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Review

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Constrained lattice density functional theory and its applications on vapor–liquid nucleations

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Abstract Vapor–liquid phase transition occurs via a nucleation process, and depending on the role of foreign objects, nucleation can be either homogeneous or heterogeneous. In this review, we focus on the recently developed constrained lattice density functional theory (CLDFT) and its applications on vapor–liquid nucleation. We also review the recent theoretical advance on the stability of nanobubbles. Based on CLDFT, a pinning and supersaturation mechanism has proposed to interpret the surprising stability of surface nanobubbles. The mechanism can interpret most characteristics of nanobubbles. More importantly, the mechanism suggests that the critical nucleus can be stabilized under the condition of contact line pinning. Thus, CLDFT studies provide an alternative way to measure the critical nucleus that is difficult to measure experimentally in the bulk solution, through stabilizing it with surface roughness or heterogeneities.

Keywords Phase transition · Heterogeneous nucleation · Constrained lattice density functional theory · Nanobubbles

1 Introduction

In principle, liquid water would immediately transform into vapor above 100 °C and into ice below 0 °C under one atmospheric pressure. However, in reality, there exists liquid water at a temperature higher than 100 °C or lower than 0 °C. In fact, solid, liquid, or gas can persist in a metastable state when temperature or pressure exceeds the transition point [1]. The delayed phase transition is ascribed to the difficulty of forming small objects of the new phase [2]. According to the Gibbs' nucleation theory, first-order phase transition occurs via a nucleation process featured with the formation of small nucleus. If the nucleus exceeds a critical size, it grows further and induces the new phase, whereas the smaller one tends to decay and disappear finally. The nucleus in the critical size is called critical nucleus, and the corresponding free energy cost for its formation is the free energy barrier. Thus, nucleation corresponds to a thermally activated process to overcome the free energy barrier between the metastable and stable states.

In most situations, the nucleation process is the limiting step to control the whole rate of phase transition. It was thus of special significance in many scientific fields and industrial applications and was extensively studied in the past decades. Because of its small volume and short lifetime, the new nucleus is hardly observed in experiments directly, and as a result the experimental studies often rely on theoretical assumptions to analyze the size of critical nuclei and nucleation barriers. On the theoretical aspect, there are several typical methods that are used to explain the nucleation mechanism, including classical nucleation theory (CNT), computer simulation, and density functional theory (DFT).

On the basis of Gibbs' nucleation theory, Becker and Doring [3], Volmer and Weber [4], and Oxtoby et al. [5, 6] proposed and developed CNT. CNT estimates the free energy barrier to nucleation by treating the nucleus of the new phase as composed of a bulk core surrounded by an interface. In CNT, capillarity approximations have been used. It means that the microscopic clusters also have a surface tension just like macroscopic liquid drops or bubbles. By using vapor to liquid nucleation as an example, at

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constant temperature and chemical potential a nucleus is generated from a metastable gas phase, and the fluctuation of the free energy is given by

$$\Delta G = G - G_0 = \Omega - \Omega_0 = \Delta\Omega, \quad (1)$$

where G_0 and Ω_0 are Gibbs free energy and grand potential of the metastable gas phase, and G and Ω correspond to those in the presence of the nucleus. Based on CNT, we can obtain

$$\begin{aligned}\Delta\Omega &= \Omega - \Omega_0 \\ &= \left(-p_l V_l - p_v V_v + 4\pi R^2\gamma\right) - \left(-p_v V\right) \\ &= -(4\pi/3)R^3\Delta p + 4\pi R^2\gamma,\end{aligned} \quad (2)$$

in which

$$V_l = (4\pi/3)R^3, \quad (3)$$

$$V_v = V - V_l, \quad (4)$$

$$\Delta p = p_l - p_v, \quad (5)$$

where γ represents surface tension, and V_l, p_l and V_v, p_v are the volume and pressure of liquid and vapor, respectively. With $\frac{\partial\Delta\Omega}{\partial R} = 0$, the radius of the critical nucleus (R^*) and the free energy barrier of the nucleation ($\Delta G(R^*)$) can be obtained as

$$R^* = 2\gamma/\Delta p, \quad (6)$$

$$\Delta G(R^*) = \Delta\Omega(R^*) = (16\pi/3)\gamma^3/(\Delta p)^2. \quad (7)$$

When the radius of nucleus is smaller than R^*, the free energy decreases with the radius; otherwise, it decreases with the increase of radius. It means that only for the nucleus with a radius larger than the critical one the nucleus would grow spontaneously.

CNT plays an important role in explaining various nucleation results of first-order phase transition. For example, it succeeded in forecasting the supersaturation of gases in the past decades. However, because of its unrealistic assumptions embedded, CNT is questionable for a small cluster which has a site of 20–50 molecules. In such cases, both the obtained classical nucleation rate and the size of critical nucleus were proved to be incorrect [7–10], and the nucleation rate was found to be three orders of magnitude larger than that from CNT prediction [11]. Thus, new methods or theories are required to be developed for nucleation study.

Computer simulation serves as a powerful tool to study the microscopic process of nucleation [12, 13]. However, the probability for the formation of critical nucleus depends exponentially on the height of the energy barrier. When the nucleation energy barrier is of a number of $k_B T$ (where k_B is the Boltzmann constant and T is temperature) the formation of critical nucleus would become a rare event. Thus, it is difficult to observe nucleation events by direct computer simulation in most cases. Instead, special computer simulation techniques to sample rare events, including umbrella sampling techniques [14, 15] and the forward flux sampling method [15], should be applied. Those techniques are, however, often featured with increasing implementation difficulty and sometimes uncontrollable computer time. In general, the brute force approach that simply runs simulations for a sufficiently long time has limit use for the nucleation far from the spinodal decomposition, although sometimes it was employed via placing a preexisting spherical nucleus in the metastable phase to evaluate the critical nucleus [16, 17]. Alternatively, DFT can be used for vapor–liquid nucleation [18–23]. With the same question, DFT was designed for stable and metastable states, and its applications on unstable transition states, just like critical nucleus, were rather limited.

In this review, we give account of the recent development in computer simulation and DFT studies on the vapor–liquid nucleation. In particular, the primary goal of this article is to review the development of the constrained lattice density functional theory (CLDFT) and its applications on vapor–liquid nucleation and also to describe the recent advance on the stability of nanobubbles. It is beyond the scope of this review to touch upon other topics and other types of nucleation systems, such as crystal and polymer nucleation.

2 Constrained lattice density functional theory

Obviously, traditional DFT is limited and only suitable for stable and metastable state of system. For unstable transition state, just like nucleation process, this method breaks down. Therefore, CLDFT was proposed to obtain the nucleus morphology and nucleation barrier [24–27]. This method introduces an appropriate constraint into classical LDFT to achieve a transition state, and its validity has been proved by recent investigations [28, 29].

On the theoretical side, CLDFT has been developed to understand nucleation at a molecular level. Within the framework of classical lattice density functional theory [24], the grand potential can be expressed as

$$\begin{aligned}\Omega = k_B T \sum_i \left[\rho_i \ln\rho_i + (1-\rho_i)\ln(1-\rho_i)\right] \\ - \frac{\varepsilon_{ff}}{2}\sum_i\sum_a \rho_i\rho_{i+a} + \sum_i \rho_i(\varphi_i - \mu),\end{aligned} \quad (8)$$

where ρ_i is the local density at site i, and a is the vector from a site i to its nearest neighbor site. ε_{ff} is the interaction between fluid and fluid, and φ_i is the fluid–solid interaction exceeding the nearest neighbor of site i. μ is the given chemical potential. At a constant chemical potential, the