Constructing explicit magnetic analogies for the dynamics of glass forming liquids

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By defining a spatially varying replica overlap parameter for a supercooled liquid referenced to an ensemble of fiducial liquid state configurations, we explicitly construct a constrained replica free energy functional that maps directly onto an Ising Hamiltonian with both random fields and random interactions whose statistics depend on the liquid structure. Renormalization group results for random magnets when combined with these statistics for the Lennard-Jones glass suggest that discontinuous replica symmetry breaking would occur if a liquid with short range interactions could be equilibrated at a sufficiently low temperature where its mean field configurational entropy would vanish, even though the system strictly retains a finite configurational entropy. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3009827]

I. INTRODUCTION

The commonalities and contrasts between the glassy behavior of supercooled liquids and quenched disordered magnetic systems have been long studied. Both exhibit a diversity of long lived states with no apparent structural long range order. These states challenge the paradigms of standard many body physics. Starting in the 1980s, the disordered magnetic systems came under control, but only in the mean field limit, through the concept of broken ergodicity using replica methods that allowed averaging over quenched disorder. Despite the absence of quenched disorder, there is an analogy between the first order breaking of ergodicity predicted by mode coupling theory for structural glasses and the phase transition predicted for spin glasses that lack up-down symmetry (Potts spin glasses).[1,2] In mean field theory, the asymmetric spin glasses exhibit a Kauzmann entropy crisis[3] like that for supercooled liquids.

The analogy between glass forming liquids and mean field spin glasses is however incomplete. The observed dynamics of supercooled liquids fits the mean field mode coupling paradigm only modestly well.[4] The main problem with the mean field theory is its neglect of important activated motions that allow a supercooled liquid to reconfigure locally. The most convincing evidence for this is the near Arrhenius dynamics with large activation energy seen in structural glasses in the aging regime.[5]

Activated motions have infinite barriers in the mean field limit. Describing activated motions requires accounting for the finite interaction range. Accompanying a paucity of exact results,[6] even the empirical situation remains controversial for finite range random magnetic systems.[7,8] For the random field Ising magnet (RFIM), arguments based on renormalization group (RG) theory and droplet arguments do work well,[9–11] but controversy remains as to the extent Ising spin glasses partake of mean field versus droplet features.[12] Nevertheless, useful analogies between glass forming liquids and disordered magnets have been drawn showing how droplet arguments give the Vogel–Fulcher law.[13] Similar arguments have also been adduced using replicas.[3,14,15]

By applying density functional theory to determine the parameters in these droplet arguments,[16] one predicts a large number of confirmed quantitative results for liquids.[5] The resulting random first order transition (RFOT) theory bears some resemblance to the nucleation picture of ordinary first order phase transitions. The theory's core is an analogy to the random field Ising magnet in a field. The average field in the magnet is related to the configurational entropy density of the liquid.[13,16] Tarzia and Moore[17] suggested that supercooled liquids are related to Ising spin glasses in a field. When an average field is present, corresponding to a finite configurational entropy in the liquid, both the random field magnet and the spin glass have the same symmetry: neither model is expected to have a phase transition, although this is still somewhat controversial.[18] While both magnetic analogies agree on this point, the activated dynamics in the two different analogical magnets differ because the interface energies in spin glass droplets have weaker scaling than the random field ferromagnet. To quantify this distinction in this paper, we construct explicitly the analogy between a structural glass forming liquid and the corresponding short range disordered ferromagnet.

Replica methods, along with liquid state theory, allow an explicit mapping of the free energy landscape of a glass forming liquid onto a disordered Ising magnet. Using this explicit construction we may eschew droplet arguments entirely. Simulating the analogous magnet shows that the mapping reproduces, however, the main features of the RFOT analysis. The mean activation barrier and its fluctuations, which give rise to a nonexponential relaxation, can be com-

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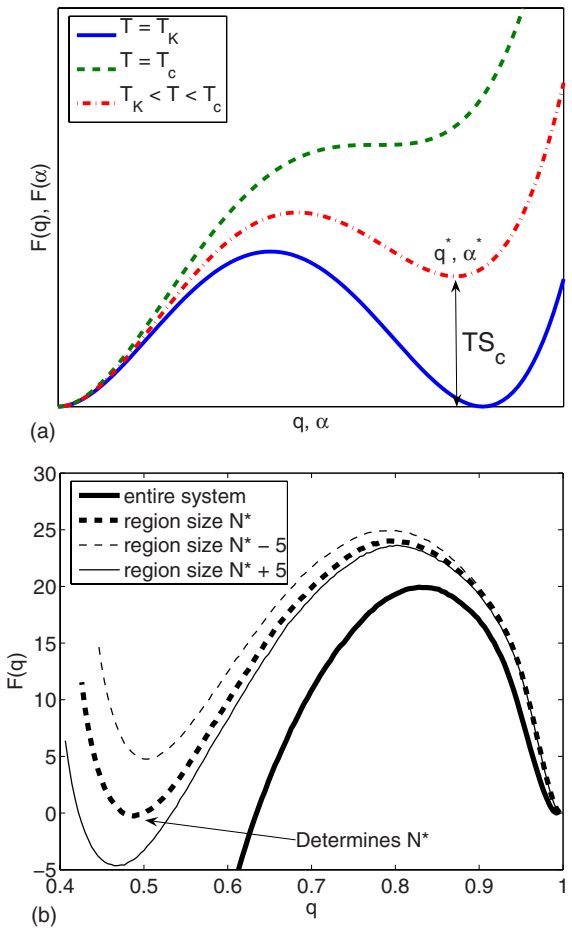

FIG. 1. (Color online) (a) Schematic mean field free energy profiles for supercooled liquids at the dynamical crossover temperature (dashed line), the Kauzmann temperature (solid line), and an intermediate temperature (dot-dashed line). In the mean field, the particle localization α and the structural overlap q are equivalent reaction coordinates. The secondary free energy minimum at $T_K<T<T_c$ demonstrates the existence of metastable structural states in supercooled liquids. (b) Free energy profiles calculated for the finite range Ising magnet analogous to the LJ liquid. The minimum size needed to escape the free energy minimum and thus reconfigure the liquid at $s_c=1.10$ is $N^*=148$ particles.

puted using importance sampling methods for the analog. Approximate arguments can place the analog system onto a phase diagram previously deduced for disordered magnets using RG. This construction suggests that under thermodynamic conditions when the mean field estimate for the configurational entropy would vanish, the liquid would still undergo a phase transition having one step replica symmetry breaking (RSB) despite the exact configurational entropy remaining nonzero.[19,20]

II. THEORY

The analogy yields a description of a structural glass in terms of discrete spinlike variables tied to the liquid structure equilibrated at one time. The structural glass is statistically homogeneous but nonuniform with a density $\rho(\mathbf{x})$ that is not translationally invariant. Liquid state theory provides a free energy as a functional of such a density $\mathcal{F}[\rho(\mathbf{x})]$. While the complete equilibrium free energy $F=-k_BT\ln Z$ assumes all phase space can be sampled, close to the glass transition there is trapping in locally metastable states which manifests itself as extensively many local minima described by a configurational entropy density $S_c=\ln N_{ms}$. This nonergodic behavior can be captured by a construction due to Monasson[21] in which an external random constraining pinning field couples m replicas of the system through an attractive potential. Each replica's density field is $\rho^k(\mathbf{x})$. The free energy of the m replica system is

$$F(m,\beta)=\lim_{g\to 0+}\left[-\frac{1}{\beta m}\ln\int\prod_{k=1}^{m}\mathcal{D}\rho^k(\mathbf{x})\times\exp\left\{-\beta\sum_k\mathcal{F}[\rho^k(\mathbf{x})]-\frac{g}{2m}\times\sum_{k,j,k<j}\int d\mathbf{x}[\rho^k(\mathbf{x})-\rho^j(\mathbf{x})]^2\right\}\right]. \quad (1)$$

The typical free energy of a metastable frozen state, $\tilde{F}=\partial mF(m,\beta)/\partial m|_{m=1}$, differs from the complete equilibrium free energy by an amount $\delta F=\tilde{F}-F=\partial F(m,\beta)/\partial m|_{m=1}=TS_c$. In contrast to Monasson's thoroughly field theoretic formulation, we separate the m replicas into one fiducial probe copy of particles interacting through the Hamiltonian $H(\{\mathbf{x}_i^f\})=\Sigma_{i<j}u(\mathbf{x}_i^f-\mathbf{x}_j^f)$ and $m-1$ others described by density fields. Here u is the microscopic interparticle potential. The pinning field on the other replicas is $\rho^f(\mathbf{x})=\Sigma_i\delta(\mathbf{x}-\mathbf{x}_i^f)$. We can write

$$F(m,\beta)=-\lim_{g\to 0}\frac{1}{\beta m}\ln\int\mathcal{D}\{\mathbf{x}_i^f\}e^{-\beta H(\{\mathbf{x}_i^f\})}\int\prod_{k=1}^{m-1}\mathcal{D}\rho^k(\mathbf{x})\times\exp\left\{-\beta\sum_{k=1}^{m-1}\mathcal{F}[\rho^k(\mathbf{x})]-\frac{g}{2m}\times\sum_{k=1}^{m-1}\int d\mathbf{x}[\rho^k(\mathbf{x})-\rho^f(\mathbf{x})]^2-\frac{g}{2m}\times\sum_{k=1}^{m-1}\sum_{j=1,k<j}^{m-1}\int d\mathbf{x}[\rho^k(\mathbf{x})-\rho^j(\mathbf{x})]^2\right\}. \quad (2)$$

In calculating the free energy with respect to the probe replica we ignore peripheral interactions not involving the probe, thus decoupling the partition function

$$F(m,\beta)=-\lim_{g\to 0}\frac{1}{\beta m}\ln\int\mathcal{D}\{\mathbf{x}_i^f\}e^{-\beta\mathcal{H}(\{\mathbf{x}_i^f\})}[Z_q]^{m-1} \quad (3)$$

such that each replica is constrained by a potential to the vicinity of the fiducial copy,

$$Z_q=\int\mathcal{D}\rho(\mathbf{x})\exp\left\{-\beta\mathcal{F}[\rho(\mathbf{x})]-\frac{g}{2m}\int d\mathbf{x}[\rho(\mathbf{x})-\rho^f(\mathbf{x})]^2\right\}. \quad (4)$$

For a glassy system, when $TS_c=(\partial F(m,\beta)/\partial m)|_{m=1}$ is finite, in the limit $m\to 1$, the replicated free energy is dominated by a saddle point corresponding to the spontaneous

ordering of replicas in phase space. The saddle point solution to the free energy is found by minimizing the exponential's argument,

$$\frac{\delta}{\delta\rho(\mathbf{x})}\left[\beta\mathcal{F}[\rho(\mathbf{x})]+\frac{g}{2m}\int d\mathbf{x}[\rho(\mathbf{x})-\rho^f(\mathbf{x})]^2\right]_{\rho=\tilde{\rho}}=0. \quad (5)$$

The free energy functional can be written, à la density functional theory, as the sum of an entropic cost to localize the density and an interaction term,

$$\beta\mathcal{F}[\rho(\mathbf{x})]\approx\int d\mathbf{x}\rho(\mathbf{x})\ln\rho(\mathbf{x})+\beta F_{\text{int}}[\rho(\mathbf{x})]. \quad (6)$$

While the free energy functional $\mathcal{F}[\rho]$ is globally minimized by a uniform equilibrium solution with mean density ρ_0, $\mathcal{F}[\rho]$ also has local minima corresponding to frozen aperiodic densities. The g coupling, even as g vanishes, picks out one particular minimum around the structural state ρ^f. Thus $\mathcal{F}[\rho]$ can be analyzed in terms of the similarity, or overlap $q=\int d\mathbf{x}(\rho(\mathbf{x})-\rho_0)(\rho^f(\mathbf{x})-\rho_0)$, between $\rho(\mathbf{x})$ and $\rho^f(\mathbf{x})=\Sigma_i\delta(\mathbf{x}-\mathbf{x}_i^f)$. A schematic of the free energy as a function of the order parameter q as computed in Refs. 14 and 22 is shown in Fig. 1(a). The free energy difference between the large overlap solution and the small overlap solution is the excess free energy of the frozen glass over the equilibrium free energy and is determined by TS_c.

The large overlap state is well approximated by a density distribution of a sum of Gaussians centered around the particle locations of the fiducial (probe) copy $\rho(\mathbf{x})=\Sigma_i\rho_i(\mathbf{x})=\Sigma_i(\alpha_i/\pi)^{3/2}e^{-\alpha_i(\mathbf{x}-\mathbf{x}_i^f)^2}$. The localization parameters $\{\alpha_i\}$ determine the local overlap. Near the large overlap minimum, $q(\alpha_i\gg\rho_0^{2/3})=\Sigma_i((\alpha_i/\pi)^{3/2}-\rho_0)$. In the opposite limit, near the global free energy minimum, the density ansatz reduces to the mean density and $q(\{\alpha_i\}\to 0)=0$.

For large values of $\{\alpha_i\}$ the particles are localized very near the fiducial locations $\{\mathbf{x}_i^f\}$ and F can be evaluated by using the independent oscillator approximation[23,24] which decouples the particles at the individual site level. Within this approximation F_{int} can be expressed as a sum of effective potentials between the interacting density clouds, $\beta V_{\text{eff}}(|\mathbf{x}_i^f-\mathbf{x}_j^f|;\alpha_j)\equiv-\ln\int d\mathbf{x}_j\rho_j(\mathbf{x}_j)e^{-1/2\beta u(\mathbf{x}_i^f-\mathbf{x}_j)}$,

$$\beta F_{\text{glass}}(\{\mathbf{x}_i^f\},\{\alpha_i\})=\sum_i\frac{3}{2}\ln\frac{\alpha_i\Lambda^2}{\pi e}+\sum_{ij}\beta V_{\text{eff}}(|\mathbf{x}_i^f-\mathbf{x}_j^f|;\alpha_j). \quad (7)$$

The localization parameters corresponding to the large overlap solution, $\{\alpha_i^\uparrow\}$, can be found by applying a self-consistency condition.[23,24] The existence of the free energy minimum at large overlap reflects the cage effect where the motion of a particle is restricted by its neighbors. To first order one may compute the potential $\beta V_e(\mathbf{x}_i-\mathbf{x}_i^f,\{\alpha_j\})\equiv\Sigma_j\beta V_{\text{eff}}(|\mathbf{x}_i-\mathbf{x}_j^f|;\alpha_j)$ and expand around small displacements of particle i, $w_i=|\mathbf{x}_i-\mathbf{x}_i^f|$,

$$\beta V_e(w_i,\{\alpha_j^\uparrow\})\approx\beta V_e|_{w_i=0}+w_i^2\frac{1}{6}\nabla^2\beta V_e|_{w_i=0}, \quad (8)$$

$$\beta V_e(w_i,\{\alpha_j^\uparrow\})\approx\beta V_e|_{w_i=0}+\alpha_i^\uparrow w_i^2. \quad (9)$$

The linear term gives no contribution because the fiducial replica becomes centered on a stationary location with all forces canceling. The localization parameter of particle i thus can be computed from the curvature of the effective potential, $\alpha_i^\uparrow=\frac{1}{6}\nabla^2\beta V_e(|\mathbf{x}_i-\mathbf{x}_i^f|=0,\{\alpha_j^\uparrow\})$, giving a self-consistent solution for $\alpha_i^\uparrow$.[24,25]

Near the uniformly low overlap state the interaction free energy F_{int} follows from the equilibrium liquid equation of state, $Z_{\text{EoS}}(\eta)$, where η is the packing fraction,[26]

$$F_{\text{liq}}^\downarrow=N\ln\rho_0\Lambda^3-N+N\int_0^\eta(Z_{\text{EoS}}-1)\frac{d\eta'}{\eta'}. \quad (10)$$

To characterize the reconfiguration events and to develop the magnetic analogy, one must also examine nonuniform solutions. At the interface between the two solutions there must be some energetic penalty due to the patching together of distinct configurational states. At an interface, one particle is in the large overlap state while its neighbor has small overlap, so the pair interaction becomes $\beta V_2^{\text{eff}}(|\mathbf{x}_i^f-\mathbf{x}_j^f|;\alpha_i^\downarrow,\alpha_j^\uparrow)=-\ln\int d\mathbf{x}_i d\mathbf{x}_j\rho_i^\downarrow(\mathbf{x}_i)\rho_j^\uparrow(\mathbf{x}_j)e^{-1/2\beta u(\mathbf{x}_i-\mathbf{x}_j)}$. The small overlap parameters $\{\alpha_i^\downarrow\}$ determine $\rho_i^\downarrow$ and are obtained in the self-consistent phonon theory by matching the entropy of the low overlap state calculated within the Gaussian density ansatz with the entropic term of the equilibrated liquid,

$$\sum_i\frac{3}{2}\ln\frac{\alpha_i^\downarrow\Lambda^2}{\pi e}=N\ln\rho_0\Lambda^3. \quad (11)$$

For any combination of the discrete values of $\{\alpha_i^\downarrow\}$ and $\{\alpha_i^\uparrow\}$, the free energy of the supercooled liquid is equivalent to a pairwise interacting model with spins located at the fiducial locations, $\{\mathbf{x}_i^f\}$,

$$\beta H=-\sum_i h_i(1-s_i)+\sum_{i<j}J_{ij}[s_i(1-s_j)+s_j(1-s_i)], \quad (12)$$

where the spin $s_i=1$ corresponds with large overlap and $s_i=0$ small overlap at a site. The average field is found from the bulk free energy difference between the states, $\Sigma_i h_i=\beta F_{\text{glass}}-\beta F_{\text{liq}}=Ns_c/k_B$, with a heterogeneous local configurational entropy resulting from the alpha variations,

$$h_i=\frac{3}{2}\ln\frac{\alpha_i^\uparrow}{\pi}+\beta\sum_j V_{\text{eff}}(|\mathbf{x}_i^f-\mathbf{x}_j^f|;\alpha_j^\uparrow)-\frac{1}{N}F_{\text{liq}}. \quad (13)$$

The interactions defined through the effective potential give the surface energies of droplets within the RFOT picture and are explicitly

$$J_{ij}=V_2^{\text{eff}}(|\mathbf{x}_i^f-\mathbf{x}_j^f|;\alpha_i^\downarrow,\alpha_j^\uparrow)+V_2^{\text{eff}}(|\mathbf{x}_i^f-\mathbf{x}_j^f|;\alpha_i^\uparrow,\alpha_j^\downarrow). \quad (14)$$

III. APPLICATION TO A SIMULATED GLASS

The mapping to the disordered Ising model should be carried out for each fiducial equilibrium liquid structure. We sample fiducial structures of the Kob–Andersen 80–20 mixture of two types of Lennard-Jones (LJ) particles at a density of 1.2 (in LJ reduced units). The pairs have interaction parameters,[26,27] $\sigma_{AA}=1.0$, $\sigma_{BB}=0.8$, $\sigma_{AB}=0.88$, $\epsilon_{AA}=1.0$,

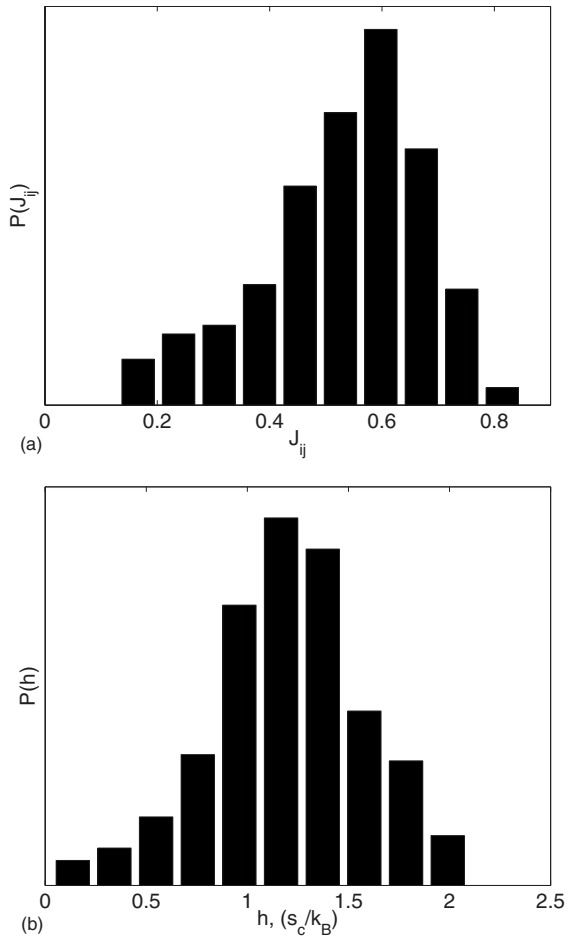

FIG. 2. The distributions of interactions and local fields of the magnet analogous to the simulated LJ two compound glasses. In this mapping $\bar{h}$ is directly related to the configurational entropy, $\bar{h}=s_c/k_B$. The fields are shown at $\bar{h}=1.2$, close to the dynamical crossover temperature.

$\epsilon_{BB}=1.5$, and $\epsilon_{AB}=0.5$. The fiducial structures were obtained by simulated annealing runs to the temperature $T_{\mathrm{MD}}=0.45$. The equilibration time for these simulations reaches a tenth of a microsecond when referenced to argon.

The parameters $\{\alpha_i^{\uparrow}\}$ $(\{q_i^{\uparrow}\})$ and $\{\alpha_i^{\downarrow}\}$ $(\{q_i^{\downarrow}\})$ are calculated for every particle. The mean rms deviation determined from $\{\alpha_i\}$ is about 0.12 particle spacings, rather close to the Lindemann parameter expected for periodic crystals $d_L\approx 0.1$ independent of the force law. The rms actually observed during the molecular dynamics (MD) run at $T_{\mathrm{MD}}=0.45$ is consistent with this estimate $d_L=0.113$.

The distribution of the calculated interactions is shown in Fig. 2(a). The interaction free energy per neighbor is $J_i \equiv 1/z_i\Sigma_j J_{ij}$, where z_i is the number of neighbors of particle i. The typical interaction $\bar{J}\equiv 1/N\Sigma_i J_i$ is directly related to σ, the mismatch free energy penalty in RFOT theory for a particle at a flat interface between regions of high and low overlap. In the Ising mapping $\beta\sigma_I=n_{bb}\bar{J}$, where $n_{bb}=3.2$ is the typical number of bonds broken by the interface. The direct calculation yields $\bar{J}=0.55$ giving $\beta\sigma_I=1.77$ not very different from the RFOT theory estimate usually used[28] $\sigma_{\mathrm{RFOT}}=3/4k_BT\ln 1/(d_L^2\pi e)=1.85k_BT$.

In RFOT theory the configurational entropy parametrizes

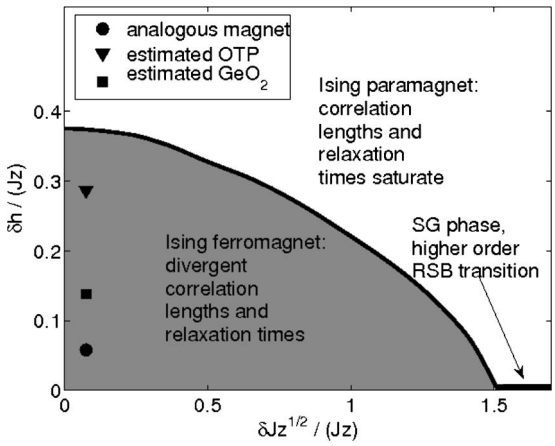

FIG. 3. Phase diagram of the Ising model with random bonds and fields adapted from Ref. 32. The parameters calculated for the magnet analogous to the LJ liquid (circular mark) indicate that the liquid would undergo a true phase transition at the ideal glass transition. The triangular and square marks indicate estimates of where the glass forming liquids, OTP and GeO_2, would fall on the phase diagram.

a liquid's descent into the glassy regime. In harmony with many experimental observations,[29–31] the dynamic crossover and the laboratory glass transition occur at universal critical entropies of $s_c(T_c)=1.12k_B$ and $s_c(T_g)=0.82k_B$, respectively.

Because of the rapidly increasing equilibration time scales, it is impossible presently to obtain proper fiducial structures directly at very low temperatures via MD. We can, however, treat the configurational entropy, and therefore the average field, as variable in order to extrapolate to find the magnetic system analogous to a liquid equilibrated at a much lower temperature, eventually extrapolating all the way to the ideal glass transition by taking $\bar{h}=\frac{1}{N}\Sigma_i h_i\rightarrow 0$. The presence of even a small average field is thought to destroy the phase transitions of both spin glasses and the random field Ising magnets, but at zero field, a transition to a phase with long range correlations can still occur. Would a transition occur for the liquid analog when $\bar{h}=0$, i.e., when the mean field configurational entropy vanishes? We answer this by appealing to a RG analysis of Migliorini and Berker[32] for the phase diagram for an Ising system in which both the fields and the interactions fluctuate randomly and independently, encompassing both the RFIM and the short range spin glasses. Their model is on a cubic lattice. We present their phase diagram in Fig. 3 in terms of the mean field theory based normalization where both the field fluctuations, δh, and the fluctuations of the interaction strength, $\delta Jz^{1/2}$, are normalized by the total interaction energy per site $\bar{J}z$. This parametrization should eliminate trivial near neighbor lattice dependence. This zero average field phase diagram is shown at a temperature $T=1$ coinciding with the established temperature of the analogous magnet. The results for the simulated Kob–Andersen liquid are indicated by the dot, suggesting that the disorder in both the fields and the interactions is sufficiently modest so that the system would undergo a phase transition to a state with infinite correlation lengths and divergent relaxation times when the field vanishes. This extrapolation implies that the Kob–Andersen LJ liquid should possess a true phase transition to a state with one step RSB

even though the renormalized configurational entropy, which would include small scale droplet excitations, strictly speaking remains finite. For such a broken replica symmetry state, the free energy landscape has divergent barriers between a finite number of collective free energy basins each one of which still has finite configurational entropy due to local defects.

According to Landau,[33] the excess heat capacity yields $\delta s_c = \sqrt{\Delta C_p k_B / N_{\mathrm{corr}}}$, where N_{corr} is the volume within which the disorder is correlated. The explicit mapping for the LJ system gives entropy fluctuations $\delta h = \delta s_c / k_B = 0.38$, smaller than a typical fragile glass forming liquid such as *ortho*-terphenyl (OTP). Assuming a similar distribution of interactions but rescaling the field fluctuations to that calculated for OTP yields the triangular position on the RG phase diagram in Fig. 3, while the square mark indicates where the strong glass forming liquid GeO_2 would lie. Even though OTP is rather fragile, we see that it would still be expected to obey one step RSB.

Our extrapolations neglect any structural changes that occur in an actual fluid upon cooling, yet we can test how well the direct dynamics of the extrapolated analog model corresponds to droplet analysis. Escape from the metastable ($s=1$) large overlap state corresponds with a large scale activated, structural rearrangement of the liquid. Directly simulated escape times are shown as circles in Fig. 4(a). The relaxation time grows rapidly at the dynamical crossover temperature appearing to diverge as s_c, $\bar{h} \to 0$. Below the dynamic crossover the growth in relaxation time is well fitted by $\ln \tau / \tau_0 \sim s_c^{-\psi}$. The proportionality constant for the inverse linear fit ($\psi=1$) is $22 k_B$, while droplet arguments in RFOT theory predict a slightly larger value $\ln \tau / \tau_0 = 32 k_B / s_c$. $\psi=2$, corresponding to the unwetted result from RFOT theory,[16] actually gives a closer fit to the relaxation time curve. This is consistent with what we have already seen in Fig. 3, that the analog magnet underestimates the disorder in the field moving the system away from the critical line where wetting is dominant.

The average overlap of the liquid frozen density fields maps onto the magnetization in the analog magnet, $q = 1/N \Sigma_i s_i$. This coordinate can be used to monitor escape from the local minima. We create free energy profiles for this local collective reaction coordinate using the weighted histogram analysis method[34–36] (WHAM). The resulting free energy profile, calculated with $\bar{h} = s_c / k_B = 1.1$, is shown as a thick solid line in Fig. 1(b). The metastable minimum at large overlap is separated from the global minimum at small overlap by a free energy barrier that accounts for the relaxation time according to $\tau = \tau_0 e^{\beta F^{\ddagger}}$.

The global overlap is not an ideal reaction coordinate for reconfiguration, as it averages over reconfiguration events occurring at spatially distinct regions. By selecting a spherical region at random and only permitting motion within that region, the overlap becomes a good reaction coordinate. This is the magnetic analogy of the landscape "library construction"[30] and is similar to the technique recently used to calculate the surface tension near a first order transition.[37] By varying the region size, the minimum size to irreversibly

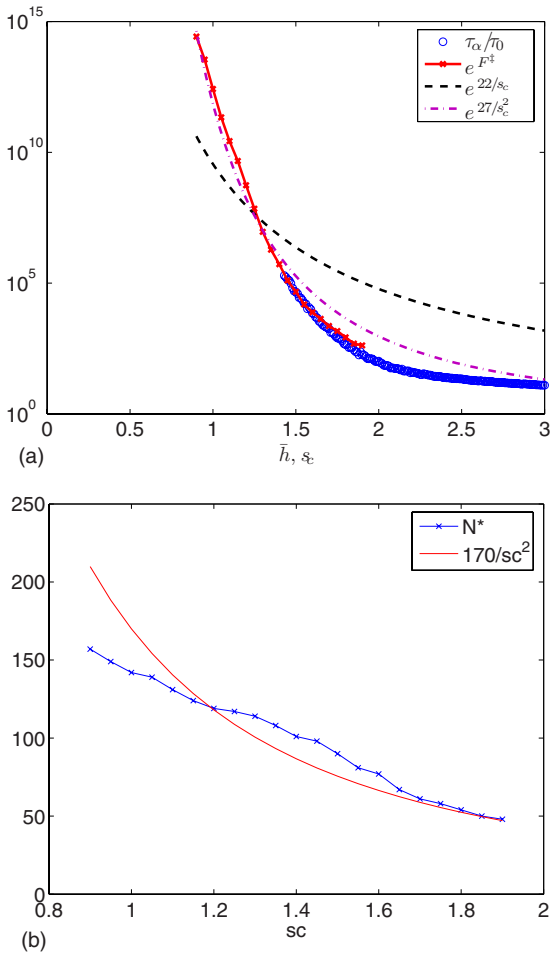

FIG. 4. (Color online) (a) Relaxation times of the Ising model analogous to the LJ liquid (circles). The solid line gives relaxation times calculated from free energy barriers. The dashed lines show fits using relations derived in RFOT theory (see text). (b) The minimum region size able to irreversibly reconfigure.

escape a minimum and reconfigure the liquid, N^*, can be determined. Free energy profiles for several region sizes around N^* are shown in Fig. 1(b). The free energy barriers computed for regions of size N^*, converted to relaxation time, are shown in Fig. 4(a). Using WHAM and the library construction allows descent much further into the glassy regime than is possible via direct simulation. The predicted minimum reconfiguration size is shown in Fig. 4(b). At high temperatures, $s_c > 1$, the growth of region size with decreasing s_c is consistent with $N^* \propto s_c^{-2}$ expected from RFOT theory, but at low temperatures the growth falls off as the result of finite size effects since the cluster size approaches the simulated system size itself. The free energy barrier is also underestimated for the low temperature range.

Not all cooperatively rearranging regions are created equal. The resulting dynamic heterogeneity of the liquid is seen in Fig. 5, showing a collection of free energy profiles for different regions at $\bar{h} = s_c / k_B = 1.1$. There is clearly a spread of relaxation times which can give rise to the stretched exponential relaxation behavior $\phi(t) = e^{-(t/\tau)^{\beta_{KWW}}}$ common to glassy systems. If the relaxation is entirely heterogeneous, the stretching exponent, β_{KWW}, was shown in Ref. 28 to be related to the spread of free energy barriers,

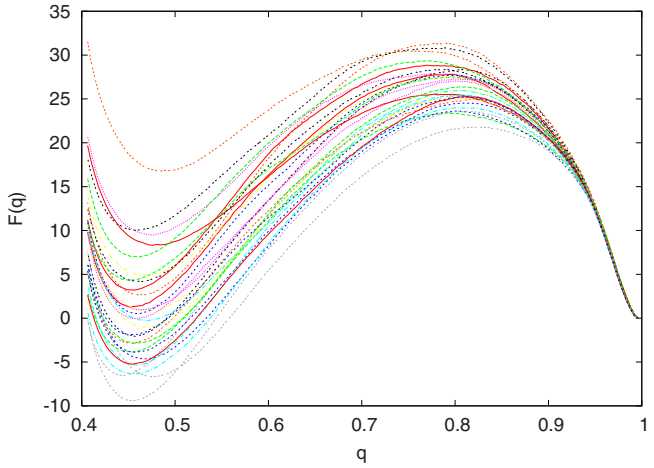

FIG. 5. (Color online) Free energy profiles for different regions at $\bar{h}=s_c/k_B=1.1$. The distribution of free energy barriers gives rise to the stretched exponential relaxation behavior common to glassy systems.

$\delta F^{\ddagger}$, through the relation $\beta_{KWW}\approx(1+(\delta F^{\ddagger}/k_BT)^2)^{-1/2}$. Xia and Wolynes[28] argued that regions do not reconfigure completely independently, so free energy barriers larger than the mean are lowered by facilitation effects of neighboring regions. Using the barrier distribution corrected in this way for facilitation yields a nonexponentiality parameter nearly independent of temperature, $\beta_{KWW}\approx 0.6$, a value characteristic for fragile liquids.

IV. CONCLUSION

Using a mixed density functional/atomistic replica formalism, the dynamics of the structural glass forming liquids can be mapped onto a general disordered Ising model. This mapping allows a computationally inexpensive route to low temperature dynamics, which is impossible currently by direct simulation. Using this information from the replica density functional, one can guide MD simulations carried out at complete atomic detail to more easily reach low temperature structural states.

Our results suggest that the Kob–Andersen liquid should demonstrate one step RSB at a sufficiently low temperature even though its configurational entropy including local droplet excitations, strictly speaking, will not vanish. The system is, in this sense, closer to the random field Ising magnet than it is to the Edwards Anderson short range spin glass model. The results from the simulation are consistent with droplet based predictions using the existing RFOT theory estimates.

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[1] T. R. Kirkpatrick and P. G. Wolynes, Phys. Rev. A **35**, 3072 (1987).
[2] T. R. Kirkpatrick and D. Thirumalai, Phys. Rev. Lett. **58**, 2091 (1987).
[3] T. R. Kirkpatrick and P. G. Wolynes, Phys. Rev. B **36**, 8552 (1987).
[4] S. P. Das, Rev. Mod. Phys. **76**, 785 (2004).
[5] V. Lubchenko and P. G. Wolynes, Annu. Rev. Phys. Chem. **58**, 235 (2007).
[6] *Spin Glasses and Random Fields*, edited by A. P. Young (World Scientific, Singapore, 1997).
[7] E. Marinari, G. Parisi, F. Ricci-Tersenghi, J. J. Ruiz-Lorenzo, and F. Zuliani, J. Stat. Phys. **98**, 973 (2000).
[8] G. Parisi, Physica A **386**, 611 (2007).
[9] D. Huse and D. S. Fisher, Phys. Rev. B **35**, 6841 (1987).
[10] W. L. Mcmillan, Phys. Rev. B **31**, 340 (1985).
[11] J. Villain, J. Phys. (France) **46**, 1843 (1985).
[12] D. Huse and D. S. Fisher, J. Phys. I **1**, 621 (1991).
[13] T. R. Kirkpatrick, D. Thirumalai, and P. G. Wolynes, Phys. Rev. A **40**, 1045 (1989).
[14] M. Dzero, J. Schmalian, and P. G. Wolynes, Phys. Rev. B **72**, 100201 (2005).
[15] S. Franz and G. Parisi, J. Phys. I **5**, 1401 (1995).
[16] X. Xia and P. G. Wolynes, Proc. Natl. Acad. Sci. U.S.A. **97**, 2990 (2000).
[17] M. Tarzia and M. A. Moore, Phys. Rev. E **75**, 031502 (2007).
[18] T. Temesvári, e-print arXiv:0809.1839v1.
[19] M. P. Eastwood and P. G. Wolynes, Europhys. Lett. **60**, 587 (2002).
[20] F. H. Stillinger, P. G. Debenedetti, and T. M. Truskett, J. Phys. Chem. B **105**, 11809 (2001).
[21] R. Monasson, Phys. Rev. Lett. **75**, 2847 (1995).
[22] Y. Singh, J. P. Stoessel, and P. G. Wolynes, Phys. Rev. Lett. **54**, 1059 (1985).
[23] M. Fixman, J. Chem. Phys. **51**, 3270 (1969).
[24] J. P. Stoessel and P. G. Wolynes, J. Chem. Phys. **80**, 4502 (1984).
[25] M. Mézard and G. Parisi, Phys. Rev. Lett. **82**, 747 (1999).
[26] R. W. Hall and P. G. Wolynes, J. Phys. Chem. B **112**, 301 (2008).
[27] W. Kob and H. C. Andersen, Phys. Rev. Lett. **73**, 1376 (1994).
[28] X. Xia and P. G. Wolynes, Phys. Rev. Lett. **86**, 5526 (2001).
[29] J. D. Stevenson, J. Schmalian, and P. G. Wolynes, Nat. Phys. **2**, 268 (2006).
[30] V. Lubchenko and P. G. Wolynes, J. Chem. Phys. **121**, 2852 (2004).
[31] V. N. Novikov and A. P. Sokolov, Phys. Rev. E **67**, 031507 (2003).
[32] G. Migliorini and A. N. Berker, Phys. Rev. B **57**, 426 (1998).
[33] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley, Reading, MA, 1969).
[34] A. M. Ferrenberg and R. H. Swendsen, Phys. Rev. Lett. **61**, 2635 (1988).
[35] A. M. Ferrenberg and R. H. Swendsen, Phys. Rev. Lett. **63**, 1195 (1989).
[36] A. N. Drozdov, A. Grossfield, and R. V. Pappu, J. Am. Chem. Soc. **126**, 2574 (2004).
[37] C. Cammarota and A. Cavagna, J. Chem. Phys. **127**, 214703 (2007).