COMPUTATIONAL STUDY OF NON-STATIONARY CLUSTER SIZE DISTRIBUTION AND RATE OF NUCLEATION IN CASE OF PRE-EXISTING CLUSTERS

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The dynamics of a cluster-type system formed by constant total number of molecules, M, is studied when clusters change their sizes by nearest-size transitions (the Szilard model) with time-dependent boundary conditions and non-zero initial cluster size distribution. We compare these results to those reported previously [5], when non-stationary cluster size distribution was considered under the condition that only monomers are present in the system at the initial moment t=0, and describe the effect of arbitrary pre-existing clusters on the time evolution of the interacting clusters with different sizes, n. The average group size problem is also solved, and the process of relaxation in the system is studied.

1. Introduction

The process of nucleation can begin in the presence of clusters formed previously in the system, and one may expect that these pre-existing clusters could be a factor affecting the kinetics of nucleation [1–4]. For instance, the pre-existing clusters are able to grow spontaneously right after initial moment and will thus cause an increase in the non-stationary nucleation rate at the earliest stage of the process. Also, the pre-existing clusters can exert influence on the concentration of supernuclei in the system and the nucleation delay-time, so the effects of the pre-existing clusters on the rate of non-stationary nucleation [2], homogeneous nucleation of crystals in vitrified melts, and 2d and 3d heterogeneous nucleation of condensed phases on foreign and own substrates [1, 3] were widely studied.

In general, nucleation itself is the process of random generation of those nanoscopically small formations of the new phase that have the ability for irreversible overgrowth to macroscopic sizes. In case of the cluster approach, these nanoscopically small formations of the new phase are considered as a group of clusters of a certain number n of molecules (or atoms) in them. The cluster itself is regarded as separated from the old phase by a phase boundary and that makes it possible to say which of all M molecules in the system are still in the old phase and which of them already belong to the new phase [1]. In [5] a model based on the cluster theory was developed and used to simulate the dynamics of complex systems with different sizes M. In particular, the role of attachment probability was described by comparison between this model and other kinetic models of random growing networks and herding phenomena, and the size effect on the formation of clusters, under the condition that only monomers are present in the system at the initial moment, was elucidated. Therefore, it is worth looking further into the role of pre-existing random generated clusters with different

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sizes in the non-stationary cluster size distribution, and we present in this paper our findings relating to this intriguing matter.

2. The Model

In [5] a detailed description of the model is given. The following two basic assumptions, which allow a mathematical formalism to be developed, are indispensable in the framework of the Szilard model: 1) There exist clusters in the initial state which consist of different number n of molecules (or atoms) (n=1, 2, …); 2) Transformations of n-sized clusters into m-sized ones at time t occur with certain frequencies f_{nm} (n, m=1, 2, …). Denoting $f_n=f_{n,n+1}$, $f_{n-1}=f_{n-1,n}$, $g_n=f_{n,n-1}$, $g_{n+1}=f_{n+1,n}$, where $f_{nm}=0$ for $|n-m|>1$ and $f_{nm}\neq 0$ for $|n-m|=1$, the clusters will change size by nearest-size transitions. This is illustrated in Figure 1 in which the arrows symbolize the number of forward $n\rightarrow n+1$ and backward $n\rightarrow n-1$ transitions, and the quantity f_nZ_n, for example, gives the number of $n\rightarrow n+1$ transitions undergone by the n-sized clusters per unit time, divided by the number of interacting clusters $N(t)$, where $N(t)=\sum_{k=1}^{M} n_k(t)$, M is a number of molecules (or atoms) in a closed system ($M=const$), and $n_k(t)$ is number of groups (clusters) of size k at time t. The evolution of the process is sought to be described by the function $Z_n(t)$, which represents the solution of the kinetic master equation and characterizes the time-dependence of the concentration of clusters of size n:

$$\frac{dZ_n(t)}{dt} = f_{n-1}Z_{n-1}(t) - g_nZ_n(t) - f_nZ_n(t) + g_{n+1}Z_{n+1}(t) \quad (1)$$

By definition, $f_0=0$, $g_1=0$, $Z_{M+1}=0$, and $Z_n(t)$ and M are connected by the relation $N(t)\sum_{n=1}^{M} nZ_n(t) = M$, where the initial cluster size distribution $Z_n(0)$ is considered to be *a priori* known. Note that one time step in this formulation corresponds to one update in the numerical simulation under time-dependent $Z_1(t)\neq 0$ and $Z_M(t)\equiv 0$, and non-zero random initial cluster size distribution $Z_n(0)\neq 0$ (n=1, 2, 3, …, M-1). So equation (1) becomes a set of M-1 homogeneous ordinary linear differential equations of first order in the M-1 unknowns $Z_1(t)$, $Z_2(t)$, $Z_3(t)$, …, $Z_{M-1}(t)$. In this case the problem can be solved in a straightforward manner, and the solution $Z_n(t)$ given in [5] takes a new form without the stationary cluster size distribution part, and i=1, 2, …, M-1. The d_i is the only parameter affected by the non-zero initial cluster size distribution, $Z_n(0)\neq 0$, and now it is given by the following determinant of order M-1:

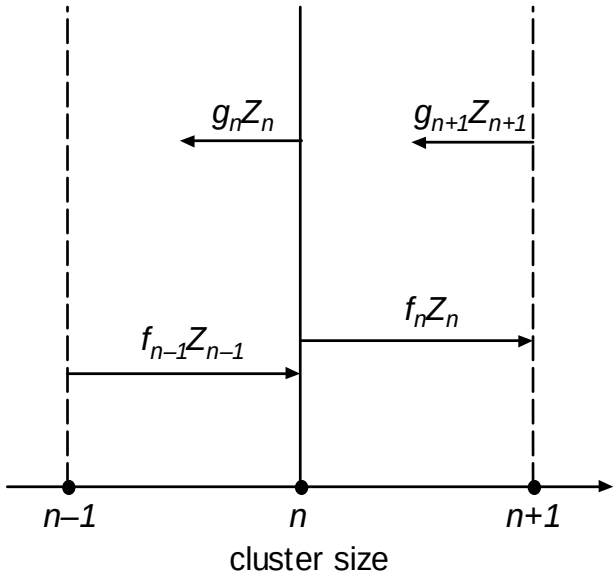

Fig.1. Schematic presentation of the possible changes in the size of a cluster of n molecules by nearest-size transitions. The quantity of n-sized clusters diminishes because of $n\rightarrow n-1$ and $n\rightarrow n+1$ transitions, and increases due to $n-1\rightarrow n$ and $n+1\rightarrow n$ transitions, and these processes are represented by arrows leaving size n and those ending at size n, respectively.

$$d_i = \begin{vmatrix} a_{11} & a_{12} & a_{13} & \cdots & a_{1,i-1} & Z_1(0) & \cdots & a_{1,M-1} \\ a_{21} & a_{22} & a_{23} & \cdots & a_{2,i-1} & Z_2(0) & \cdots & a_{2,M-1} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ a_{M-1,1} & a_{M-1,2} & a_{M-1,3} & \cdots & a_{M-1,i-1} & Z_{M-1}(0) & \cdots & a_{M-1,M-1} \end{vmatrix}, \qquad (2)$$

where a_{ni} are the same constants described in [5] with the help of transition frequencies f_n and g_n.

We can now determine the non-stationary rate $J(t)$ of nucleation at pre-existing clusters in the system. For n=1, 2, …, M-1

$$J(t) = \sum_{i=1}^{M-1} (d_i / d')(f_n a_{n,i} - g_{n+1} a_{n+1,i}) \exp(-\lambda_i t), \qquad (3)$$

where λ_i>0 is the ith eigenvalue, i.e. the ith root of the characteristic equation [5], and d' is a determinant of order M-1:

$$d' = \begin{vmatrix} a_{11} & a_{12} & a_{13} & \cdots & a_{1,i-1} & a_{1,i} & \cdots & a_{1,M-1} \\ a_{21} & a_{22} & a_{23} & \cdots & a_{2,i-1} & a_{2,i} & \cdots & a_{2,M-1} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ a_{M-1,1} & a_{M-1,2} & a_{M-1,3} & \cdots & a_{M-1,i-1} & a_{M-1,i} & \cdots & a_{M-1,M-1} \end{vmatrix}. \qquad (4)$$

For M>5 we must resort to numerical methods for solving the problem, because the exact analytical solution can be found only for $M \leq 5$.

3. Results and Discussion

Time evolution of the interacting n-sized clusters was numerically simulated for M=7 and g_i/f_i ={0.229, 1.458, 2.466, 2.835, 0.686}, i=2, 3, …, 6, and the results for n=2, 3, …, 6 in both cases of arbitrary pre-existing clusters (solid curves) and when only monomers are present in the system at the initial moment t=0 (broken curves) are shown in Figure 2.

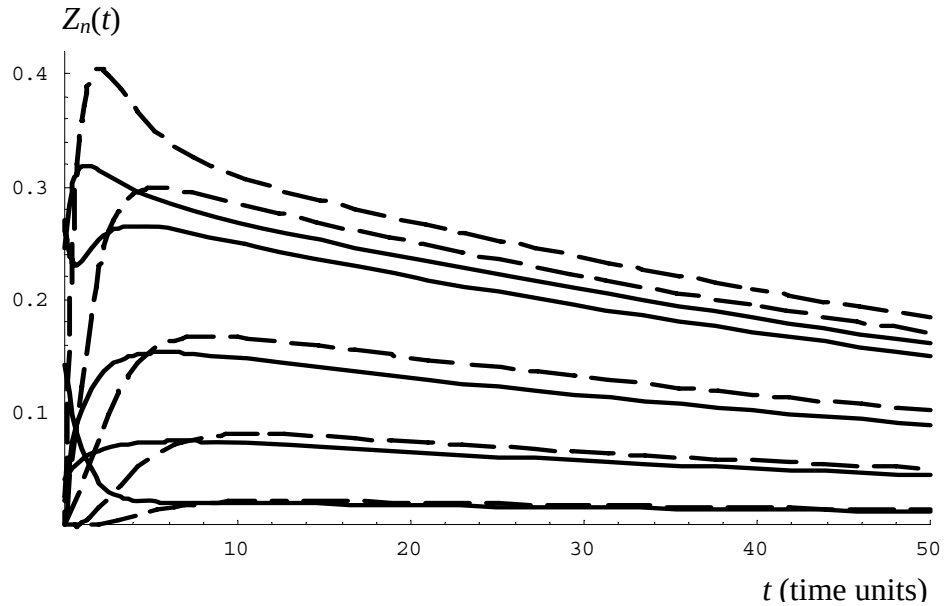

Fig.2. Time dependences of the concentration of clusters of size n in case of arbitrary pre-existing clusters (solid curves) and when only monomers are present in the system at the initial moment (broken curves) for M=7 (n=2, 3, 4, 5 and 6, from top to bottom).

We can conclude that the impact of pre-existing random generated clusters with different sizes n=1, 2, …, 6 on the non-stationary cluster size distribution in the short time limit depends on the size of clusters, and it is stronger for smaller groups. For large t the effect vanishes, and this is expected since the pre-existing clusters cannot affect the cluster distribution at equilibrium. They can only shorten the time needed for the establishment of the final distribution, and this fact can be clearly seen on the figure, regardless of the size n of clusters. Time dependence of the average group sizes, $M/N(t)$, represented in Figure 3 for both types of initial conditions by solid and broken curves respectively, also indicates that the system relaxes towards equilibrium faster in case of pre-existing random generated clusters. The sum $\sum_n nZ_n(t)$ was calculated between the limits 2 and M-1. In particular, it is important to note that these results give us more flexibility in choosing initial conditions, especially in case of evolution of large groups in the time limit $t\to\infty$, i.e. for late stages of cluster formation, because the accuracy of analytical solutions will not be affected since the difference between particular results obtained by applying different initial conditions is insignificant.

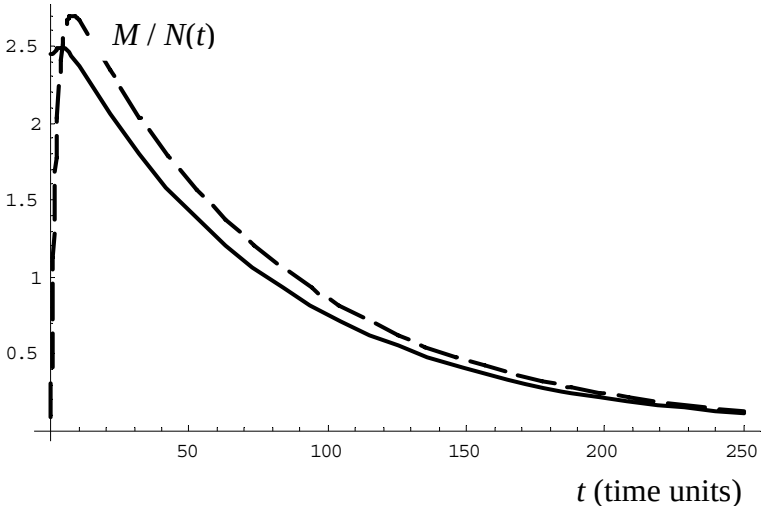

Fig.3. Time dependences of the average group sizes for M=7. Solid curve represents the result in case of pre-existing random generated clusters with different sizes n=1, 2, … 6, and broken curve that for only $Z_1(0)\neq 0$.

In this paper the non-stationary cluster size distribution in a network of agents (i.e. atoms or molecules) which evolves randomly has been studied at early and late stages of clusters formation, when they are expected to grow and decay mainly by gaining and losing monomers, because a relatively low cluster concentration at the early stage and an immobile stable structure at the late stage would require a single-agent mechanism of cluster formation. The advanced stage could be characterized additionally by merge of clusters of various sizes into a new bigger one (coagulation effect), and the contacts between them begin to have an increasingly important role in the size changes. So the more specific features, such as new agents entering the system (open structure), preferential attachment, coagulation effect etc, have been applying to the system to study both random and preferential dynamics of cluster-structures.

References

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