

# Cluster growth mechanisms in Lennard-Jones fluids: A comparison between molecular dynamics and Brownian dynamics simulations



Jiyun Jung, Jumin Lee, Jun Soo Kim\*

Department of Chemistry and Nano Science, Ewha Womans University, Seoul 120-750, Republic of Korea

## ARTICLE INFO

### Article history:

Received 30 October 2014

In final form 7 January 2015

Available online 14 January 2015

### Keywords:

Lennard-Jones fluid

Cluster growth

Cluster coalescence

Ostwald ripening

Brownian dynamics simulation

Phase separation

## ABSTRACT

We present a simulation study on the mechanisms of a phase separation in dilute fluids of Lennard-Jones (LJ) particles as a model of self-interacting molecules. Molecular dynamics (MD) and Brownian dynamics (BD) simulations of the LJ fluids are employed to model the condensation of a liquid droplet in the vapor phase and the mesoscopic aggregation in the solution phase, respectively. With emphasis on the cluster growth at late times well beyond the nucleation stage, we find that the growth mechanisms can be qualitatively different: cluster diffusion and coalescence in the MD simulations and Ostwald ripening in the BD simulations. We also show that the rates of the cluster growth have distinct scaling behaviors during cluster growth. This work suggests that in the solution phase the random Brownian nature of the solute dynamics may lead to the Ostwald ripening that is qualitatively different from the cluster coalescence in the vapor phase.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

The assemblies of self-interacting molecules, including biological macromolecules, colloids, nano-particles, and amphiphiles, have been an important issue in many areas of science and technology [1–5]. For instance, the assembly of RNAs and proteins into nuclear structures is crucial in gene regulation and other cellular processes [3]. Also, the gelation of colloidal particles dramatically changes the material properties [4], and the self-assembly of synthetic amphiphiles into vesicles and micelles are important as molecular carriers for gene and drug delivery [5]. Therefore, extensive experimental investigations have been reported on the phase behavior and morphology of assembled structures. However, the growth mechanism for these assemblies remains less explored, probably due to the experimental difficulties in accessing these dynamic processes in sufficient spatial and temporal resolutions.

Molecular simulations have served as an alternative for providing molecular insights into many dynamic processes as well as equilibrium phenomena. The kinetics-controlled polymorphic change during the liquid–solid phase transition has been investigated by molecular simulations of Lennard-Jones (LJ) fluids [6,7]. The kinetics of the vapor–liquid phase separation and formation of liquid droplets in LJ fluids that are close to the two-phase boundary have also been intensively studied, particularly, in the

short-time regime with a view in understanding the nucleation kinetics [8–14]. However, until very recently [15–17], the kinetics of the droplet formation in the long-time regime has not been reported by molecular simulations.

Here, we investigate the phase separation and cluster growth of a one-component LJ fluid at late times, at a low density close to the coexistence boundary, by molecular dynamics (MD) and Brownian dynamics (BD) simulations. In the MD simulations of low-density LJ fluids, each LJ particle moves deterministically following Newton's equation of motion [18], modeling the particle dynamics in the vapor phase. On the other hand, the LJ particles in the BD simulations move stochastically by a random Brownian motion, mimicking that of large solutes that arises in the solution phase from the incessant collisions by the solvent molecules [19]. While MD simulations of LJ fluids have been employed in investigating the nucleation kinetics of liquid droplets in a vapor phase [8–14], BD simulations have been used to study the structural and rheological aspects of mesoscopic aggregation of colloidal particles in a solution phase [20–24]. Since it is not obvious whether two different particle dynamics described by MD and BD simulation methods would result in the same growth mechanism of phase-separated clusters, the comparison of the growth mechanisms by MD and BD simulations is our motivation in doing this work. In this work, we find that the cluster growth in BD simulations takes place by the Ostwald ripening [25] whereas the clusters in MD simulations grow via the cluster diffusion and coalescence upon cluster–cluster collision.

\* Corresponding author.

E-mail address: [jkim@ewha.ac.kr](mailto:jkim@ewha.ac.kr) (J.S. Kim).

Ostwald ripening has usually been known as the mechanism of domain growth in a solid–liquid binary mixture [25–28], in which large domains grow at the expense of smaller ones and without any direct domain–domain interaction. Smaller domains have a greater solubility than the larger ones and, thus, the dissolution of the smaller domains and the redeposition onto the larger ones lead to further growth of the larger ones. It has also been suggested that the Ostwald ripening is one of the main routes in degrading the emulsion stability by coarsening the emulsion droplets [29,30]. Although the diffusion and coalescence of liquid droplets in a vapor phase have been frequently reported in previous MD simulations [8,11,16,17], the observation of the Ostwald ripening from molecular simulations has been rarely reported [15]. Kraska performed MD simulations of a liquid–vapor phase separation of an argon gas and reported the direct observation of the Ostwald ripening in some cases out of several MD trials [15]. By observing the Ostwald ripening in BD simulations starting from an initially homogeneous distribution of self-interacting particles, our work further suggests that the molecular aggregation and cluster growth in a mesoscopic level may proceed via the Ostwald ripening.

The rest of this paper is organized as follows: we describe the simulation and analysis methods in Section 2. In Section 3, we present the simulation results based on the cluster analysis during the phase separation. Then, this work is concluded in Section 4.

## 2. Methods

### 2.1. Simulation model and methods

In this work, the kinetic mechanisms of phase separation and cluster growth are investigated by MD and BD simulations of one-component LJ fluids. The LJ fluid is a system that contains spherical particles interacting through a LJ potential,  $U(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ , where  $\epsilon$  is the attraction strength and  $\sigma$  corresponds to the particle diameter. All simulations in this work are performed using GROMACS v 4.5.4 [31], and the LJ potential is truncated and shifted at the cutoff distance of  $2.5\sigma$ .

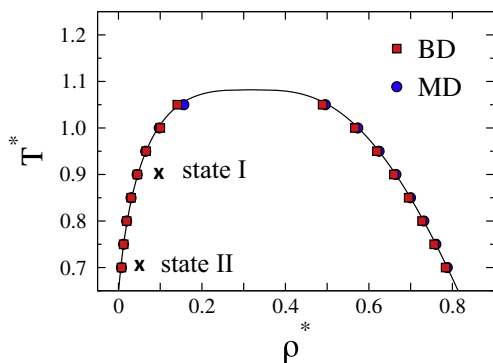
To determine the simulation conditions for the phase separation, the phase diagram in a range of simulation parameters is required. Although the phase diagram of LJ particles is well known [32–35], we also determine the phase diagram by using MD and BD simulations in order to confirm the validity of our simulation methods in this work. The phase diagram is presented in Fig. 1, in terms of the reduced temperature  $T^*$  and the reduced density

$\rho^*$ . Here, the reduced temperature is defined as  $T^* = k_B T / \epsilon$  and the reduced density is defined as  $\rho^* = \rho \sigma^3$ , where  $k_B$  is the Boltzmann constant,  $T$  is the temperature, and  $\rho$  is the number density of the LJ particles. Since the method to construct the phase diagram by MD simulations is well established [32–34] and the detailed description was provided in our previous work [35], we refer the readers to these earlier MD papers [33–35]. The phase diagram is determined by using BD simulations in the exact same way. The phase diagrams from the MD and BD simulations are in mutual agreement. The critical density and temperature are estimated as  $\rho_c^* = 0.316$  and  $T_c^* = 1.085$ , which is in good agreement with previous simulation results that were done by using the same LJ cutoff distance of  $2.5\sigma$ .

In Fig. 1, the phase separation into dense and dilute phases takes place for a system at any state point  $(\rho^*, T^*)$  within the area that is enclosed by the coexistence boundary. The phase separation of a system that is near the coexistence boundary occurs via a nucleation and growth mechanism whereas the phase separation of a system that is quenched deeply into the two-phase region occurs via the spontaneous phase separation, which is called the spinodal decomposition. In this work, we want to understand the mechanism of cluster growth that follows a nucleation process, and not that of a spontaneous decomposition. Therefore, simulations are performed for two state points of  $(\rho^*, T^*) = (0.096, 0.90)$  and  $(0.048, 0.70)$  that are near the coexistence boundary, as specified by the cross symbols and labeled as the states I and II in Fig. 1. Each system contains a randomly distributed configuration of 20,625 and 10,313 LJ particles for the state points I and II, respectively, in a simulation box of  $60\sigma \times 60\sigma \times 60\sigma$ , resulting in the reduced density  $\rho^* = 0.096$  and  $0.048$ . Although we further simulate the state point of  $(\rho^*, T^*) = (0.096, 0.70)$ , we do not present the result at that state point since the qualitative conclusions do not change compared with that at the state point of  $(\rho^*, T^*) = (0.048, 0.70)$ .

MD simulations are performed in the constant NVT ensemble. Ten, independent configurations of LJ particles are prepared and the simulations are performed for each configuration in order to ensure the validity of our conclusions. The system is evolved by integrating the Newton's equation of motion by using the leap-frog algorithm [18,31] at each time step of  $\Delta t = 0.01\tau_{MD}$ , where  $\tau_{MD}$  is the unit of MD simulation time that is defined as  $\tau_{MD} = \sigma\sqrt{m/\epsilon}$  and  $m$  is the particle mass. For an argon gas with  $m = 39.948$  atomic mass unit,  $\epsilon/k_B = 120$  K, and  $\sigma = 0.3405$  nm,  $\tau_{MD}$  is estimated 2.2 ps. Simulations are run for the time duration of  $10^5\tau_{MD}$ , in which the phase separation is completed. The temperature is controlled by using the v-rescale method with a time constant of 0.1 [36]. We confirm that the conclusions do not change when we perform another set of MD simulations that use a Nosé–Hoover thermostat method. At the given densities and temperatures, the LJ fluids separate into the liquid and vapor phases and the MD simulations provide an accurate way of modeling the condensation of a liquid droplet in the vapor phase.

BD simulations are performed by solving the position Langevin equation, as suggested by Ermak and McCammon [19], at each time step of  $\Delta t = 10^{-4}\tau_{BD}$ , where  $\tau_{BD}$  is the unit of BD simulation time and is defined as  $\tau_{BD} = \sigma^2/D$  and  $D$  is the diffusion coefficient of LJ particles. Since the diffusion coefficients of various molecules ranging from small organic molecules to proteins in aqueous solutions are about an order of  $10^{-9}$  to  $10^{-10}$   $\text{m}^2 \cdot \text{s}^{-1}$ ,  $\tau_{BD}$  is estimated 250 ps to 250 ns assuming the size of 0.5 nm to 5 nm. At each time step, LJ particles moves by an average distance of  $0.023\sigma$ . Ten independent simulations are run starting from different initial configurations for the time duration of  $5 \times 10^4\tau_{BD}$ , and we confirm that the phase separations are completed within this time duration. In the BD simulations, random Brownian motions of solute particles arising from the incessant collisions by solvent molecules are implicitly incorporated as random displacements with a Gaussian



**Fig. 1.** Phase diagrams of LJ particles obtained from MD (circles) and BD (squares) simulations. The solid line is a coexistence boundary fitted to circles, resulting in the critical density and temperature of  $\rho_c^* = 0.316$  and  $T_c^* = 1.085$ , respectively. Two cross symbols denote two state points simulated in this work, where the state I corresponds to  $(\rho^*, T^*) = (0.096, 0.90)$  and the state II corresponds to  $(0.048, 0.70)$ .

Download English Version:

<https://daneshyari.com/en/article/5373401>

Download Persian Version:

<https://daneshyari.com/article/5373401>

[Daneshyari.com](https://daneshyari.com)