstanding.

4. DISCUSSION ABOUT THE SIMULATIONS IN FIGURE 1

Parambathu et al. perform simulations to match our work. There may be serious issues. The details are discussed below:

(1) Validation

Rigorous validation is required for the method proposed by Parambathu et al. In our work, we have conducted validation through two types of simulations: surface tension of the solid−vacuum system and examination of size dependency for the solid−fluid system. Based on eq 12 of our paper,[2] whether the molecular simulations are conducted at high-compression, high-tension, or random low-stress conditions, the calculated interfacial free energy is the same due to the use of the proposed formulation.

In Figure 1 of ref 1, the solid−fluid results match our work, but the solid−vacuum results do not. The only supporting information for the results of Parambathu et al. is the statement "*We equilibrate the starting configuration taking care*". However, the challenge is how to quantify "care".

Compared to rigorously validated results in ref 2, a different result without validation may be an indication of the problem. The fact that it sometimes agrees and sometimes does not puts the result by Parambathu et al. in doubt. It may also be a consequence of the lack of robustness.

(2) "Very low pressure" and "$p^* = 0.1$" for the solid−vacuum system

To "match" our results, Parambathu et al. equilibrate the system at a "*very low pressure*" and "$p* = 0.1$" for the solid−vacuum system. There is a conflict between "vacuum" and "*very low pressure*" ($p* = 1 \times 10^{-5}$) or "$p* = 0.1$". This may not be appropriate.

Perhaps Parambathu et al. mean the simulations are conducted in an "unstressed" (or unstrained) system instead of a "*very low pressure*". If the system were unstressed, the multiplier of the second term in eq 5 (eq 12 of ref 2) would be zero. The results from the conventional test-area method should be the same as those from our method. However, it is often a challenge to create a rigorous unstressed solid−fluid or solid−vacuum system. For example, in Figure 1 of ref 1, there is still a difference between the results of "*very low pressure*" and our "solid−vacuum" results. On the other hand, Parambathu et al. mention the "*unchangeable solid*", which is only in concept and may not be a good approximation. Equation 6 in Parambathu et al. is still in need of the calculation of γ_{sl} and γ_{sv}. Then, one comes back to the challenges discussed in our paper.

The "$p* = 0.1$" may be referring to a stressed (compressed) system. Then, the results in Figure 1 exactly agree with our analyses in section 2 of ref 2. We provide a framework to quantify the effects of the strain (or stress) on the results and present a universal expression for general conditions. Figure 6 of ref 2 shows the contributions of the two terms in eq 5 (eq 12 of ref 2) and provides a clear guideline for calculations of the solid−fluid interfacial free energy density. The central panel in Figure 6 of our work is directed to address this condition. The unrealistic interfacial free energy density values in the conventional test-area method (γ_{TA}) are due to neglect of the deviatoric stress $\Delta\sigma$ (=0.5 $(\sigma_{xx} + \sigma_{yy}) - \sigma_{zz}$) in eq 14 in ref 2:

$$\gamma_{TA} = \gamma_{sf} + \frac{L_{z,s}}{2}\Delta\sigma \tag{7}$$

Generally, higher compression leads to lower $\Delta\sigma$. Note that compressive stress is defined as negative. If it is slightly compressed, γ_{TA} will be lower than γ_{sf}, which is exactly the case in Figure 1 by Parambathu et al. If it is highly compressed, γ_{TA} will be even negative. There are also conditions for which the calculated interfacial free energy density is positive but may not be correct. The right panel in Figure 6 of ref 2 shows that at high tensile stress conditions, one may get an unrealistically high interfacial free energy density without the use of our formulation. Other detailed discussions are provided on p 5845 of our paper.

■ AUTHOR INFORMATION

Corresponding Author

    Abbas Firoozabadi − *Department of Chemical and Biomolecular Engineering, Rice University, Houston, Texas 70057, United States;* ⊙ orcid.org/0000-0001-6102-9534; Email: abbas.firoozabadi@rice.edu

Author

    Tianhao Wu − *Department of Chemical and Biomolecular Engineering, Rice University, Houston, Texas 70057, United States*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.jpca.1c10259

Notes

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