An analysis on heterogeneous bubble nucleation around a nanoparticle based on density functional approach

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ABSTRACT

Density functional analyses are performed to study bubble nucleation around a nanoparticle submerged in a supersaturated LJ/s fluid in this paper. Two heterogeneous nucleation modes, i.e. core-shell mode and spherical cap mode, are considered. The minimal free energy path (MFEP) of these two nucleation modes are obtained. Effects of particle wettability and supersaturation of the bulk liquid on heterogeneous nucleation are studied. It is found that the energy barrier of the spherical cap mode nucleation is lower than that of core-shell mode nucleation. However, the difference between energy barriers of the two heterogeneous nucleation modes approaches zero when the particle becomes strongly solvophobic. The disappearance of nucleation barrier is observed for strongly solvophobic particles at high supersaturation.

1. Introduction

Due to their special properties, nanofluids (where nanoparticles dispersing in a fluid) have received enormous attentions in the past two decades [1]. Solar vapor generation [2], where nanoparticles absorb electromagnetic energy and convert it into heat to generate vapor, is a promising application of nanofluids. Recently, some experiments [3–5] have been conducted to study conditions at which bubbles could be generated under laser irradiation. Many factors, such as temperature of the nanofluids, size and shape of the nanoparticle, and parameters of the incident laser, etc., have been found to affect the threshold of incident light for bubble nucleation. However, it was difficult to observe experimentally the shape of the nanobubble and how bubbles nucleated on a nanoparticle because of its nano size. It has been speculated that there are two possible nucleation modes, namely, spherical cap mode and core-shell mode for bubbles nucleate on a nanoparticle submerged in a fluid, as shown in Fig. 1. In the spherical cap case, the bubble appears as a spherical cap residing on the one portion of the particle and the vapor bubble is in axisymmetric form. In the core-shell case, the particle is wrapped by the vapor bubble in a spherical symmetric form. The latter mode is easier to model due to its symmetry.

Many theoretical analyses based on classical nucleation theory (CNT) for bubble nucleation or droplet nucleation on a particle have been performed [6–8]. In 1958, Fletcher [6] derived the energy barrier of heterogeneous droplet nucleation on a spherical particle, in which a spherical cap nucleation mode is assumed. Later in 1975, Cole [7] carried out a similar analysis for the bubble nucleation, in which effects of size and wettability of the curved surface on the nucleation energy barrier were studied. Recently, Qian and Ma [8] presented a rigorous thermodynamic formulation of Fletcher's model. In the frame of CNT [6–8], it has been concluded that core-shell mode nucleation has the same nucleation barrier with spherical cap mode only if the contact angle of particle θ is 180° (for bubble nucleation) or 0° (for droplet nucleation). For a particle with contact angle $0° < \theta < 180°$, the spherical cap mode has a lower nucleation barrier than core-shell mode. All of the above papers on CNT assumed that the temperature in the system is uniform, and therefore bulk liquid/vapor need to be supersaturated to ensure a finite nucleation barrier to make nucleation possible. A few attempts [9–14] have been made to study heterogeneous nucleation in a non-uniform temperature field. In particular, Hsu [9], Wu et al. [10], and Quan et al. [11] performed CNT analyses on heterogeneous nucleation by assuming a superheated layer with a linear temperature gradient adjacent to the heated wall. Due to this superheated layer, bubble nucleation would occur although the bulk liquid is at a saturated condition. It should be pointed out that CNT is based on a macroscopic approach in which it is assumed that (i) the Young-Laplace equation is valid, (ii) the liquid-vapor interface is sharp and (iii) properties of the vapor are uniform which possess the same values as in the bulk phase [15]. For nucleation at high supersaturation, where the size of the nucleus is small and comparable to the thickness of interface, these assumptions are questionable and the results from CNT may not be accurate [15,16].

Density functional theory (DFT), which is based on microscopic statistical mechanics, can overcome shortcomings of CNT. DFT has been

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Nomenclature

a	Helmholtz free energy per molecule (J/molecule)
b	radius ratio of particle to critical bubble
c	direct correlation function
d	distance between the center of the bubble and the center of the particle
f	nucleation barrier ratio
F	Helmholtz free energy (J)
h	Planck constant ($6.626\ 07 \times 10^{-34}$ J·s)
i	index
k	particle-fluid interaction strength parameter
k_B	Boltzmann constant ($1.380\ 65 \times 10^{-23}$ J/K)
m	cosine of contact angle
m_0	mass of single molecule (kg)
P	pressure (Pa)
r	distance (m)
r^*	dimensionless distance
r_c	truncated distance of LJ/s potential (m)
r_s	parameter in LJ/s potential (m)
$\mathbf{r}$	position vector (m)
$\mathbf{r}_b$	position of bubble center (m)
$\mathbf{r}_p$	position of particle center (m)
R	radius of bubble (m)
R_c	radius of critical bubble (m)
R_p	radius of particle (m)
s	parameter in LJ/s potential (m)
S^*	dimensionless supersaturation
T	temperature (K)
T^*	dimensionless temperature
u	interaction potential (J)
V_{ext}	external potential from particle (J/molecule)
x	coordinate (m)
y	coordinate (m)
z	coordinate (m)

Greek symbols

γ	surface tension (N/m)
Δn	reduction of the number of molecules (molecule)
ε	energy parameter in LJ/s potential (J)
Λ	thermal de Broglie wavelength (m)

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μ	chemical potential (J/molecule)
θ	contact angle (degree)
ρ	molecular number density (molecule/m³)
ρ^*	dimensionless molecular number density
$\bar{\rho}$	weighted molecular number density (molecular/m³)
$\rho(\mathbf{r})$	density distribution (molecule/m³)
$\rho_{pl}(\mathbf{r})$	density distribution without vapor generated (molecule/m³)
$\{\rho^i(\mathbf{r})\}$	density profile series along MFEP (molecule/m³)
σ	diameter parameter in LJ/s potential (m)
ω	weighted factor
Ω	grand potential (J)
Ω^*	dimensionless grand potential
Ψ	availability (J)

Subscripts and superscripts

att	attractive
axi	axisymmetric
c	critical
f	fluid
ff	fluid-fluid interaction
homo	homogeneous
l	liquid
p	particle
pf	particle-fluid interaction
pl	particle-liquid
rep	repulsive
sat	saturated
sph	spherically symmetric
spin	spinodal
v	vapor

Abbreviation

CNT	classical nucleation theory
DFT	density functional theory
FMSA	first-order mean spherical approximation
MFEP	minimal free energy path
MFMT	modified fundamental-measure theory
NEB	nudged elastic-band

widely used to study nucleation bubble and droplet at high supersaturation in recent years [15,17–19]. Most DFT bubble nucleation studies were carried out for homogeneous cases [15,18,19] or heterogeneous cases on a flat surface [17]. There are several papers on droplets nucleation on nanoparticles [16,20–24]. Padilla and Talanquer [16] calculated droplets nucleation on spherical particles by gradient

square approximation DFT, and reported that CNT overestimates nucleation barrier at high supersaturation. A hybrid thermodynamic/density-functional theory was proposed by Bykov and Zeng [21] to study the core-shell mode droplet nucleation on a particle. Liu et al. [23] investigated effects of particle size, shape and wettability on the critical nuclei shape and nucleation barrier of vapor-liquid nucleation by constrained lattice density functional theory (LDFT). It was found that the critical nucleus structure transforms from spherical cap to core-shell with the increase of particle wettability. The paper by Liu et al. [23] implies that the relation between the energy barriers of the two nucleation modes may change with particle's wettability. However, a quantitative comparison of the energy barrier for the two nucleation modes was not given. In addition, most previous studies focused mainly on the configuration of critical nucleus, and discussion on the minimum free energy path (MFEP) of nucleation is limited. The MFEP is believed to be the most probable route for nucleation [25] which can be described by a series of configurations from pre-critical states through the critical state to post-critical states. Since the MFEP gives information not only on the critical state but also sub- and super-critical nuclei, it would offer a better understanding of the nucleation process involved. It is known that the nucleation energy barrier could disappear under
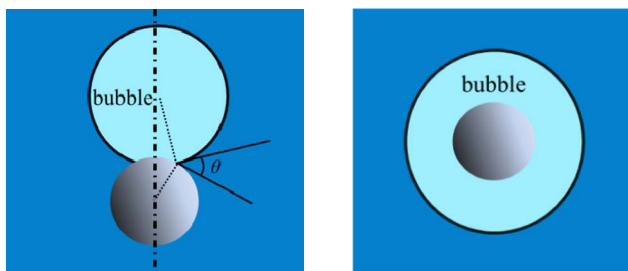
(a) Spherical cap mode   (b) Core-shell mode

Fig. 1. Two heterogeneous bubble nucleation modes.