COMMENT

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Comment

Comment on "Theoretical description of the nucleation of vapor bubbles in a superheated fluid" by Lutsko J. F.

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In a recent letter [1], Lutsko studied the bubble nucleation from a stretched fluid with negative pressure using several variants of the density functional theory (DFT). He analyzed a simple model and concluded that the apparent instability found previously by Uline and Corti (UC) [2] using DFT was merely an artifact of the constraint method [2,3] as the model predicts an unphysical negative critical radius. Unfortunately, he made several mathematical errors in [1] when he showed that this simple model combined with constraint method leads to an unphysical negative radius.

The constraint method realizes the idea of (N,λ)-cluster model based on the molecular theory of nucleation originally proposed by Weakliem and Reiss [4] in DFT. In contrast to the usual DFT based on the grand canonical ensemble, the constraints are imposed such that the system consists of N molecules and is enclosed within a spherical container of radius λ with physically reasonable boundary condition [3].

Lutsko started from essentially the classical nucleation theory (CNT) and used the free energy of bubble with radius R at the inverse temperature β:

$$\begin{aligned}&\beta\Omega\left[\rho\right]-\alpha g_{\mathrm{UC}}\left(\left[\rho\right],\Gamma\right)=\\&\quad\frac{4\pi}{3}R^3\left(f\left(\rho_0\right)-f\left(\rho_l\right)-\mu\left(\rho_0-\rho_l\right)\right)\\&\quad+4\pi\gamma R^2\left(\rho_0-\rho_l\right)^2-\alpha g_{\mathrm{UC}}\left(\left[\rho\right],\Gamma\right),\end{aligned}\tag{1}$$

where $\Omega[\rho]$ is the grand potential functional of the system with density distribution ρ and α is the Lagrange multiplier and g_{UC} is the constraint. $f(\rho)$ is the free energy per unit volume, μ is the chemical potential, γ is the surface tension of bubble, ρ_0 and ρ_l are the density of the vapor within the bubble and the surrounding liquid, respectively. Even though the definition of the grand potential Ω and the surface tension γ are different from the tradition, we follow the notation of Lutsko. Constraint g_{UC} used by UC is given by

$$\begin{aligned}&g_{\mathrm{UC}}\left(\left[\rho\right],\Gamma\right)=\\&\quad\begin{cases}+\left(\frac{4\pi}{3}\lambda^3\rho_0-N\right)\Theta\left(R-\lambda\right),\\+\left(\frac{4\pi}{3}R^3\rho_0+\frac{4\pi}{3}\left(\lambda^3-R^3\right)-N\right)\Theta\left(\lambda-R\right),\end{cases}\end{aligned}\tag{2}$$

where Γ represents a set of parameters such as the total number of atoms N in the bubble. $\Theta(x)$ is the usual step function and λ is the radius of sphere that contains the bubble. Equations (1) and (2) constitute eq. (1) of [1]. The first line of (2) represents the (N,λ)-bubble when the bubble with radius R that is larger than the container radius λ $(R>\lambda)$. The second line represents the case when $R<\lambda$.

Instead of solving (1) with unknown Lagrange multiplier α and adjusting α such that (2) is satisfied, Lutsko [1] solved (2) and (1) with $\alpha=0$ separately and determined the required chemical potential μ or the vapor density ρ_0. Now we consider the case when $0<R<\lambda$ (the second line of (2)). The condition $g_{\mathrm{UC}}=0$ gives

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

which determines the density ρ_0 from the given particle number N and bubble radius R. On the other hand, minimizing the above free energy $\beta\Omega\left[\rho\right]$ in (1) with respect to the bubble radius R gives the usual expression for the critical radius:

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

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Equations (3) and (4) constitute eq. (12) of [1]. However, the number 4 in the numerator should be replaced by 2 and the minus sign should be added to the original eq. (12) of [1]. Equation (3) can be rewritten using the pressure P defined by $-P = f - \mu\rho$ as

$$R = \frac{2\gamma\left(\rho_l - \rho_0\right)^2}{P\left(\rho_0\right) - P\left(\rho_l\right)}. \tag{5}$$

The radius R is always positive as the vapor phase is more stable than the liquid so that $f(\rho_0) - \mu\rho_0 < (\rho_l) - \mu\rho_l$ or as the liquid is stretched ($P(\rho_l) < P(\rho_0)$). The unknown chemical potential μ in (4) will be determined from the known density ρ_0 through $\mu = \partial f/\partial\rho = f'(\rho_0)$. Hence, we have

$$R = -\frac{2\gamma\left(\rho_l - \rho_0\right)^2}{f\left(\rho_0\right) - f\left(\rho_l\right) - f'\left(\rho_0\right)\left(\rho_0 - \rho_l\right)}, \tag{6}$$

which is precisely eq. (12) in [1] except that 4γ should be replaced by 2γ (that should be a typographical error) and the negative sign should be added. By expanding the free energy $f(\rho_0)$ when the density ρ_0 is small, we can derive eq. (13) of [1] but the minus sign is added. Therefore, the radius R is always positive even when $\rho_0 \to 0$.

Next, we consider the case of the bubble with radius R larger than radius λ ($0 < \lambda < R$). The condition $g_{\mathrm{UC}} = 0$ gives

$$\rho_0 = \frac{3}{4\pi\lambda^3}N. \tag{7}$$

In this case, the chemical potential μ is not the function of the bubble radius R. Again, maximizing the above free energy $\beta\Omega\ [\rho]$, with respect to the bubble radius R leads to (4). However, this critical radius R is not coupled to the particle number N through (7) as it is independent of R. Therefore, the chemical potential μ cannot be fixed by the particle number N, or the density ρ_0. Then, we have

$$\lim_{\rho_0 \to 0} = -\frac{2\gamma\left(\rho_l - \rho_0\right)^2}{-f\left(\rho_l\right) + \mu\rho_l} \simeq -\frac{2\gamma\rho_l^2}{\beta P\left(\rho_l\right)}, \tag{8}$$

which is eq. (15) of [1]. Equation (8) is unphysical because it predicts a negative radius if $P(\rho_l) > 0$. However, the liquid pressure $P(\rho_l)$ must be negative in (8) as it should be lower than the vapor pressure $P(\rho_0 \to 0) = 0$ in the stretched fluid. Again the sign of the critical radius R is always positive.

In conclusion, the negative radius R derived by Lutsko [1] is not due to the defect of constraint minimization method of DFT [2,3] or of the underling molecular theory of nucleation [4], but merely due to the mathematical error and the misinterpretation of the formula. Then the activated instability of bubble nucleation is in no way related to the mathematical defect of the constraint minimization method of DFT as Lutsko claimed [1] because the constraint method is not proved to give an unphysical result (negative critical radius). Rather, this instability is commonly expected when we use a (N, λ)-cluster model of Weakliem and Reiss [4] and its extension to DFT by constraint method, and is related to the spinodal-like instability of fluid confined within a cavity [5].

The issue of the instability of the growing nucleus should be discussed in a broader context not limited within the DFT as it cannot include the fluctuation properly [5]. Euler-Lagrange equation and its extension using nudged elastic band (NEB) method [1] can only trace the minimum free-energy path (MFEP) while the constraint minimization method [3] for (N, λ)-cluster model [4] is an attempt, though approximate, to include the fluctuation into the nucleation process. It is too hasty to negate the possibility of activated instability found by UC [2] from the calculation of MFEP [1] as the latter explores a limited portion of phase space and may not include fluctuation properly. Further attempts to merge these two streams are certainly necessary.

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