COMMENTS

Comment on "Lattice Contraction and Surface Stress of fcc Nanocrystals"

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In a recent letter,[1] Jiang and co-workers present a theory for the magnitude of the interface stress f of interfaces between a solid metal and its melt. Such a theory would indeed be highly desirable, since f is a fundamental thermodynamic parameter for which there are few reliable data. The computation supplies, as an intermediate result, a size-dependent specific Gibbs excess free energy γ, which in itself is of interest with relation to the thermodynamic functions of nanoparticles. However, we maintain that the derivation, which is based on a consideration of the mechanical relaxation of the particle subject to the surface-induced stress, is erroneous since an important part of the work of deformation is neglected. We also give a critical discussion of the criterion of vanishing γ at small size.

Let us consider a spherical particle of diameter D, and use, as a reference state, the stress-free particle; in this state the Gibbs excess free energy is $\gamma_0 A$, with γ_0 the value of γ for the unstrained surface. At equilibrium the surface stress must be balanced by a pressure in the bulk,[2] $P = 2Af/(3V)$, which induces a uniform and isotropic strain of magnitude

$$\epsilon = -4\kappa f/(3D) \tag{1}$$

where the symbols κ, A, and V denote compressibility, surface area, and volume, respectively. The excess free energy in the strained particle is the sum of $\gamma_0 A$ and of the mechanical work of deformation, which we shall now compute. We note that the strain does work against the surface stress and against the pressure in the bulk in such a way that the free energy density at the surface is decreased at the expense of an increased free energy density in the bulk. By definition, γ is the *total* Gibbs excess free energy, per area, due to the presence of the surface; this includes not only local changes of the free energy density in the interfacial regions, but also any other variations that are intrinsically related to the presence of surfaces. This applies in particular to the strain energy in the bulk, which is erroneously neglected in ref 1. In computing the work of deformation it is instructive to measure area and volume in the undeformed lattice (Lagrangian coordinates), so that these parameters are constants, independent of the strain. The scalar surface stress is then defined by $f = 1/2$ trace $(\partial\gamma/\partial\mathbb{E})$ with $\mathbb{E}$ the tangential strain tensor,[2] and the work done by the isotropic strain ϵ against f is

$$W_A = 2fA\epsilon \tag{2}$$

The work associated with the bulk strain is simply

$$W_V = \frac{9}{2}\kappa^{-1}\epsilon^2 V \tag{3}$$

By substituting eq 1 for the strain into these expressions and using $A/V = 6/D$ for the sphere, one obtains

$$W_A = -\frac{8}{3}\kappa f^2 \frac{A}{D}, \quad W_V = \frac{4}{3}\kappa f^2 \frac{A}{D} \tag{4}$$

Since ref 1 ignores the bulk term W_V, which has half the magnitude and opposite sign compared to W_A, their results overestimate the magnitude of the reduction in excess free energy due to strain by a factor of 2.

The total excess free energy per area is obtained by adding W_A and W_V to the excess in the reference state, $\gamma_0 A$, and dividing by the area; the result is

$$\tilde{\gamma} = \gamma_0 - \frac{4}{3}\kappa f^2/D \tag{5}$$

The tilde denotes the use of Lagrangian coordinates; the value of γ using laboratory coordinates is $\tilde{\gamma}/(1 + 2\epsilon)$ since the excess free energy is computed per area of the *strained* surface. With eq 1 for ϵ this yields

$$\gamma = \gamma_0 \left[1 - 4\kappa f^2/(3\gamma_0 D)\right] / \left[1 - 8\kappa f/(3D)\right] \tag{6}$$

which corrects eq 6 of ref 1.

The excess per referential area, $\tilde{\gamma}$, is always a decreasing function of $1/D$. By contrast, an inspection of eq 6 shows that γ can be either a decreasing or an increasing function of $1/D$, depending on the sign of the term $f - 2\gamma_0$. This is due to the change in the area: for instance, when $f = 2\gamma_0$ then the strain reduces the excess free energy in proportion to the area, so that their ratio, γ, is a constant.

Based on their hypothesis that small crystalline clusters are indistinguishable from the melt, ref 1 postulates that $\gamma(D_0) = 0$ where $D_0 = 3h$ with h the interatomic distance. We draw attention to the fact that this is not compatible with the predicted *increase* of γ with diminishing size for materials with $f < 2\gamma_0$; a more consistent postulate might be that $\tilde{\gamma}$, not γ, vanishes at small D. We also note that the relative volume contraction 3ϵ at D_0 estimated from eq 1 with the parameters in Table 1 of ref 1 ranges from -0.045 (Pt) to -0.11 (Al), values that cast doubt on the validity of an analysis neglecting higher order elastic constants. What is more, in the spirit of the hypothesis of indistinguishability there appears to be a contradiction between the large density increase derived for small solid particles and the well-known trend that the density of metallic melts is *less* than that in the fcc solid, by typically 5% at the melting point.

Finally, it is noted that the size dependence of γ due to the mechanical relaxation is only one among several conceivable physical mechanisms that may contribute simultaneously and additively to a size dependency of the specific excess. Specif-

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ically, curvature terms and the excess due to linear elements of the microstructure (edges) may be important on top of the strain effect. The inclusion of these additional terms in the equation for $\gamma(D)$ could significantly affect the predicted value of f.

In view of these comments it is questionable whether the theoretical results for the solid−melt interface in ref 1 can be validated by the reported agreement with experimental data for the solid−gas interface.

References and Notes

(1) Jiang, Q.; Liang, L. H.; Zhao, Z. S. *J. Phys. Chem. B* **2001**, *105*, 6275.

(2) Weissmüller, J.; Cahn, J. W. *Acta Mater.* **1997**, *45*, 1899.