NUCLEATION IN FINITE SYSTEMS: THEORY AND COMPUTER SIMULATION*†

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Abstract. The free energy of formation of a droplet in a finite system containing N particles in a box of volume V at a temperature T is examined. For certain values of the supersaturation the free energy of formation has a maximum and a minimum. The maximum gives rise to a barrier to nucleation whereas the minimum corresponds to the formation of a stable droplet in equilibrium with vapor. Vapor imperfection and the radius dependence of the surface tension of the droplet are shown to affect the barrier and associated cluster distributions at equilibrium in significant ways. The theory is compared with computer simulation results using a Lennard-Jones fluid at a temperature of 84 K.

1. Introduction

The formation of droplets or grains from a homogeneous medium is an ubiquitous phenomenon. Despite its common occurrence, little is understood about the thermodynamics and kinetics of this process (for a review see Zettlemoyer, 1969, and Abraham, 1974). Under what thermodynamic conditions are the droplets formed? Do the droplets grow adiabatically or isothermally? When there is only a finite amount of matter available how are the thermodynamics and kinetics of these droplets modified?

With the advent of high-speed digital computers it is possible to study the thermodynamics and kinetics of well-defined model systems and to throw light on the relative importance of various mechanisms of nucleation. With this knowledge a theoretician can formulate the appropriate kinetic equations and study the nucleation phenomenon. Moreover, it should be possible to test the idea underlying classical nucleation theory.

In this paper we present a study of a model Lennard-Jones fluid using computer simulation. Starting from a homogeneous vapor phase, nucleation is observed in a finite system. The final equilibrium state consists of a microcluster in equilibrium with vapor. This final state can be predicted using the ideas of classical nucleation theory which are based on macroscopic thermodynamic concepts.

In the next section we present the thermodynamics of finite systems, and in Section 3 we present the computer simulation results.

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2. Thermodynamics of Nucleation in Finite Systems

In classical nucleation theory the Gibbs free energy of formation, ΔG_F, of a spherical droplet of radius r, from an infinite supersaturated gas maintained at a pressure P is found to be

$$\Delta G_F = 4\pi r^2 \gamma - \frac{4\pi r^3}{3} n_L kT \ln S, \tag{2.1}$$

where γ is the surface tension, n_L the bulk density of the liquid droplet, $S = P/P_\infty(T) > 1$ the supersaturation, $P_\infty(T)$ the equilibrium vapor pressure at temperature T, and k the Boltzmann constant. The basic assumptions that lead to Equation (2.1) are: (a) macroscopic thermodynamics can be applied to microclusters; (b) the free energy of a microcluster is separable into a bulk and surface term; (c) the microcluster is spherical; (d) the vapor is an ideal gas; (e) the supersaturation is maintained constant; and (f) the surface free energy, $4\pi r^2 \gamma$, of a microcluster can be computed using the surface tension of a macroscopic liquid with a planar surface.

The first term in Equation (2.1) represents the work required to create a spherical surface of surface area $4\pi r^2$ and the second term represents the lowering of the free energy due to the fact that the chemical potential of bulk liquid is lower than that of supersaturated vapor. As is well known, the interplay between surface and bulk terms in Equation (2.1) leads to a free energy maximum, denoted ΔG_F^* at a 'critical radius' $r^* = (2\gamma/n_L kT \ln S)$. This is the famous barrier to nucleation, and both ΔG_F^* and r^* play a very important role in nucleation theory.

There are many situations in which the total amount of material available for nucleation is fixed. In such situations the pressure of the system cannot be kept constant during the process of condensation. This requires a modification of classical nucleation theory and has been the subject of some recent investigations (Rao *et al.*, 1978; Vogelsberger, 1978). In this paper we consider a simple model and study the total free energy of the system using thermodynamic considerations. We show that in a finite system we can still identify a 'critical droplet size' and, in addition, there exists a 'stable' droplet whose size depends on N, V and T. If the total free energy of the droplet–vapor system is lower than the free energy of the homogeneous vapor phase, nucleation occurs in a finite system. These results are shown in Section 3 to be consistent with the computer simulation results of a Lennard-Jones fluid at low temperatures.

Let us consider a model fluid where N particles are contained in a volume V at a temperature $T < T_c$ (where T_c is the critical temperature) consisting of $N_l(r)$ molecules in a spherical liquid droplet (of radius r and number density n_l) in equilibrium with $N_g = N - N_l(r)$ gas molecules constrained to move in the free volume $V_f = V - V_l(r)$, where $V_l(r) = 4\pi(r + \sigma/2)^3/3$ is the excluded volume due to the droplet and σ is the diameter of the molecules. The vapor density is then

$$n_g = \frac{N - N_l(r)}{V - V_l(r)}, \tag{2.2}$$

and the vapor pressure is then given by the virial equation of state (Hill, 1960)

$$P(r) = n_g kT\left\{1 + \sum_{k=1}^{\infty} B_{k+1}(T) n_g^k\right\}, \tag{2.3}$$

where $B_{k+1}(T)$ is the $(k + 1)$th virial coefficient. In writing Equation (2.3) it is assumed that the volume V_f is sufficiently large that the cluster integrals are volume independent. As we shall see, these virial corrections can effect the barrier to nucleation as well as the stable equilibrium.

The chemical potential $\mu_g(n_g, T)$ per molecule is also given by the virial expansion (Hill, 1960)

$$\mu_g(n_g, T) = \mu_g^0 + kT\left\{\ln(n_g kT) + \sum_{k=1}^{\infty} \frac{k+1}{k} B_{k+1}(T) n_g^k\right\}, \tag{2.4}$$

and the Gibbs free energy of the gas is $G_g = N_g \mu_g(n_g, T)$. Clearly, in the foregoing, if there is no large cluster; that is, if the system is entirely uniform gas, $n_g \to N/V = \bar{n}$.

The total Gibbs free energy is made up of three parts:

$$G_{\text{total}} = G_{\text{gas}} + G_{\text{liquid}} + G_{\text{surface}},$$

where

$$G_{\text{gas}} = N_g \mu_g(n_g, T), \tag{2.5}$$

$$G_{\text{liquid}} = N_l \mu_l(n_l, T) \tag{2.6}$$

and

$$G_{\text{surface}} = 4\pi r^2 \gamma, \tag{2.7}$$

where n_g and n_l depend on the radius of the droplet; μ_l is the chemical potential of the liquid droplet with a density n_l at a temperature T, and γ is the surface tension. Usually the surface tension is assumed to vary with the size of the droplet (Tolman, 1949), as given by

$$\gamma(r) = \frac{\gamma_\infty}{1 + \dfrac{2\delta_\infty}{r}}, \tag{2.8}$$

where γ_∞ is the surface tension of an infinite flat sheet and δ_∞ is the curvature correction.

Note that

$$\mu_l(n_l, T) = \mu_l(n_l^\infty, T) + \frac{1}{n_l^\infty}\{P(r) - P_\infty(T)\}, \tag{2.9}$$

where $n_l^\infty(T)$ is the density of the macroscopic liquid under its vapor pressure and $P(r)$ is the vapor pressure in a system with a droplet of radius r (cf. Equation (2.3)). Equation (2.9) is found by integration of $(\partial\mu_l/\partial P) = 1/n_l$ over pressure from $P_\infty(T)$

to $P(r)$ with the assumption that the liquid is incompressible. In equilibrium we also have

$$\mu_l(n_l^\infty, T) = \mu_g(n_g^\infty, T); \tag{2.10}$$

hence we obtain

$$G(r) = \{N - N_l(r)\}\mu_g(n_g, T) + N_l(r)\mu_g(n_g^\infty) + \\ + (n_l^\infty)^{-1}N_l(r)\{P(r) - P_\infty(T)\} + 4\pi r^2\gamma. \tag{2.11}$$

In a finite system where N, V and T are constant, the Helmholtz free energy $F(r)$, not the Gibbs free energy, should be minimized to find the conditions for stable equilibrium. Thus, we use the foregoing equations to compute the Helmholtz free energy

$$F(r) = G(r) - p(r)V. \tag{2.12}$$

The Helmholtz free energy of formation of a droplet of radius r from an imperfect gas of density $\bar{n} = N/V$, at fixed N, V, T is thus

$$\Delta F_F(r) = G(r) - N\mu_g(\bar{n}, T) - \{p(r) - p(\bar{n}, T)\}V, \tag{2.13}$$

where $p(\bar{n}, T)$ and $\mu_g(\bar{n}, T)$ are the pressure and chemical potential of the initial supersaturated gas of density $\bar{n}$, to be computed from Equations (2.3) and (2.4).

To study how the total free energy varies with the size of the droplet let us consider a model system of N particles in a volume V interacting via a pairwise Lennard-Jones potential

$$\begin{aligned} \phi(r) &= v(r) - v(r_0) \qquad & r \leqslant r_0 = 2.5\sigma \\ &= 0 & r > r_0 \end{aligned} \tag{2.14}$$

with

$$v(r) = 4\varepsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\}, \tag{2.15}$$

where ε and σ are the Lennard-Jones parameters ($\varepsilon = 119.4$ K and $\sigma = 3.405$ Å for liquid argon). This system has been studied extensively (Rao and Levesque, 1976; Kalos *et al.*, 1977) and the parameters γ_∞, $P_\infty(T)$, etc., are known. To apply the theory outlined above we must determine the virial coefficients corresponding to this temperature. For simplicity we use only the second virial coefficient, and we neglect the radius dependence of the surface tension (cf. Equation (2.8)). The free energy of formation of the droplet, $\Delta F_F(r)$, given by Equation (2.13) is plotted for this system in Figure 1 for $V/N = 20$, where V is in units of σ^3. This corresponds to the initial supersaturation density ratio $\bar{n}/n_g^\infty \sim 14$. Curve (a) corresponds to Equation (2.13) with only the second virial coefficient corrections, whereas curve (b) corresponds to Equation (2.13) with no virial corrections (an ideal vapor). Both curves show a

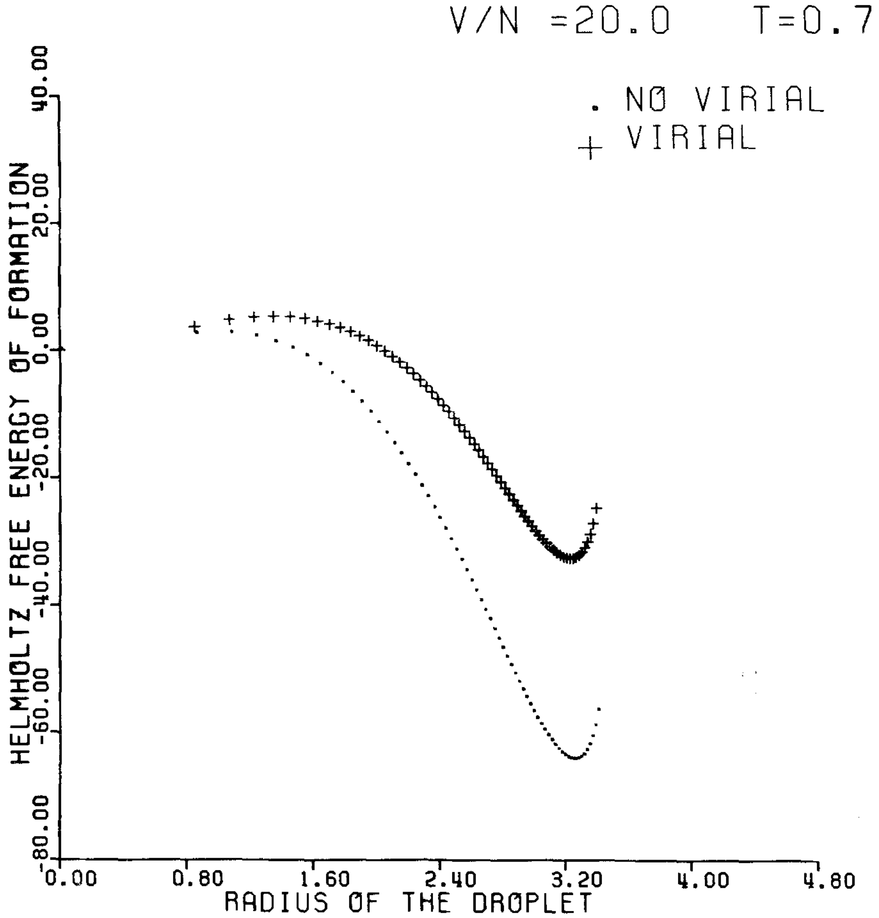

Fig. 1. $\Delta F(r)$, the Helmholtz free energy of formation of a droplet of radius r in a Lennard-Jones system for $V/N = 20$ (in units of σ^3) and a temperature of 84 K. The dots denote the free energy without the virial correction. The crosses denote the free energy with virial correction (cf. Equation (2.13)). Reduced units are used (energy in units of ε and distances are in units of σ).

maximum corresponding to a barrier to nucleation. This is similar to that observed in classical nucleation theory in that there is a barrier to droplet formation. However, there is, in addition, a minimum in the free energy of formation of the droplet. This corresponds to a 'stable cluster' which exists in equilibrium with the vapor. The stable cluster size predicted is 106 when virial correction is employed in Equation (2.13) and 110 when no virial correction is employed in Equation (2.13). Note that the effect of the virial correction is to increase the barrier to nucleation and also to destabilize the cluster. If this is correct, then the equilibrium cluster distribution of such a system must exhibit these features. The distribution of clusters will exhibit a bimodality; that is, there will be small clusters (monomers, dimers, etc.) in equilibrium with one large cluster whose size fluctuates. The mean size of the large cluster will be given by the position of the minimum in free energy of formation. In the next section we present computer simulation results supporting this picture.

3. Computer Simulation of Microclusters

Molecular dynamics (MD) and Monte Carlo (MC) simulations have been carried out on supersaturated systems (Abraham, 1974; Burton, 1977; Zurek and Schieve, 1978; Rao *et al.*, 1978). In MD an initial point in phase space is chosen, and the canonical equations of motion are solved on the computer (Berne, 1977). In this way a trajectory in phase space is generated. The bulk properties of the system are then found by time averaging the corresponding microscopic properties over the trajectory. Thus, MD allows the study of equilibrium and non-equilibrium properties; MC simulations, on the other hand, permit only the study of equilibrium properties. Here one generates a random walk in configuration space in such a way that the configurations are distributed according to the Boltzmann distribution, $e^{-\beta V(\mathbf{r}_1 \cdots \mathbf{r}_N)}$, where $V(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ is the total potential energy of the system corresponding to the configuration $(\mathbf{r}_1 \cdots \mathbf{r}_N)$. In this paper the MC method is used (Metropolis *et al.*, 1953). A system of 128 particles assumed to interact via the potential given in Equation (14) are placed in a periodically replicated box corresponding to an average density $\varrho\sigma^3 = 0.05$ (the same density used in Figure 1). The temperature of the system is set at 84 K. Starting from an initial random configuration (with a supersaturation $S \sim 14$), the MC method generates

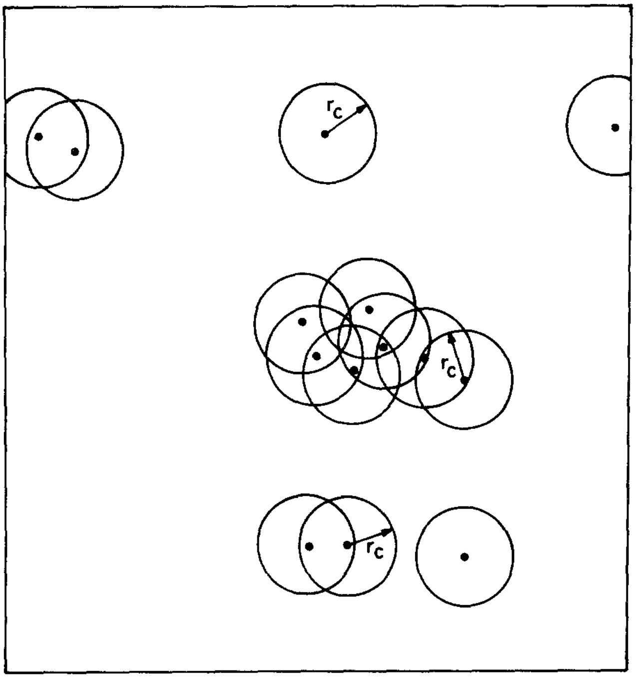

Fig. 2. A schematic illustrating the cluster definition in two dimensions.

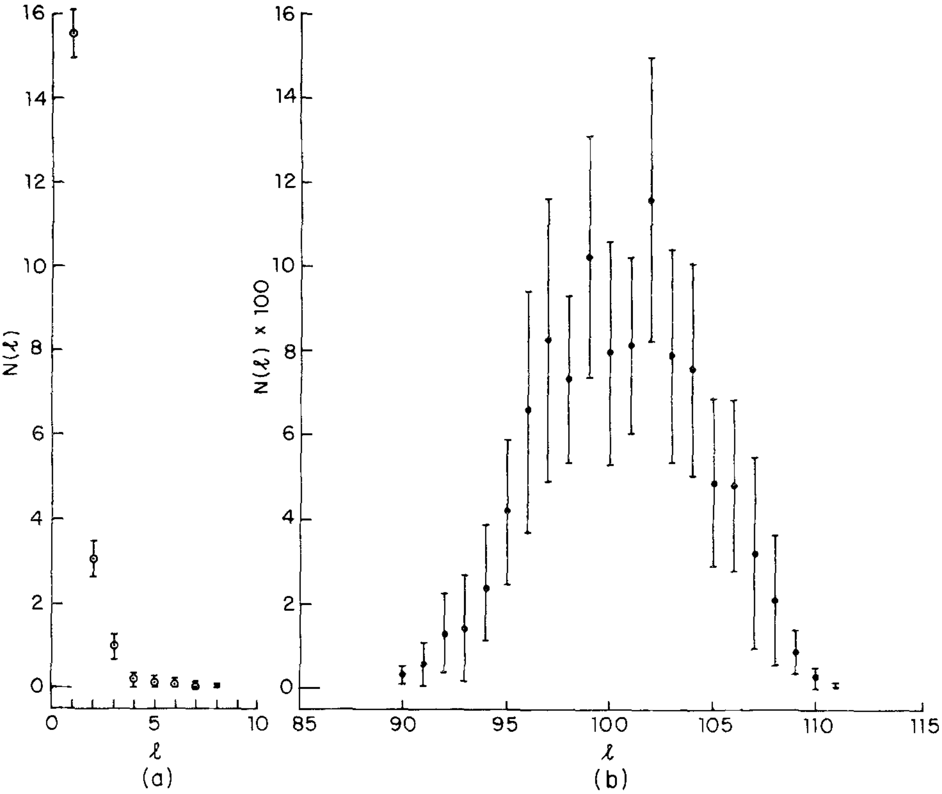

Fig. 3. (a) Distributions of monomers, dimers, etc., in the vapor phase obtained from a Monte Carlo simulation of a Lennard-Jones fluid at 84 K corresponding to an average density of $\varrho\sigma^3 = 0.05$ ($N = 128$). (b) Distribution of large clusters in the equilibrium two-phase system (droplet plus gas) from the computer simulation of the same system as in Figure 3(a).

new configuration during the simulation. After equilibrium has been established the cluster distribution is monitored. A cluster is defined as follows: *If any atom lies within a cut-off distance* r_c *of another particle, the two particles are said to belong to the same cluster.* A schematic illustration of this cluster definition in two dimensions is shown in Figure 2. The cut-off radius r_c is adjusted experimentally so that the observed cluster distributions are not sensitive to the cut-off.

An average cluster distribution is then obtained from an ensemble average over many configurations. If $N(l)$ is the number of clusters of size l, then we have

$$\sum_l lN(l) = N. \tag{3.1}$$

The probability of finding a cluster of size l is given by

$$p(l) = \frac{N(l)}{\sum_l N(l)}. \tag{3.2}$$

In Figure 3(a), $N(l)$ showing the distribution of monomers, dimers, etc., is presented from a simulation of half a million moves after equilibrium has been established. In

Figure 3(b) the distribution $N(l)$ of the large cluster sizes is plotted. It is clear that there are no clusters of sizes between 9 and 89 and the bimodal distribution predicted in the previous section is observed. The average size predicted by minimizing Equation (2.13) is 106 when virial correction is employed and 110 when no virial correction is employed, compared to the observed size 102. Thus the simple model discussed in the previous section predicts the correct features of the simulation. However, for a complete quantitative theory, other aspects have to be examined: for example, the role of the higher order virial corrections, and the curvature dependence of surface tension, etc.

4. Conclusions

We have shown that simple extension of the classical nucleation theory of finite systems seems to predict the computer simulation results rather well. Using molecular dynamics one can further study the effect of thermal accommodation in the process of nucleation, the kinetics of cluster formation and growth, etc. In future, computer results will play an essential role in understanding the detailed mechanism of nucleation, in identifying the most important processes, and in helping the theoretician set up kinetic models.

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