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Ideal glass transition in a simple two-dimensional lattice model

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We present a simple lattice model showing a glassy behavior. R matrix analysis predicts critical termination of the supercooled fluid branch at density $\rho_g=0.1717$. This prediction is confirmed by dynamical numerical simulations, showing power-law divergences of relaxation time $\tau_{1/2}$, as well as the four-susceptibility χ_4 peak's location and height exactly at the predicted density. The power-law divergence of χ_4 continues up to χ_4 as high as 10^4. Finite-size scaling study reveals the divergence of the correlation length accompanying the transition.

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Understanding the transition of supercooled liquids into a glass is considered by many to be one of the outstanding challenges of condensed-matter physics. Many liquids, when cooled fast enough to avoid crystallization, appear to freeze into solidlike structures devoid of crystalline order [1–3]. The time scales for structural relaxation in such metastable supercooled regimes increase dramatically as the temperature is lowered. For strong glass formers the relaxation times grow exponentially as $\tau=\tau_0\exp(A/T)$. Fragile glass formers exhibit relaxation times that increase more rapidly than the Arrhenius and are often fitted by the Vogel-Tammann-Fulcher functional form $\tau=\tau_0\exp[A/(T-T_0)]$, with a characteristic temperature T_0 [4].

The glass transition temperature is experimentally defined as the temperature at which dynamic relaxation times exceed those accessible in typical experiments, e.g., when viscosity hits 10^{13} P. During the past century, much interest has been focused on understanding the nature of this transition. Clearly, the glass transition temperature, defined by some viscosity cutoff value, is just an arbitrary reference point along the gradual increase in relaxation times with decreasing temperature. The question of whether there is some deeper physical meaning to the glass transition is still debated [1]. Is the fast increase in relaxation times merely a sharp crossover in the dynamics, or could it be a manifestation of a true thermodynamic transition? (Obviously, when considering a glass transition in a system exhibiting a solid phase, such as real glass formers, the notion of a thermodynamic glass transition must be interpreted in the sense of a restricted part of phase space. For simplicity, we ignore this distinction in the following.) Many theoretical studies have been applied to support either one of the competing views. For example, a popular microscopic approach is the mode-coupling theory (see [5,6] for reviews). It predicts a dynamic glass transition, characterized by ergodicity breaking, while thermodynamic (equilibrium) quantities such as the isothermal compressibility do not become singular. In contrast, the replica approach [7] predicts a structural glass transition with a pure thermodynamic origin, characterized by a vanishing configurational entropy. Other phenomenological theories, such as the random first-order transition [8,9] and the potential-energy landscape [10] to name only two, also predict a thermodynamic phase transition.

Recently, the R matrix [11,12] approach for the analysis of the Mayer cluster integral expansion has been applied to the hard-sphere fluid [13,14]. It provides the density as a function of the activity z ($z=e^{\beta\mu}$, where μ is the chemical potential and β is the inverse temperature) and predicts a critical termination of the supercooled fluid, with a power-law divergence of the isothermal compressibility. The packing fraction at which this divergence is predicted to happen is 0.556(5), which is surprisingly close to the experimentally reported glass transition packing fraction of 0.56(1). This result, therefore, strongly supports the existence of a thermodynamic glass transition for hard spheres underlying the (experimentally and numerically observed) dynamical arrest. It is desirable to have numerical measurements of the supercooled hard-sphere equation of state near the transition in order to test the validity of the R matrix approach. However, these simulations are extremely challenging. Accordingly, contradicting results have been reported regarding the existence of singularities in thermodynamic quantities for this system [15,16].

The limits of numerical methods often hamper the study of glass transition. Excluding the nonphysical kinetically constrained models, most models studied are either complex (binary mixtures) or hard to simulate (hard spheres). They are therefore limited in system size and simulation times. For example, a recent study of Lennard-Jones binary mixture [17] reports that enlarging the system to include 27 000 particles improves the quality of the extrapolation of k-dependent quantities to zero wave vector. Moreover, simulations are generally limited to time scales roughly ten orders of magnitude shorter than those near the laboratory glass transition temperature T_g and therefore to the initial stages of the glass formation process [18]. These numerical limitations might be lifted by introducing a simpler model system that still captures the essence of glassy behavior. Keeping that in mind we set to explore the glass transition is the $N3$ lattice model.

The $N3$ model is a simple two-dimensional model on a square lattice. Particles interact only through hard-core exclusion up to the third-nearest neighbor. The model is known to undergo a first-order solidification transition [19–21], where density jumps from $\rho_f\simeq 0.161$ to $\rho_s\simeq 0.191$ [21] (the closest packing density is 0.2). Like the hard-sphere case, R matrix analysis predicts a critical termination of the supercooled fluid where the isothermal compressibility power law diverges. The critical density is found to be $\rho_t\simeq 0.1717$. In concordance with hard-sphere results [14], we hypothesize that this point is indeed the thermodynamic glass transition for this system. We then study the dynamics of the model by

TABLE I. Mayer cluster coefficients nb_n and R matrix diagonal (B_n) and off-diagonal (A_n) elements for the $N3$ model.

n	nb_n	B_n	A_n
1	1	13	6
2	−13	10.777777778	5.4955088285
3	205	10.777970817	5.4246225024
4	−3521	10.762751563	5.4025047989
5	63466	10.755266974	5.3922495398
6	−1180075	10.751491280	5.3866896951
7	22423304	10.749147764	5.3834227892
8	−432957233	10.747459452	5.3814030748
9	8463267016	10.746108741	5.3801242739
10	−167059758328	10.744940022	5.3793147595
11	3323928207997	10.743879570	5.3788131550
12	−66571342665659		
13	1340690959181588		
14	−27128411793067290		
15	551181809202093940		
16	−11238651060745319617		
17	229877749269899350973		
18	−4715081436294109369498		
19	96953111901056596856377		
20	−1998044077291458477558756		
21	41259643403438186795821307		
22	−853576114433438941428139775		
23	17688270167244330924258385729		

extensive Monte Carlo (MC) simulations and find that the dynamical quantities diverge exactly at the density predicted. We therefore conclude that the dynamical arrest in the $N3$ model results from a singularity of the free energy, as predicted by the R matrix. These results support the view of a thermodynamic (also known as ideal) glass transition in this system. Furthermore, we propose the $N3$ system as a simple and convenient model system for future studies of glassiness.

In order to construct the R matrix for the $N3$ model, we extended the number of known Mayer cluster integrals to 23, using the transfer-matrix (TM) method. We have employed a diagonal-to-diagonal symmetry-reduced TM, with strip a width as large as $M=24$ (3 874 112 symmetry-reduced classes). The cluster integrals provide the exact 11×11 leading R submatrix presented in Table I (for details on R matrix construction, see [12]). The matrix elements quickly converge to a well-defined asymptotic form which we use to extrapolate additional matrix elements and obtain the equation of state (Fig. 1). Remarkably, the results, based only on low-density expansion, are in an excellent agreement with both MC data and exact TM calculations. The physical singularity is found at $z_t\sim 66.67$, which is well above the first-order transition ($z_c \simeq 39.496$), with a critical density $\rho_t = 0.1717$. Furthermore, the R matrix provides an exact formula for the critical exponent σ' associated with the termination point of the fluid [12,14]: near this singularity, the density is given by

$$\rho_t - \rho(z) \simeq (z_t - z)^{\sigma'}, \tag{1}$$

and the critical exponent is found to be $\sigma' = 0.39(2)$.

We hypothesize that this thermodynamic criticality underlies an ideal glass transition for the $N3$ model and set out to study the model dynamically looking for signatures of this glass transition. We conducted canonical (constant density) MC studies of the model in the following way: the starting configuration was generated under extreme cooling conditions (or, equivalently, infinite chemical potential). Particles were allowed to diffuse when no insertion was available. This process is known to terminate at the random closest packing (RCP) state with a density of about 86% of the closest packing density [22]. Here, we stop the cooling at the desired density (below RCP), and let the system relax diffusionally. Given enough time, the global equilibrium phase-separation state is reached. On shorter time scale the system relaxes to a disordered phase. We first measure the density-density correlation

$$C(t) = \frac{1}{1-\rho}\left(\frac{1}{N}\int_V \langle n(r,0)n(r,t)\rangle dr - \rho\right) \tag{2}$$

along the relaxation process [$n(r,t)=1$ if a particle exists at site r at time t and zero, otherwise]. Figure 2 shows the typical glassy dynamics picture: a plateau (β regime) followed by a stretched-exponential decay (α regime). Due to

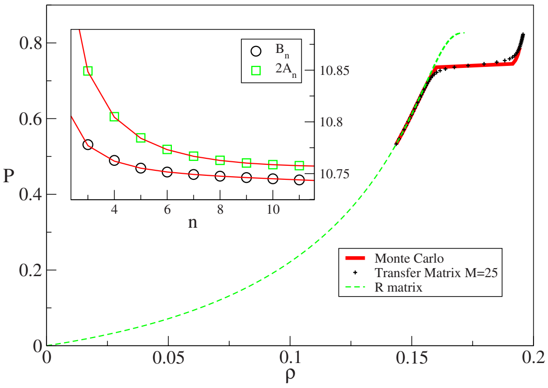

FIG. 1. (Color online) $N3$ equation of state: R matrix prediction, based on the first 23 Mayer cluster integrals (dashed line), Monte Carlo calculation on a 1000×1000 lattice (solid line), and exact transfer-matrix calculation for a semi-infinite 25 site wide strip (symbols). The latter two methods provide equilibrium results, while the R matrix extrapolates to the supercooled fluid branch. The agreement of the R matrix results with the numerical methods is excellent throughout the fluid regime. Inset shows the diagonal (B_n) and off-diagonal (A_n) R matrix elements, together with the fitted asymptotic form.

the discrete nature of the diffusion process in this model, the β relaxation stage is very short (of order one simulation time unit) and is not presented. The relaxation time $\tau_{1/2}$, defined as the time at which $C(t)=1/2$, power law diverges as the density approaches $\rho_g=0.1717$,

$$\tau_{1/2}(\rho) \sim (\rho_g - \rho)^{-\mu}, \tag{3}$$

with $\mu=0.83$ (Fig. 2, inset). In addition, we measure the four-susceptibility χ_4, [23,24]

$$\chi_4(t) = N(\langle C(t)^2 \rangle - \langle C(t) \rangle^2). \tag{4}$$

Again, a typical glassy behavior is observed (Fig. 3)—χ_4 peaks at the α phase, and the peak grows in height and shifts to higher times as the density increases. Peak heights (χ_{max}) and locations (τ_4) also power law diverge as ρ_g is approached (Fig. 3, inset). A transition to activated dynamics occurring close to the glass transition could be manifested by the onset of a slower logarithmic growth of the χ_4 peak [25]. We do not observe any such transition for χ_4 values up to 10^4.

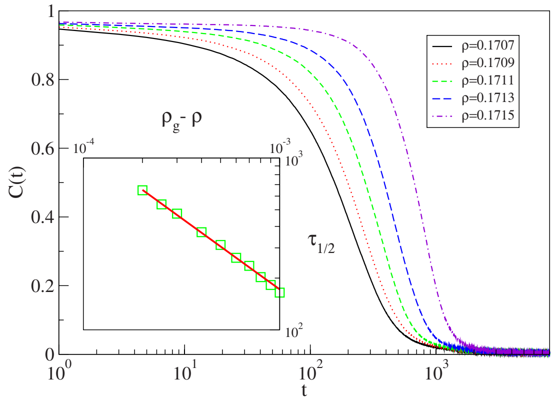

FIG. 2. (Color online) Density-density autocorrelation (2), showing the typical glassy relaxation picture, on a logarithmic time scale. The inset shows the relaxation time $\tau_{1/2}$ vs density (symbols), which is well fitted by a power law (3) diverging at ρ_g.

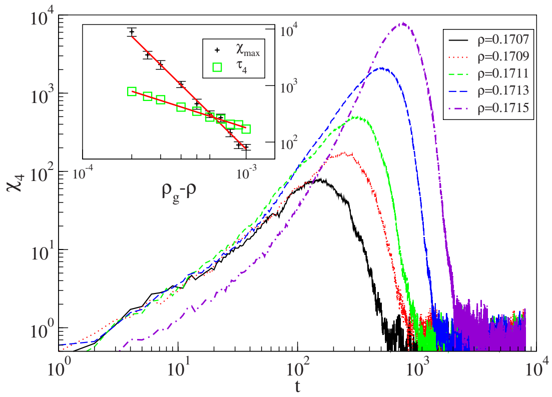

FIG. 3. (Color online) χ_4 as a function of time showing the familiar peaks. Peaks' heights $\chi_{\max}$ and locations τ_4 power law diverge as density approaches ρ_g (inset) with critical exponents of 2.85 and 0.93, respectively.

The above MC data confirm the R matrix prediction to an excellent agreement. Given that this prediction is based solely on low-density series expansion, it is remarkable that it captured quantitatively the behavior at the deep supercooled regime. This attests for the validity of the R matrix approach and its prediction of a thermodynamic criticality in the equation of state of the $N3$ supercooled fluid, and it provides a strong evidence that the glass transition in this model is indeed a thermodynamic ideal one.

The growing χ_4 peak is indicative of growing cooperative correlations in the relaxation process [26]. It measures the volume upon which diffusional moves are correlated [27]. In concordance, growing correlation lengths are seen also by the emergence of finite-size effects in the density-density correlations as shown in Fig. 4. These finite-size effects, recently highlighted by Karmakar *et al.* [28], underscore the

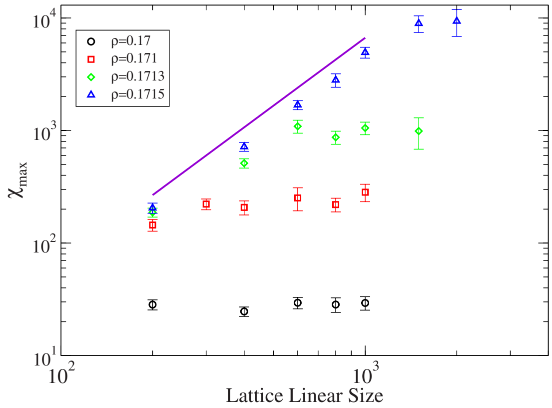

FIG. 4. (Color online) Finite-size analysis: χ_4 peak height as a function of lattice linear size, for various densities. As the density approaches ρ_g, larger lattices are needed for converged results, attesting for a diverging length scale. For lattices smaller than the correlation length, $\chi_{\max}$ is expected to grow like system's size. A straight line with a slope of 2 is presented, to guide the eye.

importance of using large systems for MC studies of glassiness, which is most difficult for popular models currently used.

Unlike the hard-sphere case, the termination density ρ_g predicted by the R matrix and the dynamical arrest occur in close proximity to the random closest packing density ρ_{rcp} [22]. Therefore, the region beyond the transition is inaccessible in this model. It is important to note that the co-occurrence of the two phenomena is not a universal trait of the R matrix analysis. For example, in the hard-sphere model the R matrix prediction for the ideal glass density is $\rho_t = 0.556(5)$, which is much lower than $\rho_{rcp}=0.64$. Hopefully, future work will find a model that is as simple as the $N3$ model but also allows access to densities beyond ρ_t. This could be achieved by studying the soft-core $N3$ model or other hard-core lattice models.

We stress that the simplicity of the $N3$ model is important not only in order to allow for analytical treatment, but to facilitate numerical studies of large systems, much larger than those typically used in glass studies. This is especially important when one approaches the glass transition, where long-range cooperative relaxation processes emerge, manifested by significant finite-size dependence. For example, at density $\rho=0.1715$, even a 1000×1000 lattice (171 500 particles; linear size of $\sim$447 particle diameters, much larger than typical three-dimensional studies) is not large enough to converge to bulk values as seen in Fig. 4. The need for a simple model then is not a matter of comfort, but a real necessity. We therefore propose that the $N3$ model, or similar models, could serve in future studies of glass formers being simple to handle, yet capturing the essence of glassiness.

In conclusion, we have applied the R matrix approach to the $N3$ model and found that its supercooled equation of state becomes singular at density $\rho_g=0.1717$, where the isothermal compressibility power law diverges. MC simulations confirm that the model shows the characteristics of a fragile glass former undergoing a glass transition at the predicted ρ_g. It thus follows that in this model the phenomenological glass transition, observed as a fragile glass dynamical arrest at ρ_g, is accompanied by a thermodynamic criticality.

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