Glass phenomenology from the connection to spin glasses

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Typical features of glass phenomenology such as the Vogel-Fulcher law, the Kauzmann paradox, and the Adam-Gibbs relationship are shown to follow from the recently discovered mapping of glasses to Ising spin glasses in a magnetic field. There seems to be sufficient universality near the glass transition temperature T_g such that study of the spin-glass system can provide semiquantitative results for supercooled liquids.

I. INTRODUCTION

Under fast enough cooling or densification, materials which are as diverse as molecular and polymeric liquids, colloidal suspensions, granular assemblies, and molten mixtures of metallic atoms may form glasses [1]. These are amorphous states that may be characterized mechanically as a solid, but lack long-range crystalline order. Despite all the work devoted to the subject, the mechanisms responsible for the vitrification processes are not well understood and the transition to the glassy state remains one of the most controversial problems in condensed matter physics.

In a recent paper [2], using an effective potential method, a replica formalism has been set up to describe supercooled liquids. This approach shows that the thermodynamics of these systems near their glass transition temperature T_g is equivalent, in the sense of "universality classes," to that of Ising spin glasses in a magnetic field h [2]. Spin-glass droplet scaling ideas [3,4] were used to discuss the consequent expected glass phenomenology. This approach would be appropriate if the length scales of cooperatively rearranging regions near T_g were many times larger than the intermolecular separation. In fact, recent studies [5] have indicated that this length scale is rather modest and only a few intermolecular distances. As a consequence, glasses are not really in the regime where droplet scaling ideas are appropriate. We shall therefore examine in this paper the glass phenomenology which arises when the correlation length is not large but instead is in the precursor regime to the droplet scaling limit. Rather to our surprise, we are able to find in this regime all the characteristic features of glass phenomenology such as the Vogel-Fulcher relation [1], the Kauzmann temperature [6], the Adam-Gibbs relation [7], etc

We shall study in particular the Edwards-Anderson (EA) Ising spin-glass model [8] in the presence of an external magnetic field h both in one dimension (1D) and in three dimensions (3D). The behavior in both dimensions is similar, but the 1D case can be studied more thoroughly as its equilibrium properties can be determined exactly by means of a renormalization group approach and its dynamical properties are accessible via Monte Carlo simulations. Even in the 1D case, the model is able to mimic most of the experimental observations on supercooled liquids. An apparent Kauzmann paradox [6] is found, accompanied by a growing (but still modest at the fields which we use) length scale ξ and by an apparent divergence of the relaxation time as in the Vogel-

Fulcher (VF) equation with $T_{VF}=T_K$ [1]. There is thus an apparent thermodynamical and dynamical singularity at a finite temperature T_K, but it is not a true transition. T_K is just a crossover temperature such that when $T \lesssim T_K$ the growth of ξ as T decreases has largely ceased. The 3D case cannot be solved exactly but has been studied within the Migdal-Kadanoff approximation (MKA) [9,10], and a similar glass phenomenology emerges. But there are some significant difference between the 1D and 3D cases, due to the fact in 1D there is no finite-temperature spin-glass transition, but only a diverging length scale as $T \rightarrow 0$ when $h=0$, whereas in 3D, there is in zero field a finite-temperature transition, and so in order to have a length scale of only a few intermolecular diameters at low temperatures, a large field has to be applied. Our work within the MKA in 3D does not provide a quantitatively accurate picture, but the results are so encouraging that it would seem worthwhile to attempt to get more quantitative results, probably by use of Monte Carlo methods. Unfortunately glass time scales are so long compared to molecular collision time scales that realistic simulations will be challenging.

The investigations presented here suggest a new framework to understand glass behavior: features of the intermolecular potential and the density determine the value of the field h and the temperature scale, but once these are fixed, there is sufficient universality left near the glass transition T_g that the mapping to Ising spin glasses in a field provides a semiquantitative account of both the thermodynamic properties of glasses and those dynamical features which can be undestood in terms of flipping and cooperative rearranging of spin domains of linear extent ξ sitting in a random effective magnetic field, requiring free energy activation over barriers.

This paper is organized as follows: in Sec. II we solve the EA Ising spin glass in an external magnetic field in one dimension by using a decimation approach and we study its dynamical properties by performing Monte Carlo simulations; we then discuss the connection to the phenomenology of glasses. In Sec. III we examine the three-dimensional case by means of the Migdal-Kadanoff approximation. Finally, in Sec. IV, we present some concluding remarks.

II. EA ISING SPIN GLASS IN ONE DIMENSION

The EA Ising spin-glass Hamiltonian in 1D in the presence of a uniform external magnetic field reads

$$\mathcal{H} = -\sum_i J_i \sigma_i \sigma_{i+1} - h \sum_i \sigma_i, \qquad (1)$$

where the spins σ_i can take values ± 1 and the nearest-neighbor couplings J_i are independent of each other and Gaussianly distributed with zero mean and standard deviation J. In principle h could be a function of temperature but we shall regard it as a temperature independent constant, whose magnitude is chosen in both 1D and 3D so that the low-temperature spin-glass correlation length ξ is of the order of a few lattice spacings and so is comparable to the glass correlation length of real glasses at T_g [5]. We evaluate the free energy of the system by using an iterative real-space renormalization group technique [9,10]. It consists of tracing out every other spin in the system, thereby generating new effective interactions between the remaining spins which sit in new magnetic fields:

$$\sum_{\sigma_{i+1}=\pm 1} \exp\left(\beta\left[J_i^{(n)}\sigma_i\sigma_{i+1} + J_{i+1}^{(n)}\sigma_{i+1}\sigma_{i+2} + \sum_{j=i}^{i+2} h_j^{(n)}\sigma_j\right]\right)$$
$$= \exp(W_{i+1}^{(n+1)} + \beta[J_i^{(n+1)}\sigma_i\sigma_{i+2} + h_i^{(n+1)}\sigma_i + h_{i+2}^{(n+1)}\sigma_{i+2}]). \qquad (2)$$

At the nth step in the decimation process, $J_i^{(n)}$ and $h_i^{(n)}$ have probability distributions, which evolve with the iteration. In 1D, the EA model has a genuine critical point at $(T=0, h=0)$, corresponding to a nontrivial fixed point of the recursion relations. Conversely, at any finite temperature and magnetic field, the system evolves toward a trivial "random paramagnetic" fixed point: the variance of the effective couplings decreases under iteration and approaches zero, whereas the effective magnetic fields have a distribution which approaches a Gaussian, with mean h (i.e., the initial value of the magnetic field) and variance $\sigma_h(T, h)$.

For each realization of the quenched disorder, the free energy f_J can be determined exactly by summing the spin-independent terms $W_i^{(n)}$ which are generated at each step of the decimation [10]. Once the average over the disorder is taken, $f = [f_J]_J$, the entropy density is obtained using $S = -\partial f/\partial T|_h$. In Fig. 1(a) the entropy is plotted versus the temperature for three different values of the magnetic field, $h = 0.05$, 0.125, and 0.2. The figure shows a temperature range in which the entropy decreases linearly and would be extrapolated to vanish at $T_K(h)$ as

$$S \simeq k_B c(h)[T - T_K(h)], \qquad (3)$$

demonstrating that the model has a "Kauzmann paradox" similar to that observed in supercooled liquids. However, below a crossover temperature $T^\star(\lesssim T_g)$, the entropy deviates from linearity and does not vanish completely except at $T=0$.

By computing the derivative of the free energy with respect to the variation of the magnetic field on two different sites, it is possible to evaluate the equilibrium connected correlation function
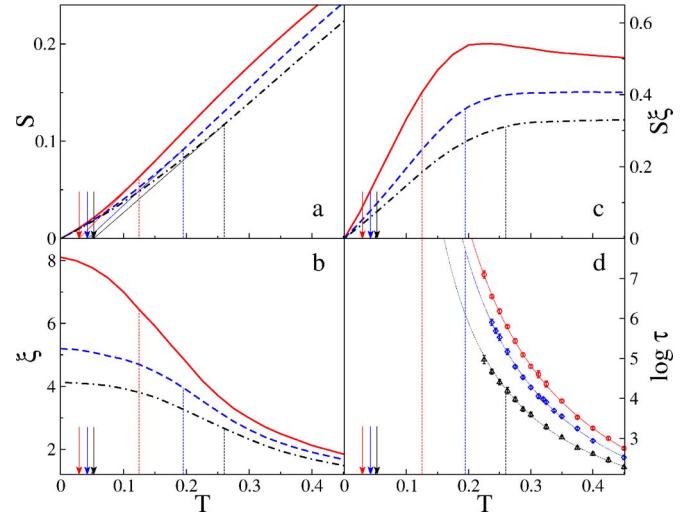

FIG. 1. (Color online) One-dimensional EA model in a field for $h=0.05$ (solid line and circles), $h=0.125$ (dashed line and diamonds), and $h=0.2$ (dash-dotted line and triangles). (a) Entropy per spin S; (b) equilibrium correlation length ξ; (c) Adam-Gibbs relation, temperature dependence of $S\xi$; (d) logarithm of the relaxation time τ as a function of the temperature. The curves correspond to the Vogel-Fulcher fits, Eq. (6), with $T_{VF}=T_K$. The arrows indicate the Kauzmann temperatures T_K, whereas the vertical dashed lines correspond to the crossover temperatures T^*.

$$\langle\sigma_i\sigma_{i+l}\rangle_c^2 = \left(T^2 \left.\frac{\partial^2 \ln Z}{\partial(\delta h_i)\partial(\delta h_{i+l})}\right|_{\delta h_i=\delta h_{i+l}=0}\right)^2. \qquad (4)$$

From the exponential decay of the correlation function $[\langle\sigma_i\sigma_{i+l}\rangle_c^2]_J \sim \exp(-l/\xi)$, we extract the equilibrium correlation length of the system, ξ, plotted in Fig. 1(b) for the same values of the magnetic field as before. ξ increases as the temperature is decreased, but at low enough temperatures ($T \lesssim T^\star$), it bends over and approaches a finite value at $T=0$, proportional to $h^{-2/3}$, as predicted by the droplet picture [3,4] on equating the energy to flip a domain of size ξ to the magnetic field energy which could be gained, $J\xi^\theta \sim h\xi^{d/2}(\sim k_B T_K)$, and for $d=1$, $\theta=-1$.

In order to establish a connection with the dynamical features of glass-forming liquids, we have studied the dynamical properties of the 1D model by performing Monte Carlo simulations of a system of 1024 spins. We have computed the spin-spin cumulant autocorrelation function, defined as

$$C(t, t_w) = \left[\frac{1}{N}\sum_i \langle\sigma_i(t+t_w)\sigma_i(t)\rangle_c\right]_J. \qquad (5)$$

For large enough waiting times t_w, the system reaches stationarity, characterized by time transitional invariance—i.e., $C(t, t_w) = C(t)$. Although the mapping established in Ref. [2] is explicit only for equilibrium quantities and might not extend to dynamical features, we find that, in analogy with glass formers, $C(t)$ is very well fitted by a stretched exponential form $C(t) \sim \exp[-(t/\tau)^\beta]$, where $\tau(T, h)$ is the system relaxation time. The spin-spin autocorrelation function is plotted in Fig. 2 for several values of the temperature.
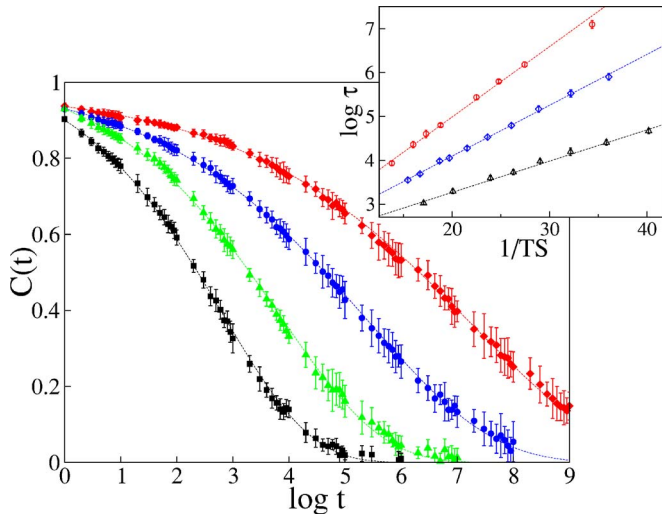
FIG. 2. (Color online) Main frame: time-dependent spin-spin autocorrelation function $C(t)$ as a a function of $\log t$ for $h=0.05$ and $T=0.45$ (squares), $T=0.35$ (triangles), $T=0.275$ (circles), and $T=0.225$ (diamonds). The data are averaged over 16–32 independent realizations of the disorder and over t_w. The dashed line correspond to stretched exponential fits $C(t) \sim \exp[-(t/\tau)^{\beta}]$ with $0.2 < \beta < 0.3$. Inset: Adam-Gibbs relation: logarithm of the relaxation time τ as a function of $1/TS$ for $h=0.05$ (circles), $h=0.125$ (diamonds), and $h=0.2$ (triangles). The straight lines are guides for the eye.

The relaxation time is plotted in Fig. 1(d) for $h=0.05$, 0.125, and 0.2 as a function of the temperature. Similarly to what happens in supercooled liquids [1] a Vogel-Fulcher law

$$\log \tau = \log \tau_0 + \frac{DT_{VF}}{T - T_{VF}} \qquad (6)$$

is able to fit quite accurately the data for each value of the magnetic field (over four to five decades), with the VF temperature T_{VF} set equal to the Kauzmann temperature T_K [1]. Again, the dynamical singularity is only apparent, since the relaxation time diverges only at $T=0$ according to an Arrhenius law. At low enough temperature τ deviates from the VF law. Such a departure starts to emerge for $h=0.2$ when $T \lesssim 0.25$. Interestingly, the onset of the deviation from the VF fit seems to coincide with the crossover temperature T^* at which the entropy deviates from linearity. This behavior is consistent with the Adam-Gibbs (AG) relation [7] $\log \tau = A_{AG} + B_{AG}/TS(T)$, which holds in the temperature range explored by the simulations, as shown in the inset of Fig. 2. The original derivation [7] of the AG equation relies on the assumption of the existence of correlated regions of size ξ rearranging cooperatively and on the hypothesis that $S\xi^d \sim$ const. As shown in Fig. 1(c), this relation seems to hold in the intermediate temperature window explored in the simulations, whereas it breaks down below T^*.

One might wonder whether the whole entropy, S, which we have calculated, plays the role of the "configurational entropy" for supercooled liquids in the AG relation. When $T < T_K$, the thermodynamics is dominated by the flipping of the few single spins for which the local field is comparable to

T. For $T > T_K$, the thermodynamics is dominated by the excitation of "droplets" of size ξ. Hence it is tempting to regard the very-low-temperature entropy in our spin-glass simulations as being the contribution to the entropy from a single state and that the configurational entropy is that which arises when many droplets are thermally excited. We have studied also the "configurational entropy" which is obtained by subtracting from S the linear contribution which fits the very-low-temperature entropy. However, the same qualitative results were found with this definition of S.

Due to the success of the AG relation, it is natural to expect that the dynamics of the system will be dominated by the flipping of spin domains of size ξ. Since the variance of the the effective couplings decreases under iteration and approaches zero after a few iteration steps, whereas the effective magnetic fields are Gaussianly distributed with mean h and variance $\sigma_h(T, h)$, one might guess that the dynamics of the system is equivalent to that of a chain of noninteracting spin domains of linear extent proportional to ξ, sitting in a random external field. Notice that this situation has been studied in Ref. [11]. Taking into account the time to pass a spin flip through the domain, which involves the breaking of the largest bond in the domain whose magnitude will be denoted by L_i, the time to reverse each spin domain will be of the form $\tau \propto \exp[(2L_i + 2h_i)/T]$. If the distribution of the L_i is also Gaussian, the distribution of the sum $(L_i + h_i)$ will be another Gaussian of variance $\sigma_L^2 + \sigma_h^2 T$. According to Ref. [11], this leads to the following expressions for the relaxation time $\tau \simeq \exp[4(\sigma_h^2 + \sigma_L^2)/T^2]$ and for the stretching exponent $\beta \simeq C[1 + 4(\sigma_h^2 + \sigma_L^2)/T^2]^{-1/2}$, with a constant $C=1$. We have verified that these formulas work quite well in describing the dynamics of the system in one dimension (with $\sigma_L \simeq 0.22$). Nevertheless, they are not *perfect*: the constant C is larger than 1 ($C \simeq 1.5$) and σ_L is too small. These discrepancies could be because the time it takes to flip the spins by breaking the largest bond on a line of spins of length ξ has not been handled with sufficient accuracy. The largest bond has its own probability distribution, which is just not a Gaussian. A full theory would be complicated. However, in 3D much larger values of the external field have to be taken to keep the magnitude of the correlation length only a few lattice spacings at low temperatures, so one could reasonably expect that the relaxation time is dominated just by the random fields alone.

The fragility D and the Kauzmann temperature T_K [see Eq. (6)] are both affected by the magnetic field h. More precisely, D decreases as h is increased (i.e., stronger glasses are described by larger fields), whereas T_K (and T^*) increases as h is increased. In the main frame of Fig. 3, the dependence of T_K on the fragility is plotted. We also plot the behavior of another two important quantities: the jump in the specific heat ΔC_p and the stretching exponent β (at $T=0.3$). The former can be estimated by (arbitrarily) setting $T_g \simeq T^*$, so that $\Delta C_p \sim c(h)T^*$, $c(h)$ being the slope of the entropy in the linear regime [see Eq. (3)]; the latter can be directly computed from numerical simulations.

Interestingly enough, β is found to be an increasing function of D, whereas ΔC_p decreases as D increases, in agreement with observations on supercooled liquids [12].
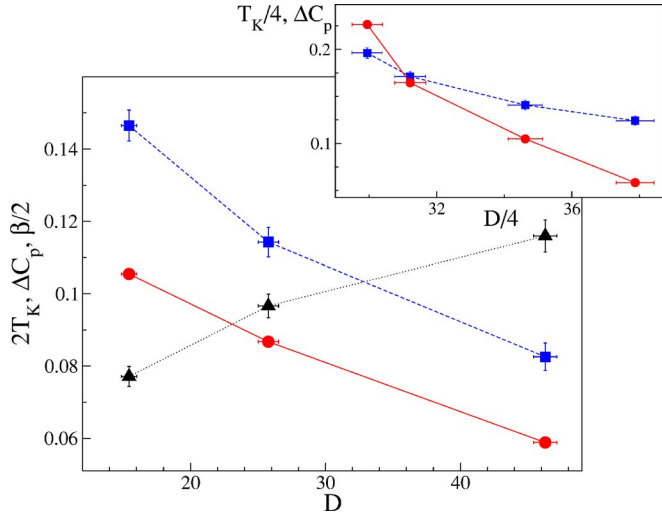
FIG. 3. (Color online) Main frame: Kauzmann temperature T_K (solid line and circles), jump in the specific heat ΔC_p (dashed line and squares), and stretching exponent β (dotted line and triangles) as a function of the fragility D extrected from the VF fit of $\log \tau$ in 1D. Inset: Kauzmann temperature T_K (solid line and circles) and jump in the specific heat ΔC_p (dashed line and squares) as a function of the fragility D extracted from the VF fit of $\exp[4\sigma_h^2/T^2]$ in 3D.

III. RESULTS IN THREE DIMENSIONS

We now turn to the 3D case, which is most relevant for real supercooled liquids. We have evaluated the free energy of the EA spin-glass model in a field by means of the MK approximation, a real-space renormalization group technique that gives approximate recursion relations for the flow of the coupling constants and magnetic fields distributions [9,10]. We have used the "bond moving" procedure, where the bonds on the 3D lattice are moved before each decimation step, so that no higher-order couplings are generated [10]: in a d-dimensional lattice, 2^{d-1} bonds are superimposed and added up, whereas the "naked" spins that are left behind have no couplings. Taking the trace over the spins that are on the main bonds leads to the coupling constants, according to Eq. (2), between neighboring spins on the coarse-grained lattice. The decimation procedure is iterated n times on a lattice of size $L=2^n$. There is a flexibility in the MK renormalization scheme as to how the fields are moved. We have treated the field terms as belonging to bonds: when a bond is moved we also move all its field terms to the end that is to be traced over next [10].

In 3D, within the MKA, when $h=0$ and $T<T_c$, $T_c \simeq 1.78$, the variance of the effective couplings grows indefinitely under iteration. For finite values of the magnetic field there is no evidence of a de Almeida–Thouless line [13]. The variance of the couplings might grow initially for low enough fields and/or temperatures, but it always decreases and eventually vanishes after a sufficient number of iteration steps, just like in 1D. The average value of the field distribution equals the initial value of the uniform magnetic field h, whereas the width of the distribution saturates at a finite value $\sigma_h(T,h)$.
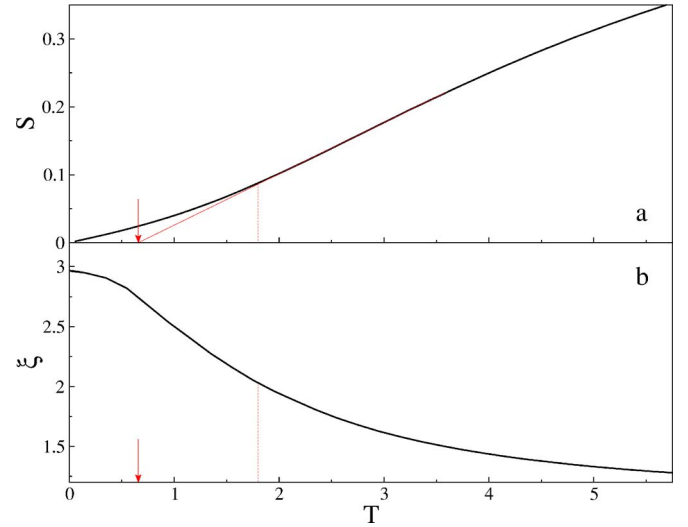

FIG. 4. (Color online) Three-dimensional EA model within the MK approximation for $h=2.0$. (a) Entropy per site S; (b) correlation length ξ. The vertical arrows and the vertical dotted lines correspond, respectively, to T_K and T^*.

The temperature dependence of the entropy per spin and the correlation length ξ, obtained within the MKA from the exponential decay of the variance of the effective coupling, $J_{ij}^{(n)}$, which decreases as $\exp(-2^n/\xi)$ at large n, are plotted in Figs. 4(a) and 4(b) for $h=2.0$, showing a scenario very similar to that found in 1D: there is a temperature range in which the entropy per site, S, is linear and is extrapolated to vanish at a finite Kauzmann temperature T_K; a crossover occurs at a higher temperature T^*, where the entropy deviates from linear behavior. The correlation length ξ grows as the temperature is decreased and approaches a finite value at $T=0$.

We also mention that, similarly to the 1D case, there is a modest range of values of the external magnetic field h (for $1.8 \lesssim h \lesssim 2.5$) for which the AG relation $S\xi^3 \sim$ const holds in the temperature region $T \gtrsim T^*$. This AG relation, however, breaks down below T^* and at high temperatures and in contrast to the 1D case is of less utility.

Due to the magnitude of the relaxation times, standard Monte Carlo simulations of the 3D model are more challenging than in the 1D case, and we will leave them for future investigations. However, since the values of interest of the magnetic field are much larger than in 1D, one can surmise that the flipping of a spin domain of size ξ sitting in a random external magnetic field Gaussianly distributed and with variance σ_h^2 is the dominant dynamical process; hence, the energy barriers involved in such processes might account reasonably well for the system's relaxation time, leading to $\ln \tau \simeq 4\sigma_h^2/T^2$ [11]. Following this hypothesis, we have verified that $\exp[4\sigma_h^2/T^2]$ can be well fitted by a VF law with $T_{VF}=T_K$ for $T>T^*$. From the VF fit of this quantity it is also possible to extract the fragility D in the 3D case. In the inset of Fig. 3, T_K and ΔC_p are plotted as a function of D, showing they have very similar behavior to that found in 1D.

The domain size ξ according to droplet scaling is given by equating the cost of flipping a droplet of size ξ, ξ^θ, to the field energy which might be gained, $h\xi^{d/2}$. As in 3D the ex-

ponent θ is small (≈ 0.2) [3], it follows that $\sigma_h^2 \sim h^2 \xi^d$ $\sim$ const., which implies that the AG relation $\ln \tau \simeq A/TS$ should hold.

The stetching exponent β would be expected to be $[1+4\sigma_h^2/T^2]^{-1/2}$, provided again that the time taken to pass the domain wall through the domain is not significant.

One feature of the MKA study in 3D is that the configurational entropy seems to be smaller than the quoted values near the glass transition, perhaps by as much as a factor of 3 [12]. In the derivation of the mapping to spin glasses [2] one can see that the field h will be a function of both the temperature and density, rather than simply being a temperature-independent constant as we have assumed here throughout for simplicity. Allowing for this temperature dependence could significantly change the entropy. For example suppose $h^2 = h_0^2 + b^2 T^2$; then, the high-temperature limit of the entropy is $S = \ln[2\cosh b]$ and, by adjusting b, can be made as large as desired.

IV. CONCLUSIONS

The mapping between supercooled liquids and spin glasses in an external magnetic field, proposed in Ref. [2], thus seems to provide a semiquantitative explanation of the properties of supercooled liquids including the Kauzmann paradox, the Vogel-Fulcher behavior of the relaxation time, the stretched exponential decays of correlation functions, a growing length scale, and the Adam-Gibbs relation in the regime $T \gtrsim T_g$, which is the precursor regime accessed by the experiments, where the correlation length is growing with temperature but is still only a few intermolecular distances. The droplet scaling limit studied in Ref. [2] is appropriate only when the correlation length is much larger than this. The large time scales which exist below the glass transition temperature T_g prohibit the taking of equilibrium data below it, and so the apparent thermodynamic and dynamical singularities at T_K cannot be accessed. In our scenario, T_K is only a crossover temperature at which the growing correlation length saturates to a constant value.

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