

Kinetic and Numerical Approaches to Nucleation and Growth during a first order Phase Transition

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ABSTRACT

Novel nanostructures are created during first order phase transitions. Embryos of the new phase are formed by aggregation of particles which diffuse in the local field. Two model independent approaches to nucleation are described : a dynamic density functional theory using the stochastic equation and a molecular dynamics simulation. A comparison makes it possible to confront the two approaches and to verify results for the local particle density, the mean square displacement and cluster dynamics on an atomic level. An analogy between the single particle paths and the conformation of a stiff polymer chain is demonstrated.

Keywords: molecular dynamics, density functional, nucleation, phase transition, clusters

1. INTRODUCTION

Nanoscale heterostructures are used in numerous applications. Original production strategies must be developed for the ongoing development of sensors, magnetoelectronic devices and smart materials. Nucleation phenomena have been the subject of extensive experimental work and provide a promising path for the preparation of new materials. In a first order phase transition, embryos of the emerging phase are formed by spontaneous aggregation of particles which diffuse in the local field. A typical situation occurs in vapour deposition. A vapour of metal atoms is brought rapidly to a point inside the coexistence zone and evolves from the initial single phase state by clustering of atoms into liquid droplets. The droplets grow with time or disappear, resulting in a broad distribution of cluster sizes. One of the current goals of material science is to find the means to control or even narrow the size distribution, allowing eventually for the preparation of well-defined quantum dot assemblies.

Experiment and theory have long been used to explore and understand nucleation and growth processes and more recently numerical simulation has

also been applied. Many fundamental questions still remain unclear. Some problems encountered are the large scales of size and time which need to be spanned, the nonequilibrium nature of the phenomena with resultant lack of a strong theoretical basis and the large number of physical parameters which can affect the behaviour. On the other hand, model independent methods can be used and two examples will be described in the following.

2. STOCHASTIC EQUATION

Dynamic density theory is a mesoscale approach which studies the temporal and spatial variation of the local particle density and, in particular, the dynamics of the particles inside the cluster and in the interfacial region between the high density cluster and the low density vapour. The dominating mechanism in cluster evolution is single particle diffusion in the presence of the self-consistent local chemical potential field. The instantaneous motion of the individual atoms is replaced by an average and the statistics of the single particle paths is considered. By weighting the probability for a given path to occur in a Gaussian distribution around the classical trajectory, the probability for a particle to be at a certain point in space with a given velocity can be expressed using a functional integral [1]. The method is well-known in polymer physics where the path of the particle is replaced by the conformation of the monomers of the chain [2]. «Stiff» polymer chains display a coupling of the position and the orientation of the individual monomers. In the analogous diffusion problem, a coupling between position and velocity occurs and the most probable paths are those for which the velocity is «persistent» in the initial direction. The dynamics of the system is strongly affected on the small scale of the evolving droplet. This is demonstrated by calculating the probability distribution for a spherical liquid cluster in a vapour. Details are given in [3] and the results are described in the following.

The density of atoms is found to be different in the vicinity of a growing or shrinking cluster relative to

the stationary critical cluster. The excess or lack of atoms on an average causes the cluster to evolve as atoms at the surface are incorporated or lost. Far inside the cluster, the atomic density and the resulting self-consistent field are constant and the particles diffuse freely with a mean square displacement proportional to the time t . The dynamics outside the cluster are affected by the radial field due to the presence of a local density gradient along the radius of the cluster. The density drops within the interfacial region from the liquid value at the surface to the low density of the vapour. Particles persist in radial paths, motions which rotate around the cluster tend to decay rapidly. The particles diffuse in the interfacial region with a mean square displacement in t^2 . The probability to find a particle, initially at the cluster surface, at a distance r from the center after a time t is approximated by a Gaussian $P(r,t)$ with

$$P(r,t) = \frac{1}{\sqrt{2\pi Dt}} \exp\left[-\frac{(r-\ell + \frac{2Dt(1+2\sigma/kTn_0\ell)}{\ell})^2}{4Dt}\right] \times \sum Y_{LM}(\vec{r}) \exp[-L(L+1)Dt/\ell^2]$$

D is the diffusion constant, ℓ the cluster radius, σ the surface energy and n_0 the vapour density. $Y_{LM}(\mathbf{r})$ are the spherical harmonics. Particles tend to be drawn toward the cluster surface. As the cluster radius increases, the constraints on the single atoms weaken and the cluster growth accelerates.

Growing clusters are found to be more probable than shrinking clusters. A critical size exists. Below the critical radius close to the stationary cluster size, the probability to observe a cluster decreases with size and it is more probable for a cluster to shrink. Above the critical size, the probabilities increase with size and the situation is reversed.

3. MOLECULAR DYNAMICS

A Molecular Dynamics (MD) simulation was performed for Lennard-Jones clusters consisting of particles interacting via the 12-6 Lennard-Jones potential $u(r) = D_0 \left[\left(\frac{a}{r} \right)^{12} - 2 \left(\frac{a}{r} \right)^6 \right]$ using the (P, T) -ensemble method described in [4,5]. Evolution of clusters was investigated at different reduced temperatures $T^* = T/D_0$. The equation of motion for the j th atom includes the interaction with the Berendsen thermostat:

$$\ddot{\mathbf{r}}_j = \frac{1}{2\tau_0^2} \sum_{i \neq j} \left[\left(\frac{a}{r_{ij}} \right)^{14} - \left(\frac{a}{r_{ij}} \right)^8 \right] (\mathbf{r}_j - \mathbf{r}_i) + \frac{1}{\tau_f} \left[\left(\frac{T^*}{T_0^*} \right)^{1/2} - 1 \right] \dot{\mathbf{r}}_j$$

where $\tau_0 = \left(a/2^{1/6} \right) \sqrt{M/24D_0}$ is the MD time scale; $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$; M , the atom mass; τ_f , the temperature relaxation time;

$$T_0^* = \frac{M}{3D_0(g-1)} \sum_{j=1}^g (\mathbf{v}_j - \mathbf{v}_{cm})^2,$$

the temperature of the cluster, g , the number of particles in the cluster, \mathbf{v}_{cm} , the velocity of cluster center of mass. Simulations were performed in a spherical cell, whose surface was a source of new atoms. The atoms that reach the surface from inside were removed from the system. The procedure of vapor atom generation at the surface of simulation cell was adjusted so that almost an ideal atomic gas with the Maxwell distribution over velocities and fixed temperature T_0^* and number density (pressure) was realized in the cell in absence of the cluster. The radius of the cell was equal to $16a$. At the beginning of the simulation run, a spherical cluster was placed in the center of the cell, and vapor atom generation begun. During the simulation, the evolution of the cluster was traced, and the physical quantities of interest were recorded and averaged.

The processes of atom condensation and evaporation took place on the surface of the cluster. According to the temperature and vapor pressure preassigned in each individual run, the cluster could grow or evaporate. In the first experiment, the density profiles of growing (circles in Fig. 1) and evaporating (triangles) clusters were investigated. The density ρ is expressed in units $a^3/\sqrt{2}$ as the function of cluster equimolar radius $r = (3g/4\pi\rho)^{1/3}$. The results shown in Fig. 1 were obtained at $T_0^* = 0.704$; at $g = 350$, the rate of cluster growth was $dg/dt = 0.154$, the rate of evaporation, $dg/dt = -0.239$ (the time is expressed in MD units). The difference in density profiles is clearly seen in Fig. 1, although the difference is rather small.

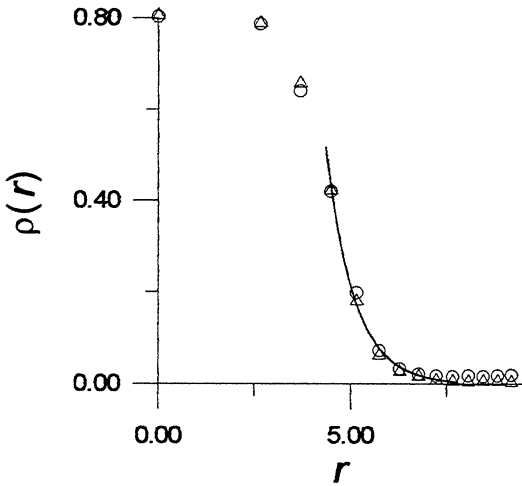


Fig. 1: Density profiles for growing (O) or evaporating (Δ) clusters

In the next series of numerical experiments, the diffusion of individual atoms inside the cluster was studied. A typical trajectory of the atom, which starts at the center of the cluster and ends on its surface, is shown in Fig. 2. The coordinates are given in units $a/2^{1/6}$. It is seen that a typical Brownian diffusion takes place in the neighborhood of cluster center; near the surface, the trajectory becomes much smoother.

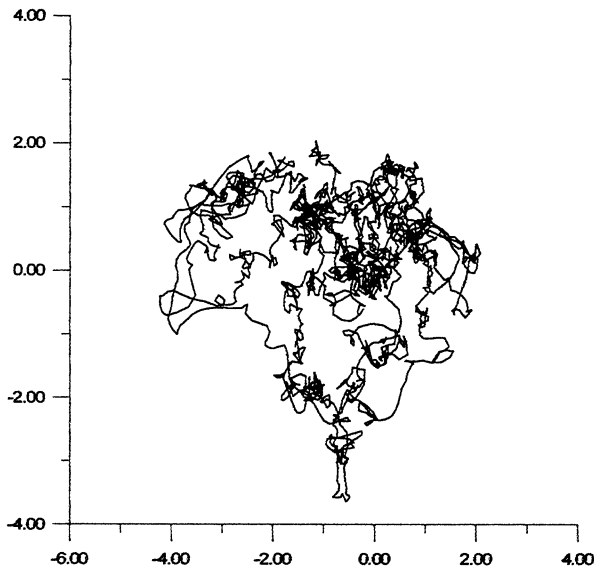


Fig. 2: Single particle path inside the cluster

The displacement and velocity correlation functions

$$\eta^2 = \frac{\langle (\vec{r}(t + \Delta t) - \vec{r}(t))(\vec{r}(\Delta t) - \vec{r}(0)) \rangle}{\langle (\vec{r}(\Delta t) - \vec{r}(0))^2 \rangle}$$

and

$$\eta^2 = \frac{\langle \vec{v}(t)\vec{v}(0) \rangle}{\langle \vec{v}(0)^2 \rangle}$$

are shown in Figs. 3 and 4.

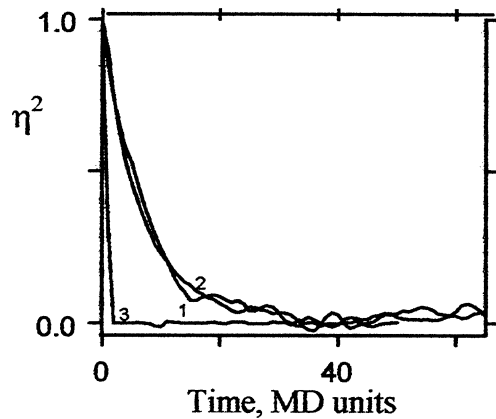


Fig.3: Displacement correlation outside the cluster (curves 1,2) and inside (curve 3)

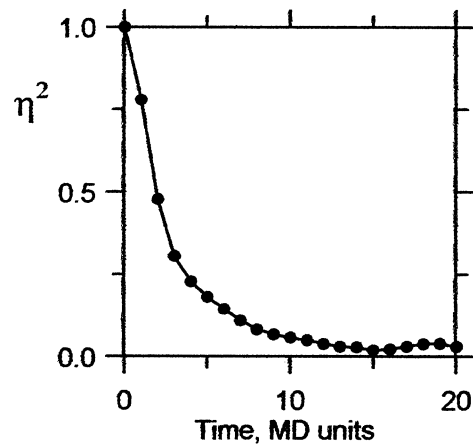


Fig. 4 : Velocity correlation inside the cluster.

These quantities were calculated for the trajectories of atoms starting within the spherical layer restricted by the inner and outer radii r_{\min} and r_{\max} , respectively.

The average square displacement

$$\rho^2 = \langle (\bar{r}(t) - \bar{r}(0))^2 \rangle,$$

is given in Fig. 5.

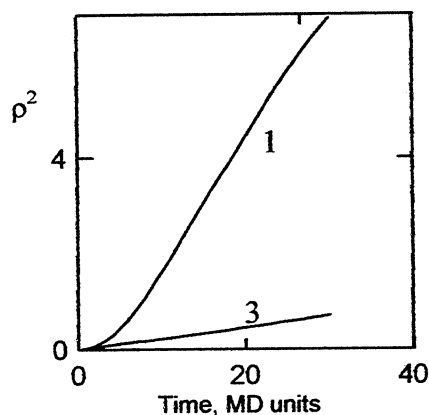


Fig. 5: The average square displacement

In Figs. 3 and 5, curves 1 and 3 correspond to the critical size cluster (which is in the state of unstable equilibrium with the vapor) with $g = 800$, 2 corresponds to $g = 100$. Curves 1 and 2 were calculated for the interfacial region with $r_{\min} = 7.2$, $r_{\max} = \infty$ (curves 1), and $r_{\min} = 4.0$, $r_{\max} = \infty$ (curves 2). Curves 3 correspond to cluster core: $r_{\min} = 0$, $r_{\max} = 3.5$. Curves 1 and 2 in Fig. 3 can be fitted to the dependence $\xi(t) = \exp(-t/\tau)$ with $\tau \approx 7.5$, which appears to be independent on cluster size. Curve 3 in Fig. 3 is close to $\xi(t) = \delta(t)$. In Fig. 5, curve 1 exhibits the quadratic behavior near $t = 0$; curve 3 is straight with the slope corresponding to the diffusion coefficient of $D = 0.02$ (in MD units) in the cluster core.

The velocity correlation function calculated for the same conditions as curve 1 in Fig. 3 is fitted by the function $\eta^2 = a \exp(-\tau/b) + c \exp(-\tau/d)$, where $a = 0.90383$, $b = 1.16178$, $c = 0.10644$, $d = 8.2496$. It is quite similar to the displacement correlation function. Note the existence of a nonzero scale of the correlation decay in the interfacial region. Figs. 3-5 are indicative of the intensification of transfer

processes due to the directed motion of particles, which resembles the turbulent diffusion. Therefore, the interfacial region cannot be described by the classical Fokker-Planck equation.

4. CONCLUSIONS

Nucleation theories are based on hypotheses and simplifications whose validity is still unclear and which are difficult to verify by experiment. A comparison of the analytical theory and the numerical simulation makes it possible to confront the results of the two approaches and to verify the conclusions on an atomic level. It can be concluded that

- particle paths tend to conserve the direction of the classical path and the persistent diffusion model leads to a valid description of the particle dynamics.
- growing and shrinking clusters can be distinguished by an excess or lack of particles in the interfacial region.
- a critical size exists. Below this size, it is more probable to observe that a cluster will shrink, above, growing clusters must dominate.
- the mean square displacement far inside the cluster is given by free diffusion but in the interfacial region a nonlinear time dependence occurs.

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REFERENCES

- [1] A. ten Bosch, *Physica A*262, 396, 1999
- [2] M. Doi, S.F. Edwards, «*The Theory of Polymer Dynamics*», Clarendon Press, 1986
- [3] A. ten Bosch, *J. Chem. Phys.* 110, 12251, 1999
- [4] D.I. Zhukhovitskii, *J. Chem. Phys.* 103, 9401, 1995
- [5] D.I. Zhukhovitskii, *J. Chem. Phys.* 110, 777, 1999