

The Ultimate Fate of Supercooled Liquids: supplementary material

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This supplementary material displays in figure 1 the temperature dependence of the probability p for a region of size n_v to have local structural characteristics sufficiently stabilizing such that a nanocrystal can be formed, as well as the analogous quantity p_{hetero} for heterogenous surface nanocrystallization. We also reproduce in figures 2, 4, and 5 many of the figures from the main paper with material parameters corresponding to a strong glass former, methanol. The figures here and in the main paper are drawn using an experimentally observed phenomenological form for the temperature dependence of the configurational entropy[1] $s_c(T) = s_c(T_g)(1 - T_K/T)/(1 - T_K/T_g)$, where $s_c(T_g) \approx 0.82k_B$ is a nearly universal value when measured per independently mobile molecular unit[2]. The temperature dependence of $\Delta\epsilon(T) = T_m s_c(T_m)(1 - \log(T_m/T) * T_K/(T_m - T_K))$ is calculated from $s_c(T)$ using the thermodynamic relation $d\Delta\epsilon = T ds_c$. The surface mismatch exponents used were $y_\alpha = 1/2$ and $y_x = 2/3$. The amorphous surface mismatch penalty is $\sigma_\alpha = -(3/4) \log(d_L^2 \pi e) 4\pi (4\pi/3)^{-y_\alpha} k_B T_K$, a value found approximately from density functional theory[3, 4]. Numerically this is $\sigma_\alpha \approx 11.3k_B T_K$. The crystal surface tension is chosen to give approximately correct experimental values for the nucleation rate in the normal crystallization regime. The temperatures $T_K = 200$, $T_g = 246$, and $T_m = 329$ used in the paper are taken from the measured values for o-terphenyl[5], a fragile glass former. For this liquid we have used $\sigma_x \approx 4.5k_B T_K$. In this supplementary material we have also looked at the strong glass former, methanol, for which the value $\sigma_x \approx 9.3k_B T_K$, along with the temperatures, $T_K = 64$, $T_g = 106$, and $T_m = 175$ [2, 6] have been used. The material values listed above are used to find unambiguous curves for the figures. The curves are approximate, but our arguments do not strongly depend on such details.

FIGURES

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- [1] Richert, R.; Angell, C. A. *J. Chem. Phys.* **1998**, *108*, 9016–9026.
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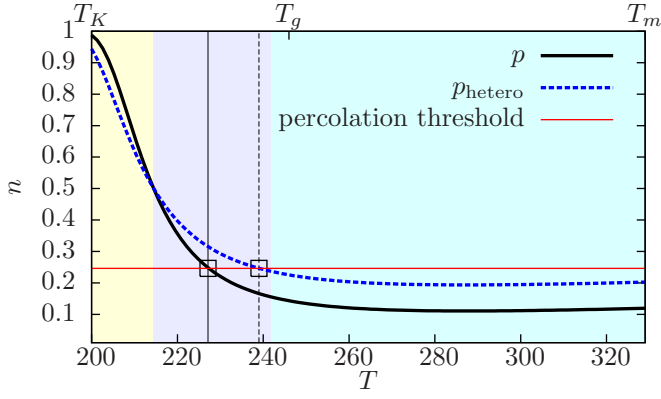


FIG. 1. The probability for a region of size n_ν to have local structural characteristics sufficiently stabilizing such that a nanocrystal can be formed. When the probability is greater than the threshold value (shown here assuming a bcc lattice) a percolative network of nanocrystallites can form in the liquid. The probability for heterogeneous crystal growth p_{hetero} is also shown and crosses the threshold at a higher temperature than homogeneous nanocrystal nucleation.

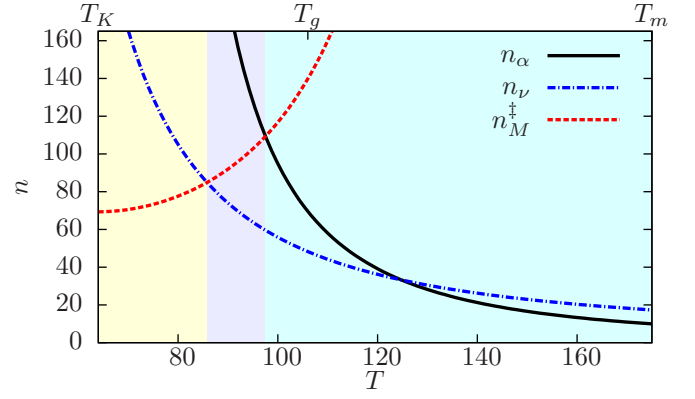


FIG. 2. Panel *a*: The temperature dependence of the relevant sizes corresponding to the various reconfiguration processes. n_α is the size of a typical amorphous reconfiguration. $n_M^‡$ is the transition state size of classical crystal nucleation. n_ν is the number of particles which take part in the nanocrystallization process. Within the shaded region on the right classical nucleation theory is valid. In the shaded region on the left direct nanocrystallization can take place. Crystallization in the center region takes place through fluctuational, percolative nanocrystallization.

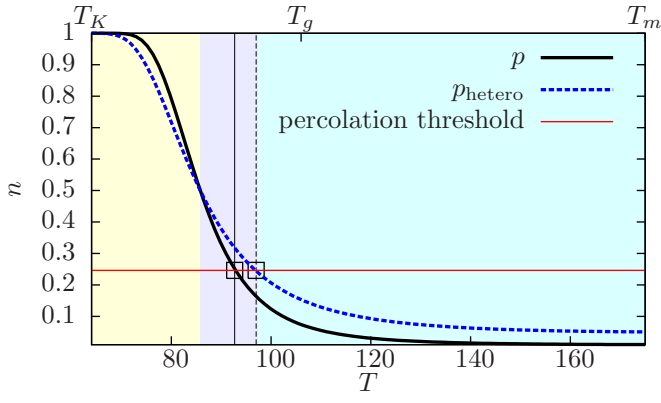


FIG. 3. Panel *b* describes the probability for a region of size n_ν to have local structural characteristics sufficiently stabilizing such that a nanocrystal can be formed. When the probability is greater than the threshold value (shown here assuming a bcc lattice) a percolative network of nanocrystallites can form in the liquid. The probability for heterogeneous crystal growth p_{hetero} is also shown and crosses the threshold at a higher temperature than homogeneous nanocrystal nucleation.

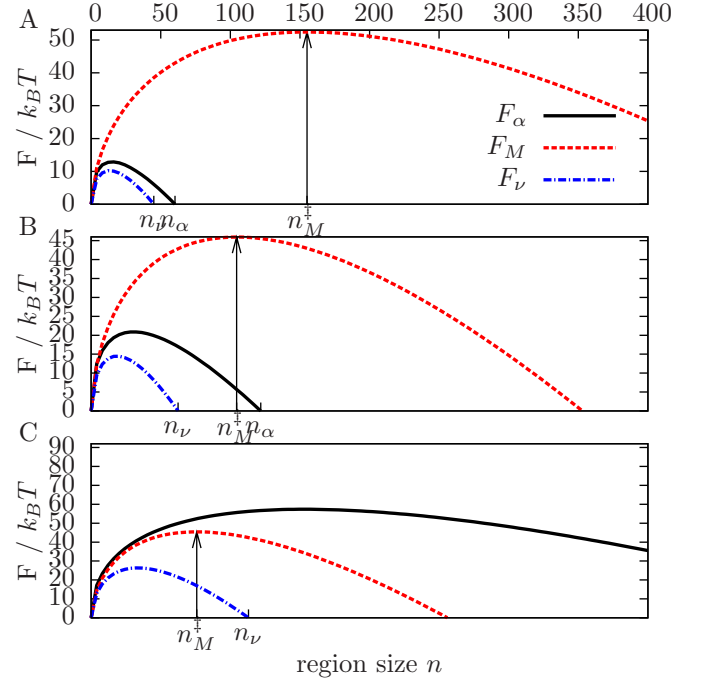


FIG. 4. Free energy profiles of α relaxation (F_α), bulk crystallization (F_M) and nanocrystallization (F_ν) at the three temperature regimes shaded in figure 2.

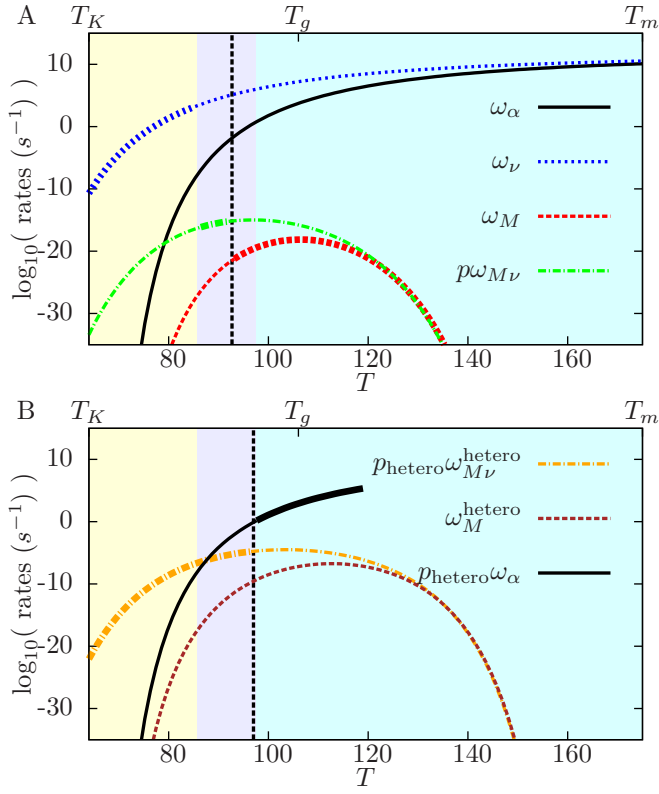


FIG. 5. Panel *a* shows the temperature dependence of nucleation rates for α relaxation (ω_α), bulk crystallization (ω_M), nanocrystallization (ω_ν), and percolative fluctuational nanocrystallization ($p\omega_{M\nu}$). The temperature regimes are shaded as per figure 2. The homogeneous percolation transition, as in figure 3, is marked with a vertical line. Rates are indicated as the inverse time to see a nucleation event within a microscopic volume. Since a single crystal nucleus would spread rapidly through the system the rate at which a sample of volume V would crystallize is $\sim \omega_M V$, a rate much faster than that appearing in the figure. Panel *b* shows rates for heterogeneous crystal surface nucleation. At high temperatures the surface nucleation rate is proportional to ω_α . At the heterogeneous percolation temperature (marked by a vertical line) the crystal growth rate switches to be $p_{\text{hetero}}\omega_{M\nu}^{\text{hetero}}$. The resulting web of crystallites percolates the system somewhat below the glass transition temperature. For both panels the important rates for crystal nucleation and growth are emphasized with a thick line.