Molecular Theory of Homogeneous Nucleation Using a More Sophisticated Kinetic

Andrey L. Itkin[1]

Institute of High-Performance Computing and Databases, Russia

Abstract. We use a recent *non ad hoc* model of microcluster (MM) proposed by Prof. Howard Reiss and co-authors [1,2] together with a more rigorous theory of the nucleation kinetic equation. It is shown that this model satisfactory predicts at least qualitative features of nucleation and the nucleation rate is insensitive to the connectivity distance d_c.

INTRODUCTION

Recently a new *non ad hoc* model of microcluster (MM) has been proposed by Prof. Reiss and co-authors [1,2] based on generalization of n/v-Stillinger's model. This model has been selected on the basis that it offered the best chance for constructing a non ad hoc theory of the nucleation rate in the sense that predicted rates would be insensitive to the magnitudes of the parameters, especially the "connectivity distance". What further the authors of MM reasonably decided to do was just to guess how they could utilize this comprehensive cluster model to get a proof of MM. At the present time unless a precise experimental technique is available to measure the cluster distribution of size, and perhaps exclusive volume as well as to register clusters' isomers, apparently the only way to carry out such verification could be as follows. One has to choose some appropriate kinetic theory, introduce the MM cluster definition in this theory and then try to predict available experimental data on nucleation rate based on such a combined approach.

The authors of [1,2] chose a simplest and so far the most popular classical nucleation theory (CNT) as *it is* to derive a nucleation rate. Thus, they used MM mostly to derive an equilibrium distribution of the clusters and also to calculate an averaged formation rate constant of the cluster containing j molecules and having an arbitrary volume between minimum and maximum admissible ones. In other words, they did not do any modification of CNT to make it more appropriate to the considered situation when clusters in addition to the number of molecules have also some additional characteristics, in particular cluster's volume. In such a form all this approach faces two problems. The first one is that now an *ad hoc* element present in the *combined* model in sense that nobody made efforts to derive kinetic equations of nucleation for MM clusters. And consequently, nobody proved that the original form of CNT can be used to make a proof of MM. Second, it turned out that nucleation rate

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[1] Currrent position: IBES International, One World Trade Center, 18 fl., New York, NY 10048-1818, itkin@chem.ucla.edu

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obtained as a result of such amalgamation more or less depends on d_c - a connectivity distance which is not a fundamental parameter. The authors of MM argued qualitatively that the final expression obtained for the nucleation rate contains several terms depending on d_c that could compensate each other, but they did not show it explicitly. Finally they expressed a hope that an account of more sophisticated cross-sections describing an interaction between two molecules could improve the situation. And later they made some modifications of MM [3] and introduce reasonable arguments why the nucleation rate could be less sensitive to the magnitude of d_c but they did not overcome this inconsistency completely.

This report aims to show that this inconsistency is not a problem of MM, but rather a problem of CNT which can not be used, at least in its original form, to derive a nucleation rate of the MM clusters. For instance, MM is developed for a *finite* system with N molecules placed in volume V at temperature T while CNT has been originally developed for an *open* system. It means that CNT considers number density of monomers n_1 as an external parameter while for the finite system it has to be determined from the conservation condition that the total number of monomers (both free and inside all clusters) is constant.

At present more comprehensive theories have been elaborated, for instance [4], that are able to describe closed systems in a proper way and allow one to overcome many problems of CNT. In particular, refer to our recent paper [5] where such an approach is discussed in detail. Thus, the idea of this work is just to eliminate using CNT and instead put the MM definition of the cluster into the basis of a more comprehensive kinetic theory and then to *derive* appropriate macroscopic kinetic equations from more general ones.

THEORY

Certainly, this is a very cumbersome task because as mentioned either in [1] based on a general form of cluster's partition function inherent to the MM one can not expect to derive an equilibrium cluster distribution of sizes in an explicit form. Therefore, instead we use a simpler model of the microcristalline cluster, but what is important this model does not contradict MM and even more, it is a particular case of MM under some assumptions made. But for this model all integration can be explicitly carry out and all assumptions made within our formalism to derive proper macroscopic kinetic equations can be verified. Thus, there is an *ad hoc* element in our theory but i) in a considerably less degree than in CNT and ii) this ad hoc element has no relation at all to the MM because we use an original *non ad hoc* MM just within the frame of our approach.

We consider our system as a canonical ensemble while in [1,2] the authors considered only a constant pressure ensemble. Nevertheless, their approach can be adopted also in case of a canonical ensemble as, for instance, they showed for a simple model in [6]. Therefore we use an equilibrium distribution of the n/v-Stillinger cluster in a canonical ensemble N_{iv} which gives the equilibrium number of clusters having i molecules and volume between v and $v+dv$.

Usually in view of a great complexity the Helmholtz free energy A_{iv} of the n/v-Stillinger cluster is evaluated by means of MC simulation under a given potential function $U(\mathbf{r})$. Then, for instance in [2] the equilibrium distribution of clusters have been substituted to the usual CNT expression in order to get the nucleation rate. Therefore, this approach doesn't touch the kinetic scheme of nucleation, but mainly takes care about the form of the equilibrium distribution of clusters with allowance of the excluded volume. Even in this sense this work is not completed because for a *closed* system the equilibrium number of monomers is not a parameter of the theory known in advance. Instead, it has to be found from the conservative law which for a closed system can be written in the form $\Sigma_i \Sigma_v i N_{iv} = N$. As shown in [4] a general method to find equilibrium density of monomers is to substitute expression for N_i into this equation and then solve the obtained equation regarding N_1 further restoring a *real* equilibrium distribution of clusters substituting this found value of N_1 into the expression for N_{iv}.

Unfortunately, even if this procedure could be directly applied to N_{iv} represented in a general form, the final distribution can be obtained only numerically so further it is very difficult to analyze it within the frame of a certain nucleation theory. That is why in this work we give a simple example of the cluster for which this procedure can be fulfilled analytically. We consider clusters located in nodes of some structure. In other words, such a model is more appropriate to explore nucleation in liquids. Nevertheless, with the help of such an example we are able to examine the model [1] within the frame of a more comprehensive kinetic scheme and just to explore how much the "connectivity distance" influences the nucleation rate.

Equlibrium Density of Monomers

For such a system one can apply a well-known method called "normal mode approximation". Applying further a method of [4] one can obtain the equilibrium number density of monomers that in the thermodynamic limit at $N \Delta T$, $V \Delta T$, $n = const$ coincides with thermodynamic equilibrium number density $n_{1e}(T) = N_{1e}/V$.

Quasisteady Distribution of Clusters

The equilibrium distribution of clusters given in [1] with N_1 found above can be now utilized to determine the vapor nucleation rate in the considered system. However, at this point we have to attract already kinetics of nucleation while so far we operated only with thermodynamics. In this report we demonstrate that the initial equations that are a subject of consideration in CNT have to be somewhat modified in the case of the clusters characterizing not only by the number of molecules in the cluster but the cluster's volume as well. There is a clear analogy between this case and the case of clusters with nonequilibrium distribution of the internal energy described and explored in detail in [4] because in the cited literature the concentrations of the clusters also were considered as a function of two variables - the number of molecules and the average internal energy. Therefore, our method is based on the physical ideas and mathematical methods developed in that book. The solution is the following. Nonequilibrium quasisteady concentrations of clusters coincide with that given in [4] where the rate constant of clusters' formation K_j^+ depend upon the minimum possible volume v_0 which can have a cluster with j molecules inside. Same is true for the nucleation rate I. The main difference is that while v is a function of d_c, v_0 does not depend on d_c. Indeed, imagine that we increase d_c that is the *maximum* distance for the molecule which is a part of the cluster from the another one. But it does not influence the configuration with the *minimum* volume when the average distance between the centers of molecules in the cluster is about the diameter of the molecule, i.e. about a parameter of the potential.

DISCUSSION

How does our I depend upon d_c. The only terms that could pretend this role if we associate d_c with the parameter of the potential σ_0 are the frequencies of intercluster vibrations ω. It can be shown that in such a case $d_c \propto \sigma_0$ and $\omega \propto 1/d_c$. Therefore with the d_c increase the nucleation rate stops to depend on d_c at all. It is also possible to argue why it is not correct to associate d_c with the parameter of the potential. If this is true, the nucleation rate does not depend on d_c at all. Thus, in both cases the present approach gives much more satisfactory results that the theory which uses a very perspective MM model [1] combined with the CNT.

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