Extension of Classical Nucleation Theory for Uniformly Sheared Systems

Anatolii V. Mokshin,† Bulat N. Galimzyanov,‡ and Jean-Louis Barrat*†

†Kazan Federal University, 420000 Kazan, Russia
‡Laboratory for Interdisciplinary Physics, UMR 5588, Université Grenoble 1 and CNRS, 38402 Saint Martin d’Hères, France

(Dated: May 7, 2014)

Nucleation is an out-of-equilibrium process, which can be strongly affected by the presence of external fields. In this letter, we report a simple extension of classical nucleation theory to systems submitted to an homogeneous shear flow. The theory involves accounting for the anisotropy of the critical nucleus formation, and introduces a shear rate dependent effective temperature. This extended theory is used to analyze the results of extensive molecular dynamics simulations, which explore a broad range of shear rates and undercoolings. At fixed temperature, a maximum in the nucleation rate is observed, when the relaxation time of the system is comparable to the inverse shear rate. In contrast to previous studies, our approach does not require a modification of the thermodynamic description, as the effect of shear is mainly embodied into a modification of the kinetic prefactor and of the temperature.

PACS numbers: 45.50.Dd, 83.50.Ax, 64.60.qe, 83.10.Tv

I. INTRODUCTION

Homogeneous crystal nucleation is the route by which the crystallization in a supercooled liquid is initiated, at least in the absence of impurities or of a spinodal instability. A general physical understanding this phenomena is provided by the classical nucleation theory (CNT), which takes into account the thermodynamic and kinetic aspects properly to treat the formation of the crystalline nuclei that are able to grow. Nevertheless, despite the strong theoretical background of the CNT, there are still debates on some fundamental questions. One example is the issue of the mechanisms, – spinodal decomposition or nucleation – by which the structural ordering is started in a simple one-component system at extremely deep supercooling.

Imposing external driving fields (e.g. a shear flow) leads to nonequilibrium steady state of the system and, thereby, impacts on the nucleation process in a complex manner. This is verified by several studies of the shear-induced effects on the structural ordering in colloidal suspensions, polymers, 2D dusty plasma and glasses. Although kinetic models for nonequilibrium nucleation have been proposed, the possibility of a simple extension of the CNT to nonequilibrium situations is still open. Moreover, it was recently found that the mechanism of the shear-induced structural ordering depends also on the character of the applied shear. According to results of Ref. 8, the nucleation mechanism, which is realized in colloidal suspensions under homogeneous shear field, is changed into crystallization through the ‘front propagation’ scenario for inhomogeneous, wall-driven shear. Interestingly, such an ordering mechanism was not observed for the model glassy systems under inhomogeneous wall-driven shear flow, where the nucleation events were clearly detected. Nevertheless, the lack of a comprehensive study of the impact of the homogeneous shear on the structural ordering in glassy materials (especially, at deep supercooling) motivates further investigations.

In this paper, we study the influence of an homogeneous shear drive on the crystal nucleation in a bulk glassy system on the basis of the nonequilibrium molecular dynamics. We analyze in detail the morphology of the ordered structures and the statistics of the nucleation events, that allows us to obtain independently all the ingredients that enter the nucleation rate and to evaluate directly the mechanisms of the ordering. The nucleation rates obtained at several temperatures and values of the shear rate indicate that the steady shear deformation can either enhance or suppress crystal nucleation, depending on the magnitude of γ. They can be described quantitatively using an extension of CNT involving an effective, shear rate dependent temperature.

II. SIMULATION DETAILS

Molecular dynamics simulations are performed for a single-component glass forming system, made of particles interacting via a short-ranged oscillatory potential, suggested originally by Dzugutov [17]. At zero pressure, this system is characterized by a melting temperature \( T_m \approx 1.02 \varepsilon/k_B \), and a glass transition at \( T_c < T_{MCT} = 0.4\varepsilon/k_B \). An applied pressure \( P = 14\varepsilon/\sigma^3 \) shifts the system melting and glass temperatures to the values \( T_m \approx 1.51\varepsilon/k_B \) and \( T_c \approx 0.65\pm0.1\varepsilon/k_B \), respectively. Simulation cells of fixed volume \( V = \ell^3 \) (\( \ell = 20.03\sigma \)) containing an amorphous sample with periodic boundary conditions were prepared by quenching from a well
equilibrated melt at the temperature $T = 2.3\epsilon/k_B$ to the temperatures $T = 0.05$, $0.1$, $0.15$, $0.3$ and $0.5\epsilon/k_B$, below $T_c$, with the quenching rate $0.001\epsilon/(k_B\tau)$. At each temperature, a set of hundred independent configurations (each is consisting of 6 912 particles) was prepared in view of a statistical analysis.

After the quench, an homogeneous shear flow is imposed by means of the SLLOD algorithm supplemented by Lees-Edwards periodic boundary conditions [18]. Here, the $x$-axis is associated with shear direction, the $y$-axis corresponds to gradient direction and the $z$-axis coincides with vorticity direction, and the shear rate has a constant value $\dot{\gamma}$ throughout each run. Constant temperature and pressure conditions are ensured by using the Nosé-Hoover method with an external pressure $P = 14\epsilon/\sigma^3$ that promotes crystallization in the system. The homogeneous character of the shear flow is verified from the linearity of velocity profiles.

III. RESULTS

A. Mechanism of ordering and crystalline structures

To identify the particles involved in the crystalline phase, the environment within the first coordination shell of each particle is analyzed in terms of the bond orientational order parameters [19], and the corresponding clusters are constructed. The time-dependent cluster size distribution $N_n(t)$ is evaluated for each run, and is averaged over independent runs. Before going to the quantitative analysis of these data, we describe briefly some qualitative aspects of the nucleation process.

The cluster data analysis reveals the following features as structural order appears in the system. The nuclei of a fcc/hcp crystal phase are homogeneously distributed, and their sizes fluctuate while they are lower than some critical size. When reaching a critical size, they start growing monotonously with time. These are clear indications that a homogeneous nucleation mechanism is at work. Similar observations are made at all shear rates $\dot{\gamma} \in [0$, $0.01] \tau^{-1}$ and temperatures, even at a deep supercooling $(T_m - T)/T_m \simeq 0.97$. Figure 1 shows, as an example, the configurations of particles generating the crystalline phases for a single amorphous sample at the temperature $T = 0.1\epsilon/k_B$ for a shear rate $\dot{\gamma} = 0.001 \tau^{-1}$ at different times after startup of the steady shear. It is seen that this type of shear-driven structural ordering differs completely from the results of Ref. [8] reported recently for shear-induced colloidal crystallization, where shear was applied through the walls and ordering appears as propagated layer by layer. Instead of the crystallization through a layering, a nucleation-growth mechanism is clearly observed here, similar to the results of Ref. [9] for a colloidal system and of Ref. [10] for flow-induced ordering in polymers.

A key ingredient in the analysis of the shear-driven nucleation will be the geometry of the nucleated clusters. To quantify this geometry, we define the pair correlation functions, $g(x, y)$ and $g(x, z)$, which are computed only for the particles involved in a critical cluster and characterize the distribution of the particles projected onto $xy$– and $xz$– planes, respectively. Our results show that the critical nucleus changes from a spherical shape in the shear-free case to a prolate ellipsoid with its long axis tilted in the $xy$–plane (see Fig. 2). Numerically, the ellipticity $\varepsilon = W/L$ grows with increasing shear rates. For the highest shear rate $\dot{\gamma} = 0.01\tau^{-1}$ it takes $\varepsilon = 0.83$ at $T = 0.05\epsilon/k_B$ and $\varepsilon = 0.75$ at $T = 0.5\epsilon/k_B$. Such flow influence on a shape of the nuclei corresponds to the recent results of Graham and Olmsted obtained within coarse-grained simulations of flow in polymer melts [10].

B. Nucleation under shear drive

We now turn to the quantitative analysis of the nucleation data, which is based on the study of the time dependent cluster distribution $N_n(t)$. In the framework of a mean first passage analysis [20], the average time $\tau(n)$, at which a cluster of a given size $n$ is observed for the first time, is analyzed together with its derivative $\partial\tau(n)/\partial n$ [21]. This allows one to obtain independently the following quantities characterizing the nucleation process: the steady-state nucleation rate $J_s = 1/(\tau_c)$ ($\tau_c$ is the nucleation time scale), the number $n_c$ of particles involved in the critical nucleus, and the Zeldovich factor $Z$ which characterizes the curvature of the free energy barrier at the top [12, 19]. In addition, the in-
terficial free energy $\gamma_m$ was estimated by means of the thermodynamic integration of the surface energy of the critical nuclei \[21]\). The different nucleation parameters are related by the general expression of the nucleation rate within the CNT \[2, 3]\:

$$J_s = g_{n_c}^+ Z \rho_{am} \exp \left( -\Delta G_{n_c} / k_B T \right).$$

(1)

Here, $g_{n_c}^+$ is the rate at which atoms attach to the critical nucleus, $\rho_{am}$ is the density of atoms in the parent amorphous phase, $\Delta G_{n_c}$ is the free energy required to form a cluster of the critical size $n_c$, that corresponds to the maximum in the free energy

$$\Delta G(n) = \Delta G_{n_c} \left[ 3 \left( \frac{n}{n_c} \right)^{2/3} - 2 \left( \frac{n}{n_c} \right) \right] ,$$

(2)

and the Zeldovich factor is defined as

$$Z^2 = \frac{-1}{2 \pi k_B T} \left[ \frac{\partial^2 \Delta G(n)}{\partial n^2} \right]_{n=n_c} = \frac{1}{3 \pi n_c^2} \frac{\Delta G_{n_c}}{k_B T}$$

$$= \frac{\gamma_m}{9 \pi k_B T} \left( \frac{36 \pi}{\rho_c^2 n_c^2} \right)^{1/3}. $$

(3)

The last equality in Eq. (3) results from the assumption that the nascent clusters have a spherical form \[2].

To interpret our results we extend the CNT above in two directions: (i) the calculation of the nucleation barrier is extended to ellipsoidal nuclei, and (ii) the temperature is considered as a free parameter, $T_\text{eff}$, in the spirit of the effective temperature concept \[22]. The shape of the nuclei is directly obtained from the simulations, and is not an adjustable parameter. Therefore, the overdetermination indicated above allows one to find independently the two unknown quantities, $T_\text{eff}$ and $g_{n_c}^+$, both of which are expected to be $\dot{\gamma}$-dependent. Thus, we have

$$J_s = g_{n_c}^+ Z \rho_{am} \exp \left( -\Delta G_{n_c} / k_B T_\text{eff} \right),$$

(4)

where $Z$ for a prolate spheroid nucleus of density $\rho_c$ with ellipticity $\varepsilon$ takes the form

$$Z = \frac{1}{n_c^{2/3}} \left( \frac{\alpha_n}{3 \pi k_B T_\text{eff}} \right)^{1/2}. $$

(5)

The term $\alpha_n$ is related with the surface contribution into the nucleation barrier $\Delta G_{n_c}$ and can be written as

$$\alpha_n = \gamma_m \left( \frac{\pi \varepsilon^2}{6 \rho_c^2} \right)^{1/3} \left[ 1 + \frac{\arcsin \left( \sqrt{1 - \varepsilon^2} \right)}{\varepsilon \sqrt{1 - \varepsilon^2}} \right].$$

(6)

For the case of spherical nuclei, $\varepsilon \to 1$, Eqs. (5) and (6) yield the last equality of Eq. (4).

C. Nucleation rate and critical size

Figure 3: (color online) Main: Nucleation rate vs shear rate at five different temperatures. The dashed line is the fit by $J_s(\dot{\gamma}, T) = J_s(\dot{\gamma} = 0, T) + (A^2 / V) \exp[-(\alpha(T) \gamma c(T))^2]$, where $A = 33$ and $n = 1/2$ are the temperature independent dimensionless parameters, $\gamma c(T)$ is the structural relaxation time defined for the shear-free cases, and $\alpha(T)$ changes from 4.5 at $T = 0.05 \varepsilon / k_B$ to 9.0 at $T = 0.5 \varepsilon / k_B$. Inset: Critical cluster size vs shear rate at the different temperatures.

In Fig. 3 we show the extracted values of the nucleation rate $J_s$ and the critical cluster size $n_c$ at different shear rates $\dot{\gamma}$ and temperatures $T$. In the shear-free limit, $n_c$ increases with temperature as expected from thermodynamics. The term $J_s$, on the other hand, is a
decreasing function of $T$, which indicates that the slowing down due to the viscosity dominates the temperature evolution. It may seem surprising to observe nucleation in very low temperature systems, in which the viscosity is effectively infinite. However, studies of aging indicate that immediately after the quench the relaxation time is finite $2^{25}$, so that the local structural rearrangements that lead to nucleation are possible.

At low shear rates, the nucleation rate increases essentially linearly with $\dot{\gamma}$, as indicated by the empirical fitting formula given in Fig. 3. In this regime, the size $n_c$ appears to be practically unchanged and a shape remains spherical. Consequently, the thermodynamic contribution can be considered as unaffected by shear-flow and the nucleation is enhanced, mainly, through the kinetic contribution $g_{n_c}$. The situation changes at moderate shear rates, $\dot{\gamma} \in [0.001; 0.005] \tau^{-1}$, where $J_s$ saturates and reaches a maximum for all the isotherms. With the further increase of shear rate, $\dot{\gamma} > 0.005 \tau^{-1}$, the nucleation rate starts to decrease. The rise of $n_c$ at shear rates $\dot{\gamma} \geq 0.001 \tau^{-1}$ is due to the transformation of the nuclei from a spherical form into prolate ellipsoids. This increase in size and the change in shape of the critical cluster at high shear rates are directly reflected in the thermodynamic aspect of nucleation, since the nucleation barrier is defined by the surface area and the volume of the critical cluster. The appearance of maxima on the curves $J_s(\dot{\gamma})$ illustrates the antagonist impact of the shear flow on the nucleation process: a slow shear-flow accelerates the nucleation trough the attachment rate, whereas the high shear rates appear to destabilize the critical nuclei and reduce the probability of the particle attachment. The physical origin of the latter effect is discussed below. The fastest nucleation rates are obtained for high temperatures and intermediate shear rates, and are typically one order of magnitude higher than in the absence of shear. Note that the corresponding shear rates would be achievable in colloidal suspensions under the isothermal conditions considered here; in hard materials such as metallic glasses, they would induce an important heating that is not described by our calculations.

We mention that the observed behavior of $J_s(\dot{\gamma})$ is similar to the one detected for the same system confined by rigid walls, undergoing inhomogeneous flow [16] and for a 2D Ising model under shear [24]. Interestingly, the nucleation rate $J_s$ takes lower values in the case of homogeneous shear flow applied to a bulk glass (at the pressure $P = 14 \epsilon/k_B$) in comparison with results for a confined system (at the pressure $P_{yy} = 7.62 \epsilon/k_B$) under inhomogeneous shear drive [16]. Moreover, the maximum in $J_s(\dot{\gamma})$ observed in Fig. 3 is shifted to higher shear rates in the case of an inhomogeneous shear. Nevertheless, the results of this study provide a clear evidence that both types of shear flow – homogeneous shear in a bulk glass and inhomogeneous shear in a confined wall-driven glassy system – yield the same homogeneous nucleation mechanism. Moreover, the increase of $J_s(\dot{\gamma})$ at low shear rates is similar with that was observed by Graham and Olmsted in polymers [10], albeit no saturation in $J_s(\dot{\gamma})$ was detected in Ref. [10]. A simple extension the CNT to describe the nucleation of colloidal suspensions under shear was proposed in Ref. [9], where the term $\Delta G_{n_c}/k_BT$ and the critical cluster size $n_c$ were considered to be quadratic functions of the shear rate $\dot{\gamma}$. Such a dependence does not seem consistent with the results for a glassy system obtained above: although the cluster size $n_c$ grows with $\dot{\gamma}$ (see inset of Fig. 3), the dependence $n_c(\dot{\gamma})$ is not parabolic, whereas the dimensionless nucleation barrier $\Delta G_{n_c}/k_BT$ appears to be a decreasing function of $\dot{\gamma}$ (see Fig. 3).

**D. Effective temperature**

The evolution of $T_{eff}$ evaluated from Eqs. (5) and (6) is presented as a function of $\dot{\gamma}$ in Fig. 3(a). The extracted effective temperature reduces correctly to that of the thermal bath in the limit of low shear rate, $T_{eff}(\dot{\gamma} = 0) \rightarrow T$. This shows that the CNT is perfectly consistent with our data in the shear-free case. Interestingly, the systems quenched at low temperature are undergoing aging, which is a nonequilibrium process. Still, the fact that the obtained temperature is identical to the one of the thermal bath indicates that the fluctuations which trig-
ger a nucleation event are “fast”, and they do not involve a slow evolution within the free energy landscape. For shear rates \( \dot{\gamma} \gtrsim 0.001 \text{ s}^{-1} \), a rise in \( T_{\text{eff}}(\dot{\gamma}) \) is observed, that is very similar to the one detected in different studies of effective temperature in sheared systems \[\text{[23]}\], where the effective temperature was defined from fluctuation-dissipation relations. This rise actually compensates the free energy cost of the nucleus formation so that the Arrhenius factor \( \exp(-\Delta G_{n_c}/k_B T_{\text{eff}}) \) increases with shear rate [see Fig. 4(b)]. The inset in Fig. 4(b), on the other hand, shows that the non-monotonous behavior of \( J_n \) arises from the \( \dot{\gamma} \)-dependence of the kinetic prefactor, \( g^*_{n_c} \).

Homogeneous shear flow results in an anisotropy of nuclei growth, and \( g^*_{n_c} \) becomes direction dependent. At low temperatures, the attachment rate averaged over directions depends on the strain rate that initiates the motion, and on the probability that a particle will remain attached to the nucleus \[\text{[3]}\]. It should, therefore, be proportional to \( \dot{\gamma} \) at small strain rates; for large strain rates, compared to the time scale \( \tau_\alpha \) of inherent structural rearrangements, the new configuration can be destabilized before the attachment is achieved. The empirical form suggested by the fits in figure \[\text{[3]}\] \( g^*_{n_c} \propto \dot{\gamma} \exp[-\xi(\dot{\gamma})^n] \), accounts well for these different trends (here, \( \xi \) and \( n \) are dimensionless parameters). In general, it can be expected that the position of the maximum in \( g^*_{n_c} \) will correspond to \( \dot{\gamma}_c \propto 1/\tau_\alpha \).

IV. CONCLUSION

It appears quite remarkable, that a simple extension of classical nucleation theory involving two independently determined quantities, an effective temperature and a kinetic prefactor, describes quantitatively the data for all the considered shear rates and temperatures. Our interpretation of shear-driven ordering is different from previously proposed approaches \[\text{[3]}\], in which an empirical modification of the nucleus free energy due to strain rate was suggested, while the value of the temperature was kept fixed. Here, we take the alternative view that the shear flow produces additional fluctuations, which enhance activated processes and can be described by an effective temperature \[\text{[23]}\]. As our analysis allows one to completely disentangle the thermodynamic and kinetic factors in the nucleation rate, we are moreover able to show that the latter actually dominates the behavior of the nucleation rate at high shear rates. Low shear rates promote nuclei growth by increasing the mobility, but increasing the strain rate beyond a critical, temperature-independent value results in a strong decrease of the sticking coefficient.

V. ACKNOWLEDGMENTS

A.V.M. acknowledges useful discussions with R.M. Khusnutdinoff, A. Tanguy and E.D. Zanotto. J.L.B. is supported by Institut Universitaire de France.

[1] K.F. Kelton, Solid State Physics, ed. by H. Ehrenreich, D. Turnbull (Academic, New York, 1991). Vol. 45, p. 75.
[2] D. Kashchiev, Nucleation: Basic Theory with Applications (Butterworth-Heinemann, Oxford, 2000).
[3] J. Frenkel, Kinetic Theory of Liquids (Oxford U.P., London, 1946).
[4] F. Trudu, D. Donadio, M. Parrinello, Phys. Rev. Lett. 97, 105701 (2006); L.S. Bartell, D.T. Wu, J. Chem. Phys. 127, 174507 (2007).
[5] S. Butler and P. Harrowell, Phys. Rev E 52, 6424 (1995).
[6] M.D. Haw et al., Phys. Rev. E 58, 4673 (1998).
[7] J.J. Cerda et al., Phys. Rev. E 78, 031403 (2008); A. Zaccone et al., Phys. Rev. E 106, 138301 (2011).
[8] L.T. Shereda, R.G. Larson, and M.J. Solomon, Phys. Rev. Lett. 105, 228302 (2010).
[9] R. Blaak, S. Auer, D. Frenkel, and H. Löwen, Phys. Rev. Lett. 93, 068303 (2004); J. Phys.: Condens. Matter 16, S3873 (2004).
[10] R.S. Graham and P.D. Olmsted, Phys. Rev. Lett. 103, 115702 (2009).
[11] V. Nosenko, A.V. Ilyev, and G.E. Morfill, Phys. Rev. Lett. 108, 135005 (2012).
[12] A.V. Mokshin and J.-L. Barrat, Phys. Rev. E 77, 021505 (2008).
[13] A. Onuki, J. Phys.: Condens. Matter 9, 6119 (1997); D. Reguera and J.M. Rubi, J. Chem. Phys. 119, 9888 (2003).
[14] H. Löwen, J. Phys.: Condens. Matter 20, 404201 (2008).
[15] A. Kerrache, N. Mousseau, and L.J. Lewis, Phys. Rev. B 84, 014110 (2011).
[16] A.V. Mokshin and J.-L. Barrat, J. Chem. Phys. 130, 034502 (2009); A.V. Mokshin and J.-L. Barrat, Phys. Rev. E 82, 021505 (2010); A.V. Mokshin and J.-L. Barrat, Bulletin of the Russian Academy of Science. Physics 74, 1146 (2010); A.V. Mokshin and J.-L. Barrat, Bulletin of the Russian Academy of Science. Physics 75, 686 (2011).
[17] M. Dzugutov, S.I. Simdyankin, F.H.M. Zetterling, Phys. Rev. Lett. 89, 195701 (2002).
[18] D. Frenkel and B. Smit, Understanding Molecular Simulation (Academic, San Diego, 2001).
[19] P.J. Steinhardt, D.R. Nelson, and M. Ronchetti, Phys. Rev. B 28, 784 (1983); P. R. ten Wolde, M. J. Ruiz-Montero, and D. Frenkel, J. Chem. Phys. 104, 9932 (1996).
[20] L.S. Bartell and D.T. Wu, J. Chem. Phys. 125, 194503 (2008).
(2006); J. Wedekind, D. Reguera, and R. Strey, J. Chem. Phys. 125, 214505 (2006).

[21] A.V. Mokshin, B.N. Galimzyanov, J. Phys. Chem. B 116, 11959 (2012).

[22] L.F. Cugliandolo, J. Phys. A: Math. Theor. 44, 483001 (2011).

[23] W. Kob, J-L. Barrat, Eur. Phys. Journal B 13, 319 (2000).

[24] R.J. Allen et al., J. Chem. Phys. 129, 134704 (2008).

[25] T.K. Haxton, A.J. Liu, Phys. Rev. Lett. 99, 195701 (2007); N. Xu and C.S. O’Hern, Phys. Rev. Lett. 94, 055701 (2005).

[26] P. Ilg and J.-L. Barrat, Europhys. Lett. 79, 26001 (2007).

[27] The terms $\epsilon$ and $\sigma$ define the units of energy and length, respectively. Time, pressure and temperature units are measured in $\tau = \sigma \sqrt{m_0/\epsilon}$, $\epsilon/\sigma^3$ and $\epsilon/k_B$, respectively.

[28] These temperatures have been determined from an accurate estimate of the potential energy and density variation as well as translational and orientational order parameters at several $(P,T)$-points. The glass transition is verified by evaluating the particle pair distributions and mean square displacements.