THE KINETICS OF PHASE TRANSITIONS: II. THE ROLE OF INTERFACE BETWEEN CLUSTERS

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The present developments in the physics of complex systems, in particular, the structural relaxation of supercooled liquids and glasses, are discussed by using a stochastic cluster-based model. We are able to depict the impact of the interface between the nucleus considered as a cluster of a certain number of molecules and the liquid phase for the enhancement of the overall nucleation process. It is also shown that even a relatively simple stochastic model, which appears phenomenological if it is not agent-based, can describe precisely the outcomes from multiple agent-based simulation runs where probabilistic insight is lacking and which should be long enough to equilibrate the states of large systems.

1. Introduction

Clustering is often described by Ewens sampling formula, which admits an interpretation in terms of rational versus herding behavior [1]. An alternative model was inspired from Simon's approaches to the problem. It differs from the Ewens model both in destruction and in creation. In particular, the probability of herding does not depend on the size of the herd; this assumption destroys the exchangeability of the random partitions and forbids an analytical solution [2]. The herding models proposed by Rodgers et al. [3−5] incorporate either coagulation and fragmentation, attachment and fragmentation, growth and addition or growth and coagulation of groups of agents at each time step. We have also introduced an alternative kinetic model based on the cluster concept [6]. In terms of clusters, growth/removal is the process in which a new cluster or a free agent is introduced/removed to/from the system. Fragmentation can be defined as a process in which a cluster breaks up into isolated agents. Coagulation takes place when two clusters join making a single one. Addition can be described as a special type of coagulation in which a free agent already in the system is added at random to another cluster. Attachment is the process in which new incoming agents attach themselves to an existing cluster, and this allows both the system and the clusters to grow in size. Only restricted combinations of these ingredients cause the models to differ.

One aim of this paper is to get new insights into microscopic explanations of stochastic models, which may be compared with the agent-based computational models, and to bridge the gap between agent-based models (ABM) and stochastic processes. The application refers to the nucleation process, a widely spread phenomenon in both nature and technology, which may be considered as a representative of the aggregation phenomena in complex systems. The recent discovery of the generation and extinction of crystal nuclei at very low temperatures [7−9] suggests that stochastic generation of crystal nuclei would be considered as a result of fluctuation of complex cluster structure of the supercooled liquid. The role of both heterogeneity and the interface between clusters in the enhancement of nucleation rate has still to be explained. In particular, it was observed that nuclei could almost always be formed near the surface of the cluster instead of in the interior, and one factor favoring nucleation

near the surface would be the greater freedom of motion and, hence, a larger nucleation probability [10−12]. This is surprising, because it is known that the surface layers of the nuclei tend to be disordered and melt at significantly lower temperatures than their cores.

2. A generic stochastic model for crystal nucleation

Let us consider N atoms, which can be in three different states (cluster, liquid, and their interface), and can perform four possible moves: liquid to interface, interface to liquid, interface to cluster, and cluster to interface. One can identify four different combinations denoted with probabilities $p_1...p_4$. That is, drawing randomly one particle, it will be of type i with probability p_i. Let N=1,2,…∞ be the total number of atoms in the system, and $\{n_1, n_2, n_3, n_4\}$ are their partition into four subsets. Each subset can be called cluster; the process proper, clustering. Schematic distribution of particles in clusters is shown in Fig. 1. This diagram illustrates a potential process for the generation of a crystal nucleus in the course of irreversible structural relaxation of the nonequilibrium supercooled liquid. The number of possible partitions in this case is $P(N) = \frac{1}{3!}\prod_{i=1}^{3}(N+i)$, where $n_i = \overline{0, N}$, $i = \overline{1,4}$ and $\sum_{i=1}^{4} n_i = N$. For example, in a system of N=1000 atoms, $P(N)$ equals to 167668501! Such an interaction in the ABM model always involves an active agent and a passive one: the agents have preferences over their states and they can play both roles interchangeably. Accordingly, the number of repeated computer runs due to different possible partitions would be very large. As already mentioned in the previous section, we are able to overcome this problem by developing similar stochastic analytical models which can describe exactly the results of the agent-based computational models, and, finally, by bridging the gap between ABM modelling and stochastic processes.

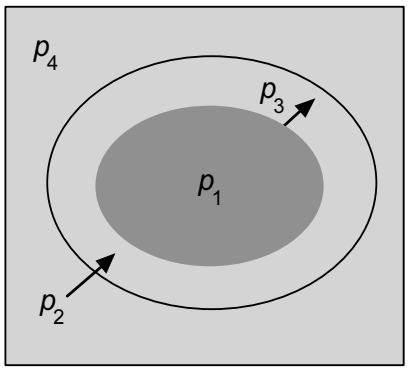

Fig. 1. Schematic diagram illustrating the distribution of particles with corresponding share in cluster, p_1, liquid, p_4, and at the interface, p_2 and p_3. The darkness represents the degree of order in the molecular arrangements, and the encircled part stands schematically for a more ordered cluster, namely, a crystal nucleus.

Let us consider further that each particle interacts with the entire group both as an aggressor (in terms of the Kolmogorov theory) and as a passive agent (in terms of the ABM models) as well. Then the mean π, namely, the stability index, takes here the form

$$\pi = p_1(p_1 - p_3) + (p_2 + p_3)(-p_1 + p_2 + p_3 - p_4) + p_4(p_4 - p_2). \quad (1)$$

or, taking into account that $\sum_{i=1}^{4} p_i = 1$, one can exclude one probability, for example, p_4, from the above equation

$$\pi = p_1(p_1 - p_3) + (1 - p_1 - 2p_2 - p_3)(1 - p_1 - p_2 - p_3) + (p_2 + p_3)(-1 + 2p_2 + 2p_3). \quad (2)$$

One can represent the distribution of states as a three-dimensional point $d(l,r,c) \equiv d(p_1, p_2, p_3, p_4) = \sqrt{l^2 + r^2 + c^2}$, where the axes are labeled l, c, and r: $l = p_1 - p_3$, $c = p_2 + p_3 - p_1 - p_4$, $r = p_4 - p_2$, and as before $l + c + r = 0$ and $d \in \left[0, \sqrt{2}\right]$. Thus different distributions of states can lead to the same point in the sphere; that is, different microscopic partitions can generate the same result on aggregate inside a sphere around the origin.

Preliminary results for the two limit cases are obvious: if all particles show the same behavior, then $d = \sqrt{2}$ and there is a maximum stability of states in such a completely asymmetrical system, but $\pi = 0$ for a homogeneous system, $p_1 = p_2 = p_3 = p_4 = 1/4$, and for combinations, such as $p_1 = p_3$ and $p_2 = p_4$ in the case of unstable steady-states.

To represent a two-dimensional graph describing the stability/instability of the system, we consider some fixed probabilities. Figure 2 depicts such dependence of the cluster instability, $1–\pi$, on the probability p_1 for a system of 100 particles, where the atoms at the liquid-cluster interface are missing (a); share of atoms at the interface p_2+p_3 is just 1/10 of their total number in the system (b); and corresponding share of particles at the interface is equal to 3/10, i.e. $p_2 = p_3 = 0.15$ (c), $p_2 = 0.1$, $p_3 = 0.2$ (d), and $p_2 = 0.2$, $p_3 = 0.1$ (e). Note that, in the absence of an interface between liquid and cluster, as we expected, the system is in a state of maximum instability for $p_1 = p_4 = 0.5$. While the number of particles at the interface, i.e., p_2+p_3 increases, the stability of the system decreases simultaneously, regardless of whether the particle flow at the interface is achieved at the expense of the liquid phase or particles in the cluster. However, particles at the liquid-cluster interface definitely accelerate the formation of clusters due to the displacement of the maximum instability in the region of smaller values for p_1. In other words, the nucleus formation is indeed a random event with a chance largely determined by the nucleation work which increases with the subnuclei size [13]; thus, a decline in share of atoms, p_1 in such a cluster, namely a decline in the critical nucleus size, would be followed by the appearance of a crossover point to the supernuclei at the lower value of the energy consumed for the cluster formation. The curves (d) and (e) in this figure also show that a greater flow from the liquid phase ($p_2 > p_3$) or from the cluster ($p_2 < p_3$) causes a minor increase in the instability of the related branches, but for $p_2 + p_3 =$ const the value of maximum π remains constant too.

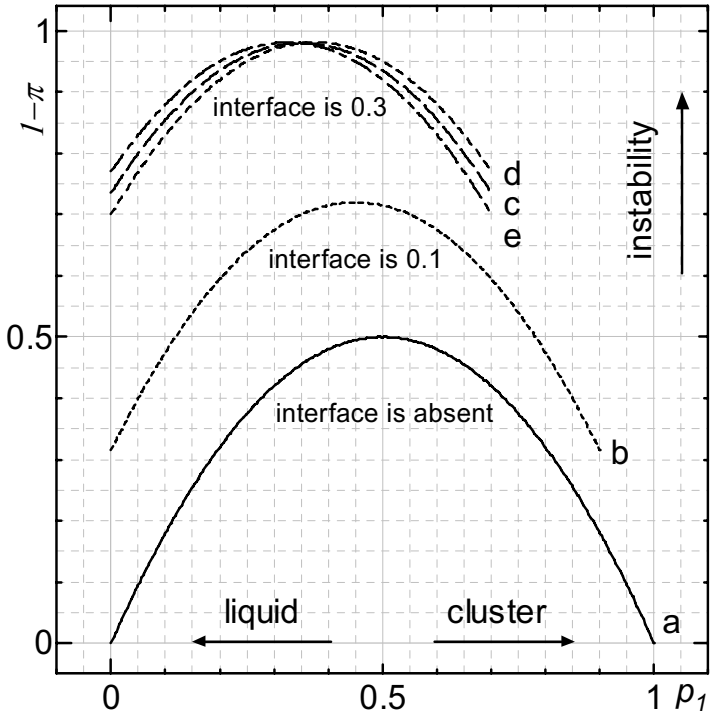

Fig. 2. Dependence of the cluster instability, $1–\pi$, on the probability p_1 for the cases: (a) particles at the liquid-cluster interface are missing; (b) share of atoms at the interface represents 1/10 of their total; corresponding share of atoms at the interface represents 3/10, i.e. $p_2 = p_3 = 0.15$ (c), $p_2 = 0.1$, $p_3 = 0.2$ (d), and $p_2 = 0.2$, $p_3 = 0.1$ (e). A total number of 100 agents in a similar ABM model is considered.

3. Conclusions

We propose a generic stochastic model for crystal nucleation. It is generally known that first-order phase transitions occur by the nucleation mechanism and that both the nucleus, a cluster of molecules or atoms, and the nucleation work, an energy barrier to the phase transition, are

basic thermodynamic quantities in the theory of nucleation. However, the critical nucleus formation is statistically a random event with a probability largely determined by the nucleation work. It is shown that, while the number of particles at the liquid-cluster interface increases, the stability of the entire system decreases simultaneously, and the nucleus formation would be definetely enhanced due to the displacement of the bifurcation point in the region of smaller clusters.

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