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Glassy behavior in systems with Kac-type step-function interaction

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We study a system with a weak, long-ranged repulsive Kac-type step-function interaction within the framework of a replicated effective φ^4 theory. The occurrence of extensive configurational entropy or an exponentially large number of metastable minima in the free energy (characteristic of a glassy state), is demonstrated. The underlying mechanism of mesoscopic patterning and defect organizations is discussed.

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Competing interactions on different length scales cause in many cases the emergence of an intermediate length scale where new structures and inhomogeneities are formed. Examples are stripe formation in doped Mott insulators [1], bubbles of electronic states of high Landau levels in quantum Hall systems [2], domains in magnetic multilayer compounds [3], and mesoscopic structures formed in self-assembly systems [4]. These systems typically exhibit a multi-time-scale dynamics similar to the relaxation found in glasses. The glassy behavior and the diverging relaxation time are believed to be the result of the competition between the interactions with different characteristic length scales [5,6]; for example the macroscopic phase separation is frustrated by competing long-range interactions [5,7]. Glassiness then arises spontaneously in the absence of extrinsic disorder due to self-generated randomness.

While there are various different scenarios for glassy behavior such as the kinetic constraint where the diverging relaxation time is purely of dynamic origin and occurs in a system with trivial equilibrium properties, the central theme of this work is based upon the random first-order transition [8], where glassiness is attributed to an exponentially large number of metastable states, originally emphasized by Kauzmann [9]. The fact that configurational entropy is needed for slow motions in glasses was first described by Gibbs and DiMarzio [10]. Below a crossover temperature T_A, an energy landscape dominated, ''viscous'' long time relaxation sets in due to an exponentially large number of metastable states, $\mathcal{N}$, i.e., the configurational entropy, $S_c=\ln\mathcal{N}$, becomes extensive. This crossover temperature T_A is often associated with the mode-coupling temperature at which the relaxation time or the viscosity exhibits a power law divergence $|T-T_A|^{-\gamma}$, within mode-coupling theory [11]. Activation processes, which are neglected in mode-coupling theories, soften the sharp transition into a crossover where for $T<T_A$ free-energy barriers and thus transition rates between the metastable states remain finite. The configurational entropy decreases with decreasing temperature, and becomes negative for $T<T_K$. A continuous (random first-order) transition, the ''ideal'' glass transition, occurs at T_K to avoid $S_c<0$. The Kauzmann temperature T_K is the temperature at which the genuine thermodynamic glass transition is expected, whereas the experimentally observed glass transition occurs at $T_g>T_K$ which depends on the cooling rate.

In Ref. [6], it was shown quite generally within the framework of a replicated φ^4 theory that the competition between short range forces (favoring phase separation) and long-range Coulomb interaction leads to an exponentially large number of metastable states and self-generated glassiness. The large phase space of fluctuations, which can lead to a fluctuation induced first-order transition [12], was shown to, alternatively, drive the system into an amorphous state, the *stripe glass*.

In this Rapid Communication we explore the extent to which *explicit* competition or frustration is necessary to cause a glassy state and what kind of interactions support such a state. A particularly interesting potential is the Kac-type step potential

$$V(x)=\alpha^2\gamma^D\phi(\gamma x), \tag{1}$$

with $\phi(y)=1$ for $y\leqslant 1$ and zero otherwise. Here, γ controls the amplitude and range of the potential, whereas the inverse length α characterizes the integral strength $\int d^Dx V(x)\propto\alpha^2$. In the van der Waals limit, $\gamma\to 0$ after the thermodynamic limit, it is known that a system of particles interacting through a potential given by Eq. (1) can be described exactly by a mean-field theory [13], where α is related to the long-range force of the van der Waals theory. In case of a step potential, mean-field theory predicts a spinodal. This model system is of particular interest since it has been used to study the glass formation and crystallization processes [14]. Using Monte Carlo simulations, the appearance of many metastable amorphous ''clump'' configurations was demonstrated in Ref. [14]. However, it is difficult, if not impossible, to enumerate the metastable states and to determine the dependence of the number of local minima, as a function of the system size, in a Monte Carlo study. We find that an analysis of a replicated φ^4 theory along the lines of Ref. [6] is useful as an alternative strategy.

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In this Rapid Communication we demonstrate that the Kac-type step-function interaction, Eq. (1), indeed causes the emergence of an exponentially large number of metastable states and a *self-generated glassy state*. In the limit of small but finite γ, no frustration between different interactions needs to be introduced explicitly, which is different from the model studied in Ref. [5,6]. We demonstrate that glassiness is due to multiple configurations of self-arrested defects, and occurs, similar to Ref. [6], once the correlation length of the system is slightly larger than the length scale of mesoscopically modulated structures. The configurational entropy, Eq. (4) below, behaves for $D=3$ and at $T=T_A$ as $S_c/V \propto \gamma^3$, where V is the volume of the system. A model of glassy behavior with the Kac-type long-ranged interaction, called a van der Waals glass, was introduced and extensively developed, including a study of its dynamics, in Ref. [15], where it is argued that proximity to the mean-field spinodal provides a long correlation length in addition to the Kac potential range, and thus leads to frustration and nonzero configurational entropy. This will be verified here using the replica approach.

We start from the model Hamiltonian

$$\mathcal{H}=\frac{1}{2}\int d^3x\left\{[\boldsymbol{\nabla}\varphi(x)]^2+r_0\varphi^2(x)+\frac{u}{2}\varphi^4(x)\right\} + \int d^3x\int d^3x'\varphi(x)\varphi(x')V(x-x'), \tag{2}$$

with $V(x)$ of Eq. (1). The usual equilibrium free energy $\mathcal{F}=-T\ln\mathcal{Z}$ is an outcome of an unconditional average over the entire configuration space. It does not permit the detection of local minima of the free energy in the configuration space. In Ref. [16], a replica approach was proposed to overcome this limitation and allows us to probe the number of metastable states. In the absence of an exact solution of the φ^4-theory, a number of approximations have been established. The self-consistent screening approximation (SCSA) [17] for an N-component φ^4 theory is correct up to a term of order $1/N$. Here, we adopt the SCSA of a replicated φ^4 theory as used in Ref. [6] and take $N=1$ at the end. Recently, it was shown that this approximation reproduces very well the generic features of the complete solution of the replica mean-field problem [18]. The free energy $\mathcal{F}(m)$ of the replicated Hamiltonian is given in terms of the regular correlation function $G(q)$ and the correlation function $F(q)\equiv\langle\varphi^a(q)\varphi^b(-q)\rangle$ between the fields in different replicas which corresponds to the Edwards-Anderson parameter signaling a glassy state. Here, a, b are the replica indices and m is the number of replicas.

Within the SCSA, the relevant part of the free energy $\mathcal{F}(m)$ is

$$\mathcal{F}(m)=-\frac{T}{m}(\mathrm{tr}\ln\mathcal{G}^{-1}+\mathrm{tr}\ln\mathcal{D}^{-1}), \tag{3}$$

which determines the configurational entropy $S_c=(1/T)(d\mathcal{F}(m)/dm)|_{m=1}$. Here, $\mathcal{G}\equiv(G-F)\mathbf{I}+F\mathbf{E}$ is the correlation function matrix with $\mathbf{I}_{ab}=\delta_{ab}$ and $\mathbf{E}_{ab}=1$. The symbol tr in Eq. (3) includes the trace of the replica space and the momentum integration. The matrix $\mathcal{D}$ is related to $\mathcal{G}$ via $\mathcal{D}^{-1}=(uT)^{-1}\mathbf{I}+\Pi$, where $\Pi=(G\otimes G-F\otimes F)\mathbf{I}+(F\otimes F)\mathbf{E}$ is the generalized polarization matrix. The symbol $\otimes$ denotes a convolution in Fourier space. The replicated Schwinger-Dyson equation can be written as $\mathcal{G}^{-1}=G_0^{-1}\mathbf{I}+\Sigma$, where Σ is the self-energy matrix and

$$G_0(q)=\frac{1}{q^2+r+\tilde{V}(q)},$$

with the renormalized mass $r=r_0+\int[d^3q/(2\pi)^3]G$. $\tilde{V}(q)$ is the Fourier transform of $V(x)$. Within the SCSA the self-energy has diagonal elements $\Sigma_G=2G\otimes D_G$ and off-diagonal elements $\Sigma_F=2F\otimes D_F$ in replica space, where D_G and D_F being, respectively, the diagonal and off-diagonal elements of $\mathcal{D}$. These equations form a closed set of self-consistent equations which enable us to solve for G and F, and then determine the configurational entropy via

$$S_c=\int d^Dq\left\{s\left[\frac{F}{G}\right]-s\left[\frac{F\otimes F}{(uT)^{-1}+G\otimes G}\right]\right\}. \tag{4}$$

Here, $s[x]\equiv -x-\ln(1-x)$.

In the limit of small and large γ it is possible to make analytic progress. For large γ the short-range part, i.e., the gradient term in Eq. (2), dominates, and $V(r)$ can be neglected. No glassy state with finite Edwards-Anderson parameter results in this ordinary φ^4 theory. The situation is more interesting in the limit of small γ, i.e., for long-range interactions. Using $\tilde{V}(q)=\alpha^2\psi(q/\gamma)$ with $\psi(z)=4\pi[\sin(z)-z\cos(z)]/z^3$, it follows for $\gamma\ll\alpha$ that now the gradient term in Eq. (2) can be neglected compared to the Kac-type interaction. The long wavelength behavior is dominated by the long-range interaction. The short-range interaction becomes effectively local and has no characteristic length scale anymore. The correlations are dominated by wave vectors which minimize $\tilde{V}(q)$. Since $\psi(z)$ is minimal (and negative) for $z=z_0=5.76$, the dominating peak in the correlation function occurs at $q_0=z_0\gamma$, independent of α:

$$G_0(q)\approx\frac{Z}{\xi^{-2}+(|\mathbf{q}|-q_0)^2}. \tag{5}$$

Here $Z=(2/c)(\gamma/\alpha)^2$ is the weight of the peak with width characterized by $\xi^{-2}=Z(r+c\alpha^2)$, where $c=\psi''(z_0)\approx 0.361$. This expansion around $q=q_0$ elucidates the correspondence with the analysis performed in Ref. [6]. A calculation along the lines of Ref. [6] determines T_A for large u ($\gg q_0^3\xi^{-2}$) as the temperature where the ratio of the correlation length ξ and the modulation length $l_0=2\pi/q_0$ becomes of order unity (larger than 2 within the SCSA). Inserting Eq. (5) into Eq. (4) yields then for the configurational entropy, at T_A, $S_c(T_A)=VC\gamma^3$, with $C\approx 6.81\times10^{-3}$. In the limit of small u a glassy state occurs as well but the criterion for l_0q_0 becomes more complex. The longer ranged the interaction,

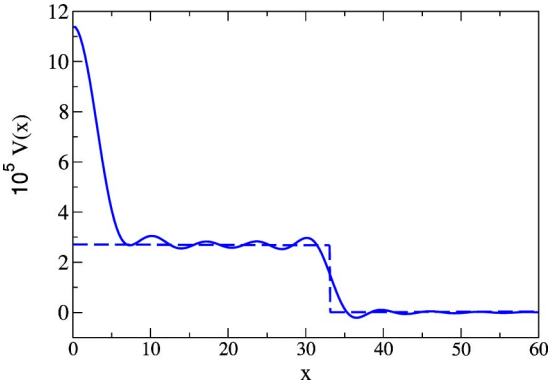

FIG. 1. Potential used in the numerical calculations (solid line) and the step-function potential with $\gamma=0.03$ (dashed line).

the smaller is the number of metastable states per unit volume. As expected, glassiness disappears in the van der Waals limit $\gamma\to 0$ [19].

While we are not able to solve the set of self-consistent equations for the bare form of the step-function potential (which has arbitrary large harmonics in its Fourier transform complicating the numerics), we found a numerical solution after adjusting the potential to the one depicted by the solid line in Fig. 1 for $r_0=0.1494>0$, $\gamma=0.03$, $u=1.79$, and $\alpha=1$ (we use units where the upper cutoff of the momentum integration is unity). The strong short-ranged repulsion is a result of the large momentum cutoff in the numerics. In Fig. 2 we show the temperature dependence of S_c. The behavior of S_c matches the entropy crisis scenario of the random first-order transition theory [8]. The mode-coupling temperature T_A and the Kauzmann temperature T_K can be unambiguously identified. Furthermore, we show in Fig. 3 the correlation functions $G(q)$ and $F(q)$. In addition to the pronounced peak at q_0 we can also see higher order structures in the instantaneous correlation function $G(q)$, which become strongly suppressed in the long time correlation function $F(q)$. A novel length scale, the *defect wandering length* λ, that determines the suppression of the long time correlations for large q emerges as a result of the off-diagonal self-energy in replica space [6] $\Sigma_F(q_0)=-(2/\lambda)^2$.

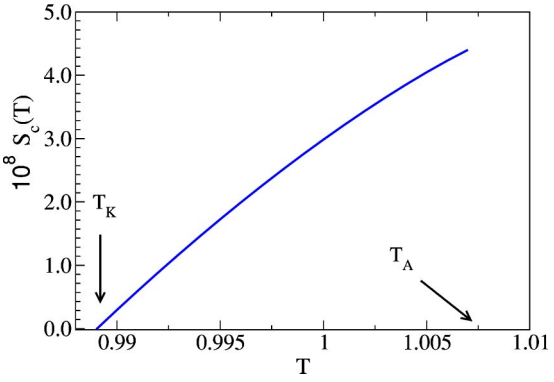

FIG. 2. Configurational entropy S_c as function of temperature for $r_0=0.1494$, $\gamma=0.03$, $u=1.79$, and $\alpha=1$.

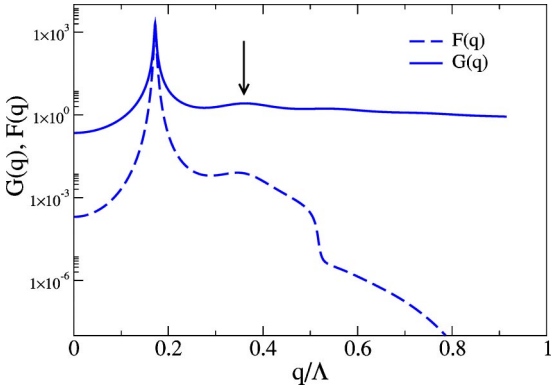

FIG. 3. Instantaneous correlation function $G(q)$ (solid line) and long time correlation function $F(q)$ (dashed line) for $\gamma=0.03$, $r_0=0.1494$, $u=1.79$, and $\alpha=1$. The arrow points at the position of the first secondary peak.

Our analysis enables us to analyze what kind of interaction, $V(x)$ of Eq. (1), can cause a glassy state. It is sufficient if the Fourier transform $\tilde{V}(q)$ of the potential possesses a minimum at q_0, with $\tilde{V}(q_0)<0$. Then the system exhibits a spinodal even for a purely repulsive interaction ($r_0>0$), in distinction to the model discussed in Ref. [5,6]. We recall that proximity to a mean-field spinodal provides a large ξ in addition to the Kac potential range, and thus self-consistently leads to frustration. One can in fact "map" the van der Waals glass [15] into the stripe glass [6]. Note, in the case of a Kac-type Gaussian potential [20] with $\phi(x)=\exp(-x^2)$, the Fourier transform of this potential is monotonic. A modulation length l_0 at the mesoscale does not occur and no glassy behavior is anticipated in the absence of the short-ranged gradient term. This agrees with the conclusion reached in Ref. [14]. In this case, both, the gradient term in the Hamiltonian and $r_0<0$ are necessary in order to find glassiness at mesoscales.

From these considerations it seems to follow that, for the model, Eq. (1), the free-energy landscape of metastable states which causes glassiness originates from configurations of mesoscopic defects. The origin of the glassiness has been discussed in detail in Ref. [6] in terms of the defect wandering length λ which depends on ξ and l_0. In the parameter region where the system acquires modulation at l_0, the mesoscopically ordered state constitutes the global minimum of the free energy $\mathcal{F}$, or the ground state. With respect to this ordered array of mesoscopic structures, excitations such as dislocations are termed defects. The defect-wandering length λ is the distance on which a defect can move freely in the lattice of the mesoscopic structure. When $\lambda<2l_0/3$, the defects are pinned by the underlying lattice of the mesoscopic structure [6]. A distribution of such pinned defects becomes a local minimum of $\mathcal{F}$. The organizations of defects should be responsible for the exponentially large number of metastable states $\mathcal{N}=\exp S_c$, where S_c is extensive. This picture is consistent with the findings of Ref. [14] that the fcc arrangement of the clumps has lower free energy than those of all frozen amorphous clump configurations. In this case, the fcc clump configuration is an ordered array of mesoscopic spherical

structures. The amorphous clump phases are the organizations of defects about the ordered lattice of these mesoscale spherical structures.

Another interesting question is whether glassiness is also possible with a microscopic l_0 of the order of the hard core radius of the atoms. The defect-pinning picture for the metastable configurations described above is intuitively clear and consistent with the three-dimensional models where l_0 is mesoscopic. Nothing in the argument forbids its application to a circumstance where l_0 is the microscopic lattice constant. To study this in more detail, we have investigated a 1D φ^4 model on a lattice in which the frozen configurations of kinks are expected to give a large number of metastable states. This occurs in the parameter regime where the continuous variable φ can be mapped to the 1D Ising model with nearest-neighbor interaction, which has been shown to have $S_c=0$ [21]. An estimate of the number of low-lying metastable states reflects *algebraic*, instead of exponential size dependence, leading to $\lim_{V\to\infty} S_c/V=0$. While the effect of dimensionality is not clear, an interesting scenario is that exponentially large number of metastable states occur only in pinned mesoscopic structures, not in trapped microscopic defect states.

In summary, we have demonstrated the emergence of glassiness (in the sense of a finite configurational entropy) in a system interacting through a Kac-type repulsive step potential. In the absence of a short-ranged interaction glassiness can occur if $\tilde{V}(q)$ possesses at least one minimum. The concept of a defect-wandering length is useful for understanding the source of the exponentially large number of metastable states. The picture of the origin of the configurational entropy as the organizations of defects in ordered arrays of mesoscopic structures is consistent with the numerical findings in Ref. [14]. The glassiness we have found is due to configurations of mesoscopic defects. Based on the analysis of a 1D Ising model, it is speculated that only pinning of defects about the mesoscopic pattern can give rise to exponentially large numbers of metastable states.

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