Elasticity and metastability limit in supercooled liquids: a lattice model

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We present Monte Carlo simulations on a lattice system that displays a first order phase transition between a disordered phase (liquid) and an ordered phase (crystal). The model is augmented by an interaction that simulates the effect of elasticity in continuum models. The temperature range of stability of the liquid phase is strongly increased in the presence of the elastic interaction. We discuss the consequences of this result for the existence of a kinetic spinodal in real systems.

Keywords: elasticity, metastability limit, supercooled liquids, nucleation.

I. INTRODUCTION

When a liquid is cooled below its freezing point without forming a crystal, it enters a metastable equilibrium phase known as supercooled. A supercooled liquid is squeezed in an uncomfortable region in the time domain: if we are too fast in measuring its properties, the system cannot thermalize and it behaves as an off-equilibrium glass; while, if we are too slow, the system has the time to nucleate the solid, and we obtain an off-equilibrium polycrystal. If at a certain temperature the relaxation time of the liquid τ_R exceeds the nucleation time of the crystal τ_N , no equilibrium measurements can be performed on the liquid state and the supercooled phase does not exist anymore. Such a temperature is called kinetic spinodal T_{sp} and it marks the metastability limit[1]. Recently we have argued that the viscoelastic response of the supercooled liquid is the main mechanism determining whether or not a metastable limit is present[2]. The central idea is that on time scales shorter than τ_R , supercooled liquids exhibit a solid-like response to strains. So, the thermodynamic drive for crystal nucleation gets depressed by an elastic contribution, which is relaxed with the passing of time.

In order to partially test this idea we study here a lattice model, without quenched disorder, that has a phenomenology similar to supercooled liquids (first order phase transition, metastability, glassy behaviour). The advantage of using a lattice model rather than a realistic structural supercooled liquid is that one can simulate for longer times and larger systems. We add in the model an *ad hoc* interaction which, we argue, simulates the effects of the elastic interaction as in

a solid. Our proposal is to study in a controlled manner how the elastic interactions affect the kinetic spinodal, neglecting, for simplicity, the relaxation of this interaction.

II. THE LATTICE MODEL

The lattice model, hereafter CTLS, without the elastic effects has been studied in Ref. [3]. The Hamiltonian is:

$$H_{CTLS} = J \sum_{i=1}^{N} (1 + \sigma_i) f_i ; \qquad (1)$$

where $\sigma_i = \pm 1$ are spins on a 2-dimensional lattice and $f_i = \sigma_i^N \sigma_i^S \sigma_i^E \sigma_i^W$ is the product of the first neighbors of the spin σ_i . We fix the units of energies and temperatures by setting $J \equiv 1$ and $k_B \equiv 1$. The following results, in the absence of elastic effects, were found in Ref. [3] and reproduced in the present study. The model present a first-order phase transition between a disordered phase (liquid) and an ordered one (crystal) at the melting temperature $T_m = 1.29$ (Fig. 1).

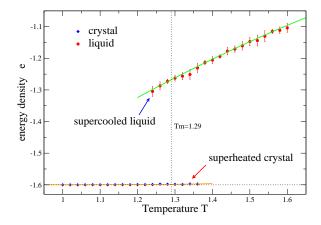


Figure 1: Equilibrium energy density of the liquid and the crystal as function of the temperature.

The system has a well defined kinetic spinodal at temperature T_{sp} . This is illustrated in Fig. 2 where we show numerical quench experiments at different temperatures. If we quench the system at a temperature $T > T_{sp}$ we see that it remains trapped in a metastable liquid state for a time much longer than the relaxation time. Finally for $T < T_{sp}$ we don't observe any plateau and the system goes down towards the ground state. Below T_{sp} the liquid phase cannot be equilibrated and therefore it becomes ill-defined.

Before introducing the elastic effects in this model we have to define a "volume" for the liquid phase and one for the crystal phase, and a "pressure". We can write a new Hamiltonian for the

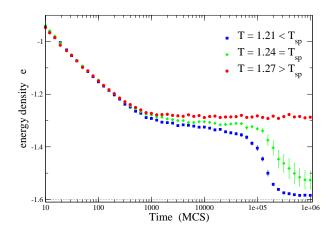


Figure 2: Quench experiments: energy density as function of time at three different temperatures for p=0.

system:

$$H = H_{CTLS} + pV , (2)$$

where p is the pressure and V is the total volume. We define an ad hoc variable V which plays the role of volume: let us assume that the volume per site for the crystal and the liquid phase (ν_C , ν_L respectively) are different as in a real crystal-liquid transition in the continuum. The total volume then can be put as:

$$V = \nu_L N_L + \nu_C N_C = N \nu_L + N_C \Delta \nu. \tag{3}$$

here N_L (N_C) is the number of sites in the liquid (crystal) phase and $\Delta \nu = \nu_C - \nu_L$. This defines the total volume as function of given quantities (ν_L, ν_C, N) and of the total number of the spins that are in the crystalline phase. To determine the latter we define a local order parameter m_i in such a way that takes the value $m_i = 1$ for every site in the crystalline phase [4] and we define the total number of crystalline sites as $N_C = \sum_{i=1}^N m_i$ [5]. We fix our units of volume by setting $\Delta \nu \equiv 1$. In this units the pressure is measure in units of $J/\Delta \nu$.

With these definitions the Hamiltonian takes the form:

$$H = H_{CTLS} + p\Delta\nu N_C + p\nu_L N. \tag{4}$$

In Fig. 3 we show the phase diagram in the p-V plane. We see that one obtains the expected behavior, indeed as the pressure increases the crystal phase, which we defined with the smallest specific volume, is favored.

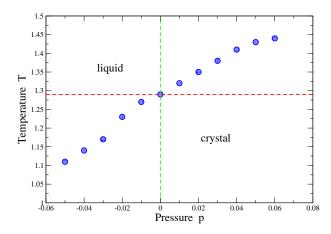


Figure 3: Phase diagram: temperature vs pressure. Negative pressures correspond to a strained system.

Sudden compression (crunching) experiments are particularly interesting because they are very similar to quenching experiments but using the pressure as control variable. We can now monitor both the value of energy density and the crystal volume.

As shown in Fig. 4 one can define a spinodal pressure $p_{sp} = 0.03$. As long as we crunch the system at a pressure $p < p_{sp}$, it remains trapped in the metastable liquid for a time much longer than the relaxation time. On the contrary, for $p > p_{sp}$ we do not observe any plateau: the system goes steadily (but slowly) to the ground state. Above p_{sp} the liquid phase cannot be equilibrated and therefore it becomes ill-defined. The same behaviour is displayed by the total crystal volume (Fig. 4).

III. INTRODUCING ELASTICITY IN THE MODEL

At low temperatures and for not too long times the supercooled liquid will show an elastic response to strains. Since the crystal has a different specific volume than the surrounding liquid phase a relatively fast nucleation process will produce strains in the liquid. The interplay between crystal nucleation and elastic stress relaxation is expressed by a self-consistent equation for the nucleation time τ_N [2]:

$$T \log \tau_{\rm N} = \frac{\sigma^3}{\left[\delta G(T) - E_{\rm elastic}(f(\tau_{\rm N})/\tau_{\rm R})\right]^2} , \qquad (5)$$

where σ is the surface tension and $\delta G(T)$ is the free energy density difference between liquid and crystal. The relaxation of elastic stress is encoded in the fact that the elastic energy depends on the ratio between a time-scale of nucleus formation, $f(\tau_N)$, and the relaxation time τ_R : for

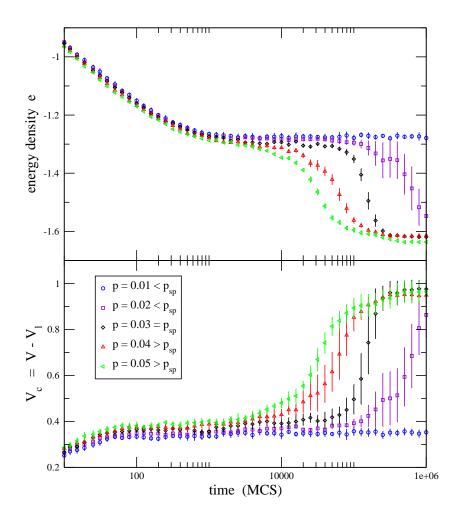


Figure 4: Crunching experiments; top: energy density vs time, bottom: crystal volume vs time.

 $\tau_{\rm R} \ll f(\tau_{\rm N}), \ E_{elastic}(\infty) = 0$, and the stress is relaxed. In [2] we assumed $f(\tau_{\rm N}) \sim \tau_{\rm N}$, whereas a more accurate hypothesis is that $f(\tau_{\rm N}) \sim (\log \tau_{\rm N})^3$ [6], coming from the fact that the time to build a nucleus scales as the square of the number of particles in the nucleus. This modification makes elastic effects quantitatively even more important. Indeed it shift the critical value of the effective elastic coupling (which now becomes $\lambda_c = 1$, see [2]). On the other hand, qualitatively, the physical picture remains unchanged. In the present numerical study we are interested to the case $\tau_{\rm R} \gg f(\tau_{\rm N})$, and thus we can assume $E_{elastic}$ constant, as in solids. This approximation is even more reasonable for $f(\tau_{\rm N}) = (\log \tau_{\rm N})^3$, since the argument of $E_{elastic}$ becomes very small as soon as we move away from the melting temperature.

Nucleation with volume mismatch in an elastic solid has been studied in different contexts[7, 8]. In the case of an isotropic systems the elastic cost for nucleation (or for any inhomogeneous

configuration) takes a simple form[8]:

$$E_{elastic} = \frac{(d-1)KG}{dK + 2(d-1)G} \int_{V} \left(\epsilon_{1}^{0}(\mathbf{x}) - \bar{\epsilon}_{1}^{0}\right)^{2} d\mathbf{x}.$$
 (6)

where d is the dimension of the system (in our case d = 2), G(K) is the infinity frequency shear (bulk) modulus, $\epsilon_1^{\circ}(\mathbf{x})$ is the trace of the stress free-dilation strain tensor and $\bar{\epsilon}_1^{\circ}$ is its mean value. We assume that G and K are the same for both phases. This formula tells us that the system tries to prevent heterogeneities. In order to implement this physics in our model we first rewrite the elastic energy as:

$$E_{elastic} = A \int_{V} \epsilon_1^0(\mathbf{x})^2 d\mathbf{x} - AV(\bar{\epsilon}_1^0)^2, \qquad (7)$$

where A = KG/(2K + 2G) (in d = 2). The trace of the strain tensor is a measure of the volume change[9], so we link it with m_i assuming a linear relationship in the spirit of Vegard's law in alloys[7]:

$$\epsilon_1^0(\mathbf{x}_i) = \delta\left(m_i - \frac{1}{2}\right),\tag{8}$$

where $\delta = (\nu_C - \nu_L)/\nu_0$ and $\nu_0 = (\nu_C + \nu_L)/2$. The hamiltonian with the elastic term (p = 0) becomes:

$$H = H_{CTLS} + E_{elastic} = H_{CTLS} + \gamma \left[\sum_{i=1}^{N} m_i^2 - \frac{1}{N} \left(\sum_{i=1}^{N} m_i \right)^2 \right], \tag{9}$$

where $\gamma = A\nu_0\delta^2$ is the effective elastic coupling constant. We stress again that we are assuming that the supercooled liquid behaves as an elastic solid. This is true only at times shorter than the structural relaxation time. At longer times the stresses that give rise to the above elastic energy cost will relax. That said, we want to test how the elastic contribution affects the kinetic spinodal when the structural relaxation time is very long. Our simulations (Fig. 5) show that the melting temperature T_m is approximately constant in γ . On the other hand, the elastic term enhance the free energy barrier to nucleation, and thus the spinodal temperature drastically decreases. As a consequence, the temperature range where the metastable liquid is defined, $T_{sp} < T < T_m$, gets wider and wider as the elastic coupling γ is increased.

IV. SUMMARY AND CONCLUSIONS

Recently we have argued that viscoelasticity is the main factor determining the existence or not of a kinetic spinodal in a supercooled liquid. Our arguments relied on the assumption that

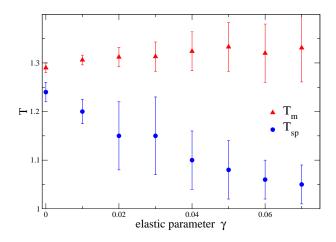


Figure 5: Kinetic spinodal T_{sp} and melting temperature T_m vs elastic parameter γ .

elasticity depress nucleation, and thus shifts the kinetic spinodal. In [2] we performed a selfconsistent determination of the nucleation time, taking into account viscoelastic effects. In this work we tested the above assumption in a microscopic model but neglecting relaxational effects.

The supercooled liquid is strongly influenced by elastic effects as expected, and our results underline the importance of these effects. Elastic effects strongly increase the range of metastability of the liquid phase. Due to technical reasons we can not increase γ beyond 0.07. This prevents us to answer the interesting question of whether the kinetic spinodal can cross Kauzmann temperature T_K , when elasticity is increased. Should this be the case, one expects this system to be an example of an ideal glass former.

V. ACKNOWLEDGMENTS

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