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

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(November 23, 2018)

We study a system with a weak, long-range repulsive Kac-type step-function interaction within the framework of a replicated effective \( \varphi^4 \)-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.

64.70.Pf, 61.43.Fs, 71.55.Jv, 74.80.-g

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, bubbles of electronic states of high Landau levels in quantum Hall systems, domains in magnetic multilayer compounds, and mesoscopic structures formed in self-assembly systems. 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: for example the macroscopic phase separation is frustrated by the competing long-range interactions. 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, where glassiness is attributed to an exponentially large number of metastable states, originally emphasized by Kauzmann. The fact that configurational entropy is needed for slow motions in glasses was first described by Gibbs and DiMarzio. 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, \( N \), i.e., the configurational entropy, \( S_c = \ln N \), becomes extensive. This cross-over 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. 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 \( \varphi^4 \)-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, was shown to, alternatively, drive the system into an amorphous state, the stripe glass. It is of particular interest to explore to what extent 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

\[
V(x) = a^2 \gamma^D \phi(\gamma x),
\]

with \( \phi(y) = 1 \) for \( y \leq 1 \) and zero otherwise. Here, \( \gamma \) controls the amplitude and range of the potential, whereas the inverse length \( a \) characterizes the integral strength \( \int d^D x V(x) \propto a^2 \). 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, where \( a \) is related to the long-range force of the van
nder van der Waals theory. For the particular 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. Using Monte Carlo simulations, the appearance of many metastable amorphous “clump” configurations was demonstrated in Ref. [14]. We find that an analysis of a replicated $\varphi^4$-theory along the lines of Ref. [6] is useful as an alternative strategy.

In this paper 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 $\gamma$ no actual frustration between different interactions is necessary, which is different from the model studied in Ref. [5,6]. We demonstrate that glassiness is due to multiple configurations of self-assisted 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 behaves for $D = 3$ like $S_c/V \propto \gamma^3$, where, $V$ is the volume of the system. A model of glassy behavior with the Kac-type long-range 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

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

with $V(x)$ of Eq. (1). The usual equilibrium free energy $\mathcal{F} = -T \ln Z$ 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. [6], a replica approach is proposed to overcome this limitation and allows us to probe the number of metastable states in models with the additional long-range interaction $V(x)$. We adopt the self-consistent screening approximation to the replicated $\varphi^4$-theory developed in Ref. [6], where 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 $F(q) = \langle \varphi^a(q)\varphi^b(-q) \rangle$ between the fields in different replicas. Here, $a \neq b$ are the replica indices and $m$ is the number of replicas. The quantity $F(q)$ equals the Edwards-Anderson order-parameter, $\lim_{t \to \infty} \langle \varphi(-q,t)\varphi(q,0) \rangle$, which becomes nonzero in the glassy state, or when ergodicity is broken.

Within the self-consistent screening approximation, the free energy $\mathcal{F}(m)$ can be expressed as

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

and the configurational entropy $S_c$ is related to $\mathcal{F}(m)$ by $S_c = \frac{1}{m} \left. \frac{d\mathcal{F}(m)}{dm} \right|_{m=1}$, where $\mathcal{G}$ is the generalized correlation function matrix, defined by $\mathcal{G} = (G - F + F \Pi)\Pi^{-1}$, where $\Pi$ is the generalized polarization matrix defined as $\Pi = (G \otimes F - F \otimes G)\Pi + (F \otimes F)\Pi$, where $\otimes$ denotes convolution in Fourier space. The replicated Schwinger-Dyson equation can be written as $\mathcal{G}^{-1} = G_0^{-1}\Pi + \Sigma$, where $\Sigma$ is the self-energy and

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

with the renormalized mass $r = r_0 + \int \frac{d^3q}{(2\pi)^3} G$. $\tilde{V}(q)$ denotes the Fourier transform of the potential $V(x)$. Within the self-consistent screening approximation the self-energy has diagonal elements $\Sigma_\alpha = 2G \otimes D_G$ 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 the matrix $\mathcal{D}$. 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

$$
S_c = \int dq \left\{ S\left[ \frac{F}{G} \right] - S\left[ \frac{F \otimes F}{(uT)^{-1} + G \otimes G} \right] \right\}.
$$

Here, $S[x] \equiv -x - \ln(1-x)$. It is obvious from the above equation that $F \neq 0$ implies $S_c \neq 0$.

In the limit of small and large $\gamma$ it is possible to make analytic progress. For large $\gamma$, i.e. short-range potentials the gradient term in Eq. (4) dominates and $\tilde{V}(q)$ can be neglected. No glassy state with finite Edwards-Anderson parameter results. The situation is more interesting in the limit of small $\gamma$, i.e. for long-range interactions. Using $\tilde{V}(q) = \alpha^2 \tilde{\psi}(q/\gamma)$ with $\tilde{\psi}(z) = 4\pi(\sin(z) - z \cos(z))/z^3$, it follows for $\gamma \ll \alpha$ that the gradient term in Eq. (4) 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 dominant peak in the
correlation function occurs at $q_0 = z_0 \gamma$, independent of $\alpha$:

$$G_0(q) \approx \frac{Z}{\xi^{-2} + (|q| - q_0)^2}. \quad (6)$$

Here $Z = \frac{2}{\pi} (\gamma/\alpha)^2$ is the weight of the peak with width characterized by $\xi^{-2} = Zr + c\alpha^2$, 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 $T_A$ as the temperature where the ratio of the correlation length $\xi$ and the modulation length $l_0 = 2\pi/q_0$ becomes larger than 2. Inserting Eq. (6) into Eq. (5) yields for the configurational entropy $S_c = VC\gamma^3$, with $C \approx 6.81 \times 10^{-3}$. The longer range the interaction, the smaller is the number of metastable states per unit volume. As expected, glassiness disappears in the van der Waals limit $\gamma \to 0$ [17].

The set of self-consistent equations is solved numerically, without assuming Eq. (6). A slightly modified Kac-potential (see Fig. 1) has been used for convenience. The major conclusions of this paper seem not affected by this modification. In Fig. 2, we show the temperature dependence of $S_c$ for $r_0 = 0.1494 > 0$ and $u = 1.79$ (we use units where the upper cutoff of the momentum integration is unity). The behavior of $S_c$ matches identically 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 $F(q)$. The typical length scale which determines the suppression of long-time correlations for larger $q$ is the defect wandering length $\lambda$ which results from the off-diagonal self-energy in replica space $\Sigma_{\phi}(q_0) = -\left(\frac{1}{\pi}\right)^2 [8]$

Our analysis allows us to determine what kind of interactions can cause a glassy state. For small $\gamma$ the short-range term will be effectively local. Competing interactions of different length scales can satisfy the glass-forming condition. Their presence is, however, not necessary. We have just demonstrated that nonzero configurational entropy can arise even if there is no explicit competition between the interaction length scales. In this case, not only does $V(q)$ possess a minimum at $q_0$, but also $V'(q_0)$ is negative. The system exhibits a spinodal when $r_0 > 0$, i.e. for a purely repulsive interaction, in distinction to the model discussed in Ref. [5,6]. The glass-forming criterion $\xi \geq 2l_0$ can be fulfilled even in the absence of the gradient term. We recall that proximity to a mean-field spinodal provides a large $\xi$ in addition to the Kac potential range, and thus self-consistently leads to frustration. One can in fact “map” the van der Waals glass [14] into the stripe glass [17]. It is thus possible to predict if glassiness occurs in a system interacting through a mesoscale potential $V(x)$. For example, in the case of a Kac-type Gaussian potential [17] 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-range gradient term. This agrees with the conclusion reached in Ref. [17]. Both the gradient term in the Hamiltonian and $r_0 < 0$ are necessary in order to find similar glassiness at mesoscales.

From these considerations it seems to follow that 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 a novel length scale, the "defect-wandering length $\lambda$" which depends on $\xi$ 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 $F$, or the ground state. With respect to this ordered array of mesoscopic structures, excitations such as ‘dislocations’ are termed defects. The defect-wandering length $\lambda$ is the distance...
on which a defect can move freely in the lattice of the mesoscopic structure. When \( \lambda < 2 l_0/3 \) [4], the defects are pinned by the underlying lattice of the mesoscopic structure. 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 \( l_0 \) on 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 3D 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 \( \varphi^4 \)-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 \( \varphi \) can be mapped to the 1D Ising model with nearest-neighbor interaction, which has been shown to have \( S_c = 0 \) [14]. A crude 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, it is thought not to change the system size dependence of the number of low-lying metastable states from algebraic to exponential. We thus conjecture that while pinning generates metastable states, the internal organizations of the defects with respect to a mesoscopically ordered state give rise to an exponentially large number of these metastable states. An extensive \( S_c \) does not occur in the case of pinned defects about a microscopic lattice because there are no internal degrees of freedom.

In summary, we have demonstrated glassiness (in the sense of a finite configurational entropy) in a system interacting through a Kac-type repulsive step-potential. We show that although the mesoscopic modulation length \( l_0 \) is due to the interaction potential alone, in contrast to the model proposed in Ref. [3], the underlying principle for glass formation is identical, i.e. \( \xi \geq 2 l_0 \). In the absence of a short-range interaction (the gradient term in the Hamiltonian) this criterion for glassiness can only be fulfilled when \( \hat{V}(q) \) 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.

KL acknowledges a Director’s Fellowship at Los Alamos National Laboratory. This research was supported by the Department of Energy, under contract W-7405-ENG-36 (KK) and W-7405-ENG-82 (JS). An additional partial support to KK by the Cooperative Research under the Japan-U.S. Cooperative Science Program sponsored by Japan Society of Promotion of Science is also gratefully acknowledged. JS acknowledges helpful discussions with P. G. Wolynes and the hospitality of the Max Planck Institute for Physics of Complex Systems, Dresden. We thank W. Klein for discussions. This work was supported by the US Department of Energy.

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