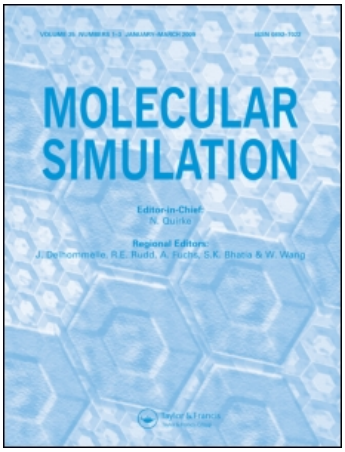

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Molecular Dynamics Simulations of Nucleation

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Molecular Dynamics Simulations of Nucleation

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Systems of many thousand Lennard–Jones (LJ) particles are quenched to a quasi-equilibrium vapor states where homogeneous and heterogeneous nucleations appear. The heterogeneous nucleation is obtained for systems confined in between planar surfaces. The effect of the surfaces on nucleation is established as well as the cluster distribution and the growth at onset of homogeneous and heterogeneous nucleation. The simulations demonstrate the surfaces "catalytic" effect on nucleation, caused by the enhanced super saturation near the surface due to the increased density. The effect of a carrier gas on homogeneous nucleation is determined for a mixture of LJ particles with inert carrier particles.

The kinetics of droplet growth is obtained from the flow of particles and sub-clusters to and from the droplets.

Keywords: Nucleation; Molecular dynamics; Simulation; Droplet growth

INTRODUCTION

The increased power of modern computers makes it possible to simulate nucleation in simple systems of many thousand particles in nanoseconds by molecular dynamics (MD) simulation [1,2]. The advantage of MD is that it serves as a kind of exact experiment which can be observed in great detail during the droplet formation and thus MD acts as an experiment by which theories and models can be tested. Traditionally, nucleation theories and models make use of mean field assumptions such as in the classical nucleation theory (CNT) [3]. The disadvantage or shortcoming of MD is that, although the dynamical behavior of hundred thousand particles in the time interval of 10–100 nanoseconds can give a realistic picture of nucleation, it is still a small number of particles and short time interval compared with a typical example of nucleation in nature. In addition, it is still not possible to make a more systematic investigation of nucleation with respect to temperature and degree of supersaturation, etc.

In an experimental determination of nucleation the quenched gas particles are often advanced to the nucleation chamber by a carrier gas [4]. This is also the case in a typical nucleation of, for example, water in the atmosphere, and this raises the question of whether the non-equilibrium nucleation phenomenon is affected by foreign particles. In fact it is well known that some salts act as seeds of (heterogeneous) nucleation for water. But typically the carrier gas is treated as an ideal gas in models like CNT. All such examples can be simulated by MD and with an insight which is much more detailed than any experiment can give. Detailed reports of homogeneous- and heterogeneous nucleation can be found in Refs. [1,2]. The present article will focus on MD simulation details concerning simulation of nucleation, and with the effect of carrier gas, i.e. nucleation of mixtures, and nucleation in system with competing phase transition.

THE MD SYSTEM

The present system consists of typical $N = 40,000$ particles and the temperature is achieved by the use of a thermostat. For computational details see Ref. [5]. The use of a thermostat, which acts instantaneously and on all particles, is a non-trivial constraint on the non-equilibrium system, since a real nucleation is associated with the release of the latent heat and associated with temperature gradients in the system. For these reasons we have also performed simulation of nucleations without a thermostat, and in the case of nucleations in a carrier gas

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the thermostat only affects the carrier gas, as in the same way the release of the latent heat by homogeneous nucleation of $H_2O(g)$ in nature is removed from the "system".

Today's standard computers can generate of the order a million timesteps for a system of $N = 40,000$ Lennard–Jones (LJ)-like particles during a day, which corresponds to 10 nanoseconds of the order. But the nature of nucleation, which is a chaotic-like phenomenon, requires an average of many individual nucleations, in order to determine the mean nucleation time, the growth, the fluxes, etc. This is, however, still practicable by use of clusters of computers. Another problem to overcome is the data collection. Most, if not all data collections have to be obtained "on the flight", i.e. directly during the time evolution in order not to drown in data. This is a non-trivial problem since many interesting data, like the distribution of clusters, can only be obtained from *correlations* between the N particles and a search, e.g. between $N \times N - 1$ particles can, without optimization, easily exceed the computer time it takes to generate the positions. Thus a program optimization is necessary in order to simulate nucleation, the cluster distribution and the fluxes, etc. For MD of particles with short-range interactions, as, e.g. (truncated) LJ particles a double sorting of particles makes it possible to run big numbers of particles on ordinary computers [6], and this sorting can also be used to obtain, e.g. the cluster distribution directly during the simulation without any significant increase in the computer time by the use of the already existing sorted list(s) of nearest neighbours [7].

THE ONSET OF NUCLEATION IN A SYSTEM WITH CARRIER GAS

Nucleation is a diffusive process where the number of particles in a cluster increases in an irregular way to a critical size where it eventually stabilizes and grows monotonically on average. This event or onset of nucleation appears in a chaotic way where only marginal changes result in the fact that this rare event is missed [1], and then the system can remain in its quasi-equilibrium state for another long period of time. Thus a precise determination of the nucleation time is very difficult and inconvenient for comparisons of different kinds of nucleation, e.g. between nucleation at a surface or nucleation in a system with a carrier gas. In these cases one would like to determine the impact of the surface and of the carrier gas on the nucleation by a comparison with the corresponding homogeneous nucleation. Instead of a direct comparison of nucleation times one can, however, compare the different quasi-equilibrium state in which the nucleation events appear.

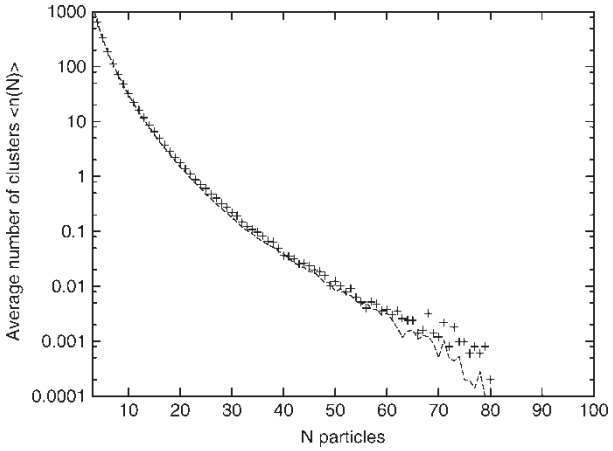

FIGURE 1 Mean number of clusters, $\langle n(N)\rangle$, in the super saturated vapor as a function of numbers of particles N in the clusters (as $ln\langle n(N)\rangle$). With full line are the mean numbers for a system of 40,000 LJ particles at $T = 0.741$ and obtained from ten million timesteps in the quasi-equilibrium state with super saturation $S = 2.17$ [1]. With points are the mean numbers (LJ-particles + carrier-gas particles) in the clusters, where 20,000 of the particles in the system are inert carrier particles, and with a supersaturation of the 20,000 LJ-particles $S = 2.29$.

The (partial) pressures, temperatures and distributions of clusters in these states can be determined very accurately from ensembles of many millions of timesteps. Figure 1 shows such a comparison of the cluster distributions in the quasi-equilibrium states before homogeneous nucleation with- and without a carrier gas. The homogeneous nucleation in a pure LJ system was determined [1] at the (reduced) temperature $T = 0.741$ and the pressure in the QE state was $P = 0.01793$. In the case of a carrier gas the $N = 40,000$ particles were divided into 20,000 LJ-particles and 20,000 truncated "LJ-particles" without attraction (i.e. the LJ-potential was truncated (and shifted) at the inter-particle distance $r = 2^{1/6}\sigma$). The 20,000 thermostated carrier particles without any attraction to any other particles in the system have no liquid state and act as perfect carrier-gas particles. The partial pressure and the temperature of the non-thermostated LJ-particles can be obtained very accurately. The system with carrier gas was scaled in size (cubic) until the two distributions were equal (Fig. 1), and where one noticed that both systems nucleated within millions of timesteps. In the CNT the nucleation is a function of the degree of super saturation $S \equiv P/P_{eq}$ where P is the pressure in the super saturated gas and P_{eq} is the pressure in (bulk) coexisting liquid and gas. The pure homogeneous nucleation was obtained for $S = 2.17$ and in the case of a carrier gas it nucleates at a partial pressure of the LJ-particles $P_{LJ} = 0.01793$ which corresponds to an increased super saturation $S = 2.29$. In the CNT one usually ignores the effect of the carrier gas on nucleation. The present simulations, however, only justify this approximation to some degree. It is also possible to answer to which

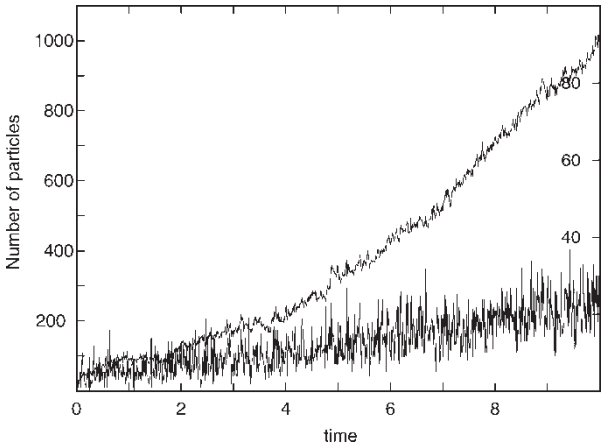

FIGURE 2 Total number of particles and carrier particles within the nucleus as a function of time (in *nanoseconds*) and at the onset of nucleation. The unit of the total number of particles is shown to the left and the unit for the number of the carrier particles, contained in the nucleus are given to the right on the figure.

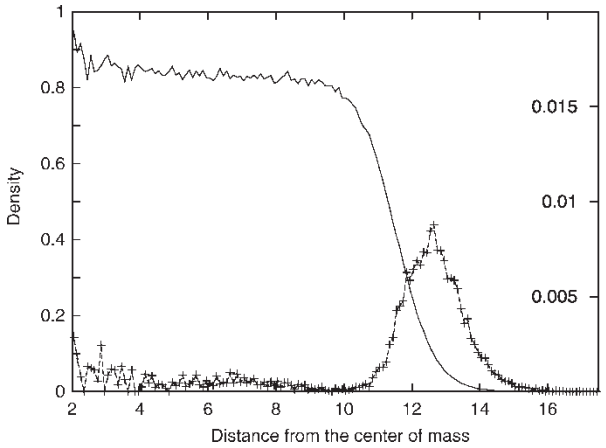

FIGURE 4 The corresponding density distributions at a later time when the nucleus has grown to $N \approx 7000$.

degree the carrier particles take part in the nucleation of the LJ-particles. The two subsystems are practically immiscible [8]; but despite this fact the successful nucleus apparently, at the onset of nucleation, contains a particle fraction of $x \approx 0.03$ carrier particles.

Figure 2 shows the total number within the successful nucleus as function of time and at the onset of nucleation and with the unit given to the left of the figure. Also shown is the number of carrier particles within the nucleus and with the unit given to the right. The increase of carrier particles "within the nucleus" as it grows, however, is entirely due to the increase of its "corona", as can be seen in Figs. 3 and 4. Figure 3 shows the density in the nucleus as a function of the distance from the center of mass is shown as a solid line, and unit given to the left vertical axis. The total density (LJ- and carrier particles) and the dashed line and + and with unit given on the right axis is for the carrier gas. Figure 3 is for a short time the interval at the onset of nucleation, whereas Fig. 4 is for a later time when the nucleus contains several thousand particles (≈ 7000). Another important aspect in nucleation is obtained by cooling the system down to a temperature below the freezing point. This is typical of what happens in nature and the question then arises as to how the nucleation appears, since the "hot" system passes from a liquid–gas supersaturated state down to a solid–gas supersaturated state. MD offers "an experimental" realization of this case by allowing the carrier gas to cool the system down below the triple-point temperature. Such an experiment shows that nucleation is to liquid

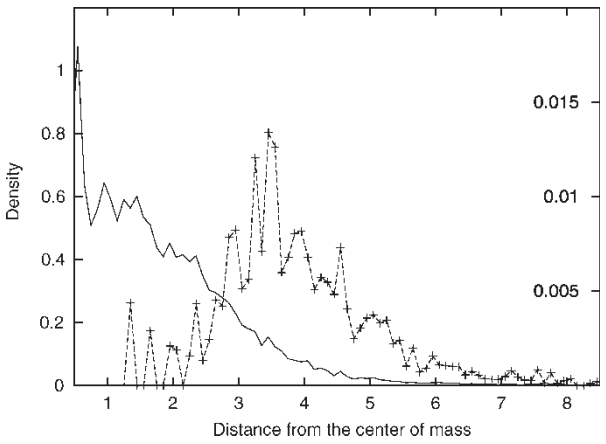

FIGURE 3 Particle density within the successful nucleus as a function of the distance from its center of mass and at onset of nucleation. The total particle density is shown with solid line and with the unit to the left in the figure. The density profile of the carrier gas, with the unit given to the right in the figure, given by dashed line and +, shows that the small amount of the carrier particles are mainly located near the surface of the nucleus.

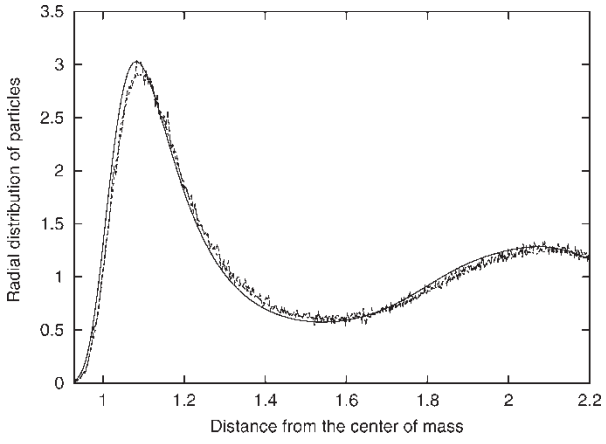

FIGURE 5 Two particle radial distribution as a function of their separation and where at least one of the particles is within a given distance from the center of mass of the supercooled nucleus. The distribution for particles near the center with at least one of the particles located in the shell-interval $[3\sigma, 4\sigma]$, with small dashes is g(r) with at least one of the particles in the shell interval $[9\sigma, 10\sigma]$, is shown by long dashes, etc, respectively. Also shown with solid line is the radial distribution function of a uniform supercooled liquid at $T = 0.741$ and $\rho = 0.85\sigma$.

droplets and that they grow as supercooled liquid-like nuclei at a temperature below the freezing point temperature, within the nuclei, before they eventually freeze. The supercooled liquid can remain for a very long time in such a state. Figure 5 shows the radial distribution of particles where (at least) one of the particles in the pair is within a given shell distance to the center of mass of the nucleus. Also shown (with full line) is the corresponding radial distribution function of a supercooled uniform liquid. As can be seen from this figure, the droplet has a distribution of pairs which is liquid-like near the center of mass as well as near the surface.

DISCUSSION

MD simulations are now at a stage where one can perform direct simulations of nucleation in systems of simple particles such as LJ particles. The MD simulations allow for a detailed insight in this non-equilibrium phenomena, which would be very difficult, if not impossible, to obtain from real experiments. Through such detailed information one can determine, for example, the impact of a solid surface on (heterogeneous) nucleation [2], and on a carrier gas, as demonstrated in this article.

References

[1] Toxvaerd, S. (2001) "Molecular-dynamics simulation of homogeneous nucleation in the vapor phase", *J. Chem. Phys.* **115**, 8913–8920.
[2] Toxvaerd, S. (2002) "Molecular-dynamics simulation of heterogeneous nucleation at a structure less solid surface", *J. Chem. Phys.*, In press.
[3] Oxtoby, D.W. (1992) "Homogeneous nucleation: theory and experiment", *J. Phys. C* **4**, 7627–7650.
[4] Grassmann, A. and Peters, F. (2000) "Homogenous nucleation rates of *n*-pentanol in nitrogen measured in a piston-expansion tube", *J. Chem. Phys.* **113**, 6774.
[5] Toxvaerd, S. (1991) "Algorithms for canonical molecular dynamics simulations", *Mol. Phys.* **72**, 159–168.
[6] Morales, J.J. and Toxvaerd, S. (1992) "The cell-neighbour table method in molecular dynamics simulation", *Comput. Phys. Commun.* **71**, 71–76.
[7] Laradji, M. Unpublished.
[8] Velasco, E. and Toxvaerd, S. (1995) "Phase stability lines and spinodals in binary immiscible mixtures", *Mol. Phys.* **86**, 845–855.