

Response to "Comment on 'Reversible work of formation of an embryo of a new phase within a uniform macroscopic mother phase'" [J. Chem. Phys. 111, 3769 (1999)]

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Kusaka correctly points out that his Eqs. (1) [Eq. (39) in Ref. 1] and (2) [Eq. (43) in Ref. 2] are equivalent. Hence, the statement in Ref. 2 that Nishioka and Kusaka¹ "arrived at a different expression for the work of embryo formation" is incorrect. Our misunderstanding stemmed from a failure to properly translate the notation of Ref. 1 into our own language. At the outset, however, we point out that nowhere in Ref. 2 is it stated that Nishioka and Kusaka's¹ result was wrong. Nevertheless, Kusaka's Comment contains several incorrect statements that we wish to clarify in this Reply.

Reference 1 applies exclusively to liquid clusters formed in a vapor. Because of the large difference in density between a liquid and a vapor, the authors of Ref. 1 assumed that the molecules in the interfacial region between the liquid cluster and the mother vapor can be regarded as belonging to the cluster. Furthermore, they assumed that the cluster establishes an internal equilibrium in a time scale much shorter than that required for it to exchange molecules with the surrounding vapor, and hence they regard the noncritical liquid cluster to be in partial equilibrium with the surrounding vapor, an equilibrium established under the *internal* constraint that the vapor and the cluster do not exchange molecules and each subsystem is in internal equilibrium. Clearly, however, time scales and diffusion are not thermodynamic considerations. In a true thermodynamic derivation, time can play no role.

This is the central point behind the introduction of *external* constraints in Ref. 2. The Gibbsian thermodynamics of interfaces applies to equilibrium situations exclusively. This equilibrium can be an unstable one (e.g., a liquid drop in contact with a vapor such that the vapor phase pressure equals the drop's vapor pressure), but it *is* an equilibrium. Because of this, matter is freely transferable between the droplet and the bulk vapor. An embryo that is not a critical nucleus is not in equilibrium with the surrounding metastable phase (e.g., a droplet that is surrounded by a vapor in which the pressure of the vapor does not equal the vapor pressure of the droplet). In this case, matter transfers *irreversibly* across the interface. Hence, in order to apply thermodynamic reasoning to this situation, we require the imposition of a constraint that prevents the irreversible transfer of matter between the bulk phase and the noncritical embryo. This is what we do in Ref. 2.

The extra-thermodynamic assumptions of Ref. 1 (rapid diffusion and equilibration, in addition to embryos that are much denser than the bulk) are only applicable to liquid droplets in a vapor. Clearly, then, the results of Ref. 1, and in particular the Comment's Eq. (1), would seem to apply only to liquid clusters in a mother vapor phase. In contrast, in Ref. 2, a thermodynamically consistent formalism is derived for calculating the reversible work needed to form a cluster (embryo) of a new phase within a uniform macroscopic mother phase. The formalism is based on the explicit introduction of a constraint in the form of an external field. The results of Ref. 2, including of course the comment's Eq. (2), are of general validity, regardless of whether the cluster is a liquid droplet in a vapor, a vapor bubble in a liquid, or a liquid droplet in a mother liquid of different composition. [Note that the explicit reference to "droplet" and "vapor" in Ref. 2 is for illustrative purposes only; the formalism is independent of the relative densities of the embryo and bulk phase.] The formalism in Ref. 2 makes no assumption about the difference in density between the embryo and the mother phase, nor about whether the diffusion of molecules in the cluster is sufficiently fast. This is all taken care of automatically through the imposition of the external field. In the limiting case in which the cluster has a much higher density than the mother phase, and rapid internal equilibrium is assumed, the physical conditions have been imposed that will result in internal equilibrium within the cluster without free exchange of mass between cluster and mother phase. This being precisely the effect of the external constraint introduced explicitly in Ref. 2, it is not surprising that the same expression is obtained for the reversible work of formation (although in Ref. 2 we failed to notice this equivalence, as the author rightly points out). But, with the method of Ref. 1, nothing can be said about vapor clusters in a liquid, for example. The method of Ref. 2 is therefore, unquestionably, more rigorous and general.

Kusaka questions the need, relevance, and appropriateness of introducing constraints. As explained above, and in greater detail in Ref. 2, without external constraints it is not possible to treat the energetics of noncritical (hence not in equilibrium) embryos thermodynamically. The extra-thermodynamic constraint invoked by Kusaka (rapid diffusion) clearly fails when the embryo is a vapor bubble in a

liquid. The approach of Ref. 2 applies unchanged. Furthermore, we point out that such constraints are routinely applied, for example, in computer simulations. This is exactly what one does, for instance, in umbrella-sampling Monte Carlo,^{3,4} where it is precisely the imposition of an external constraint via a biasing potential that allows the reversible formation of a critical nucleus. Hence, Kusaka's statement to the effect that constrained equilibria and the various thermodynamic properties associated with them are relevant if and only if the state approximates closely the actual state of the system is wrong. Nuclei in actual systems do not grow as a result of anything resembling constrained, umbrella-sampling simulations. Yet these simulations are routinely used to calculate free-energy barriers to nucleation.

Kusaka implies that the system becomes, in effect, internally constrained. However, what he misses is that the system cannot exchange work, much less reversible work, with its surroundings through the agency of an internal constraint. Thus any path, from the homogeneous metastable phase to the same phase containing a nucleus, cannot be made reversible without the aid of an external constraint capable of performing reversible work on the system, i.e., without the application of some field. Even with a constraint there can be many reversible paths connecting the initial homogeneous phase (e.g., a supercooled vapor), and the vapor containing a nucleus: this corresponds to paths defined by different constraints. Although along these paths the reversible work will differ, so too will the reversible heat interactions with the surroundings, so that the free-energy difference between the homogeneous metastable phase and that same phase with a nucleus will be independent of the path. This is a necessary requirement since the free energy is a function of state.

The existence of these different reversible paths is implicit in the design of thermodynamic potentials that can characterize the *equilibrium* state that includes the nucleus (i.e., in the absence of constraints). One such characterization involves variation of the Gibbs energy along an isothermal and isobaric path away from the equilibrium state. Such a variation is initially zero since the nucleus is in equilibrium. But, an isobaric and isothermal path can only be reversible, since temperature, pressure, and Gibbs energy are equilibrium concepts. The constraint is necessary to restore internal equilibrium (reversibility) away from the state of minimum Gibbs energy. There can, of course, be other reversible paths: in Ref. 2 we use the energy as a thermodynamic potential, and consider paths of constant entropy. Here again, entropy

and energy are equilibrium concepts. In applying these thermodynamic potentials, one is not required to specify the particular constraints that maintain the reversibility of the path during the variation, but their implicit existence must be assumed, and they cannot be "internal." This point is discussed in detail in Ref. 5.

Kusaka states that we discarded the condition that the dividing surface must be located at the surface of tension. As explained in Ref. 2, imposing the constraint of no mass exchange between cluster and vapor fixes the location of the mathematical surface separating cluster and bulk by the condition of vanishing compositional gradients within the embryo. One is therefore not free to choose the location of this surface to coincide with the surface of tension. The consequences of this are stated explicitly in Ref. 2 (clarification 6, p. 5502). It is stated there that the dividing surface is not in general located at the surface of tension, and the limiting case to which this additional degree of freedom applies is clearly identified to be that in which the cluster's radii of curvature are large with respect to molecular dimensions. The same clarification is made explicitly in the Abstract of Ref. 2. The authors of Ref. 1 do not acknowledge this explicitly, but of course this doesn't change the facts.

Kusaka states that the status of Eq. (5) is not entirely clear in Ref. 2. Equation (22) in Ref. 2 is in fact Kusaka's Eq. (5) [primed quantities in Ref. 2 denote the gradientless core of the embryo; superscript β denotes gradientless core and its hypothetical continuation to the mathematical surface separating embryo and mother phase; intensive properties are necessarily identical in these regions]. Furthermore, without Kusaka's Eq. (5), Eq. (27) in Ref. 2 does not follow from Eq. (26).

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