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Reply to the Comment by M. Iwamatsu

J. F. Lutsko

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Reply

Reply to the Comment by M. Iwamatsu

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Iwamatsu has written a comment [1] on my recent paper concerning bubble nucleation in a superheated fluid [2] in which he concludes that my analysis of a simple Density Functional Theory (DFT) model is mistaken due to mathematical errors. The point of the model was to analyze different methods of studying noncritical bubbles. In this response, I show that his analysis is incorrect and that the results given in ref. [2] stand without correction.

The problem concerns the nucleation of a vapor bubble in a superheated fluid. The part of my analysis questioned in ref. [1] is based on a simple toy model DFT in which the density profile of a bubble is spherically symmetric with constant density ρ_0 for radial coordinate $r < R$ and constant value ρ_∞ for $r > R$. It is therefore characterized by the three scalars ρ_0, ρ_∞, and R. This profile is combined with a simple square-gradient free energy model to arrive at an expression for the free energy in the grand canonical ensemble which is to say at constant temperature, T, and constant chemical potential, μ. This corresponds to the calculation of Uline and Corti (UC) [3] using a more realistic free energy model as well as my own calculations [2,4]. Then, it was shown that the resulting toy free energy function takes the form

$$\beta\Omega = \frac{4\pi}{3}R^3\left\{f(\rho_0)-\mu\rho_0\right\}+4\pi\gamma R^2\left(\rho_\infty-\rho_0\right)^2 + \left(V-\frac{4\pi}{3}R^3\right)\left(f(\rho_\infty)-\mu\rho_\infty\right), \tag{1}$$

where $\beta = 1/k_BT$ is the inverse temperature, $f(\rho)$ is the free energy per unit volume in the liquid state, γ is related to the surface tension [2], and V is the volume which is assumed to be very large (so as to approximate the thermodynamic limit). Metastable states are identified by minimizing this function with respect to the parameters ρ_0, ρ_∞, and R under conditions of fixed T and μ. The result of doing this is the identification of three states: the uniform liquid and gas (corresponding to $\rho_0 = \rho_\infty = \bar\rho$ with $\frac{d}{d\bar\rho}f(\bar\rho) \equiv f'(\bar\rho) = \mu$) and a nontrivial maximum corresponding to the critical nucleus.

To explore noncritical bubbles, UC proposed to minimize the free energy under the constraint that the total number of atoms with radius λ is some fixed number, N [3]. Given the assumed density profile, this can be expressed as an equation of the form $g(\rho_0,\rho_\infty,R;T,\mu,\lambda,N) = 0$, where the notation indicates that the quantities after the colon are parameters that are held fixed. A simple way to implement this is to introduce a Lagrange multiplier, α, and to minimize the Lagrangian function $\beta\Omega - \alpha g$ resulting in the three equations $0 = \frac{\partial\beta\Omega}{\partial x_i} - \alpha\frac{\partial g}{\partial x_i}$ for $x_i = R, \rho_0, \rho_\infty$ and the constraint equation $0 = g$. The explicit form of the Lagrangian is

$$\begin{aligned}\beta\Omega[\rho] - \alpha g_{\mathrm{UC}}([\rho],\Gamma) = &\\ &\frac{4\pi}{3}R^3\left\{f(\rho_0)-\mu\rho_0\right\}+4\pi\gamma R^2\left(\rho_\infty-\rho_0\right)^2\\ &+\left(V-\frac{4\pi}{3}R^3\right)\left(f(\rho_\infty)-\mu\rho_\infty\right)\\ &-\alpha\left\{\begin{array}{c}\left(\frac{4\pi}{3}\lambda^3\rho_0-N\right)\Theta(R-\lambda)\\ +\left(\frac{4\pi}{3}R^3\rho_0+\frac{4\pi}{3}\left(\lambda^3-R^3\right)\rho_\infty-N\right)\Theta(\lambda-R)\end{array}\right\}.\end{aligned} \tag{2}$$

Before proceeding, it is worthwhile to clarify one possible source of confusion. The constraint term involves step functions and one might worry that when differentiating with respect to the radius, these give rise to singularities. To show that this is not the case note that $(\partial/\partial R)\,\Theta(R-\lambda) = \delta(R-\lambda) = -(\partial/\partial R)\Theta(\lambda-R)$ and after a simple calculation one finds that the contribution

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of these terms is of the form $(R-\lambda)\delta(R-\lambda)$ which can be safely neglected.

The minimization of eq. (2) can be divided into two cases: the result assuming $R<\lambda$ and that assuming $R>\lambda$. In his comment on my paper, Iwamatsu claims that I have treated the case $R<\lambda$ incorrectly and hence, most of this response focusses on that case. Assuming, then, that $R<\lambda$, the Lagrangian must be differentiated with respect to the four parameters R,ρ_0,ρ_∞, and α and the result in each case set equal to zero. This gives, after dividing through by some constants,

$$\begin{aligned}
0 &= R^2\left\{f\left(\rho_0\right)-\mu\rho_0\right\}+2\gamma R\left(\rho_\infty-\rho_0\right)^2\\
&\quad -R^2\left(f\left(\rho_\infty\right)-\mu\rho_\infty\right)-\alpha R^2\left(\rho_0-\rho_\infty\right),\\
0 &= R^3\left\{f'\left(\rho_0\right)-\mu\right\}-6\gamma R^2\left(\rho_\infty-\rho_0\right)-\alpha R^3,\\
0 &= 6\gamma R^2\left(\rho_\infty-\rho_0\right)+\left(\frac{3}{4\pi}V-R^3\right)\left(f'\left(\rho_\infty\right)-\mu\right)\\
&\quad -\alpha\left(\lambda^3-R^3\right),\\
0 &= \frac{4\pi}{3}R^3\rho_0+\frac{4\pi}{3}\left(\lambda^3-R^3\right)\rho_\infty-N.
\end{aligned}\tag{3}$$

In ref. [1], Iwamatsu claims that I have neglected the terms proportional to α, but that is clearly not the case as they appear in all of the first three minimization equations. The fourth line is just the imposed constraint for the case $R<\lambda$.

It is easiest to begin with the third equation which may be written as

$$\mu=f'\left(\rho_\infty\right)+6\gamma\frac{R^2}{\left(\frac{3}{4\pi}V-R^3\right)}\left(\rho_\infty-\rho_0\right)-\alpha\frac{\left(\lambda^3-R^3\right)}{\left(\frac{3}{4\pi}V-R^3\right)}.\tag{4}$$

For fixed λ, and given the *a priori* assumption $R<\lambda$, the second term on the right is negligible in the large-volume (*i.e.*, thermodynamic) limit. The third term will also be negligible provided that $\alpha(\lambda^3-R^3)$ is bounded. Assuming this is true (an assumption that must be checked *a posteriori*) implies that $\mu=f'(\rho_\infty)$. Hence, the outer density, ρ_∞, is that of a bulk liquid or gas at the applied chemical potential. It is henceforth taken to be the density of the liquid, $\rho_\infty=\rho_l$, in order to describe bubble nucleation.

Next, the second line of eq. (3) is solved for α giving

$$\alpha=f'\left(\rho_0\right)-\mu-6\gamma R^{-1}\left(\rho_l-\rho_0\right),\tag{5}$$

and this is substituted into the first line of eq. (3) giving

$$\begin{aligned}
0 &= R^2\left\{f\left(\rho_0\right)-f\left(\rho_l\right)-f'\left(\rho_0\right)\left(\rho_0-\rho_l\right)\right\}\\
&\quad -4\gamma R\left(\rho_l-\rho_0\right)^2
\end{aligned}\tag{6}$$

or

$$R=\frac{4\gamma\left(\rho_l-\rho_0\right)^2}{f\left(\rho_0\right)-f\left(\rho_l\right)-f'\left(\rho_0\right)\left(\rho_0-\rho_l\right)}.\tag{7}$$

This is eq. (12) of ref. [2]. Contrary to the claims made by Iwamatsu in ref. [1], this was not obtained by *neglecting* the Lagrange multiplier α but, rather, by *solving* for the only value of α that extremizes the Lagrangian. Hence, Iwamatsu's criticism of this result is incorrect and the arguments given in ref. [2] stand without alteration.

The analysis is completed by invoking the fourth, so far unused, line of eq. (3) to get the inner density

$$\rho_0=\frac{3}{4\pi R^3}\left(N-\frac{4\pi}{3}\left(\lambda^3-R^3\right)\rho_l\right).\tag{8}$$

The fact that this density must be greater than zero implies that as λ becomes large, it must be the case that R remains close to λ or else the second term on the right could drive the density negative. However, $R<\lambda$ implies that $\rho_0<\frac{3}{4\pi R^3}N$ so that R being close to λ implies that ρ_0 tends to zero as λ increases. It is then easy to see that this is inconsistent with eq. (7) as discussed in detail in ref. [2]. It is also easy to show that $\alpha(\lambda^3-R^3)\sim\frac{\rho_0}{\rho_\infty}\ln\rho_0$ so that the assumption made earlier (that this combination of terms is well behaved) is shown to be true. The conclusion reached in ref. [2], that there is no solution to these equations in the large λ limit, is therefore confirmed.

For the case $R>\lambda$, Iwamatsu agrees with the mathematical result given in ref. [2], but claims that the pressure in the liquid surrounding the bubble should be negative, which would negate the contradiction in that case. However, this is clearly not correct as the density of the liquid is determined, as above, by minimizing the free energy functional and it is again found, in the large volume limit, to be that of the bulk liquid at chemical potential μ and this will certainly have positive pressure. The point again is that the various quantities are not *chosen* but, rather, are *determined* by the minimization of the assumed free energy functional under the applied constraint.

In conclusion, the calculations presented in ref. [2] have been confirmed and the criticism of Iwamatsu [1], that the Lagrange parameter α was neglected and that the equations were solved incorrectly, has been shown to be false. None of this is surprising as the results simply confirm what was observed by Uline and Corti [3] using a more complex, and realistic, DFT model. However, in the present case, it is clear that the underlying Classical Nucleation Theory model has no singularities or discontinuities and that the lack of solution of the minimization equations is solely a reflection of the artificial constraint that is introduced. In ref. [2], it was shown that such problems do not arise when another, equally plausible, constraint is used thus raising the question of the robustness of the constraint method as a description of nucleation.

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