An energy-landscape-based crossover temperature in glass-forming liquids

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The systematic identification of temperature scales in supercooled liquids that are key to understanding those liquids’ underlying glass properties, and the latter’s formation-history dependence, is a challenging task. Here we study the statistics of particles’ squared displacements $\delta r^2$ between equilibrium liquid configurations at temperature $T$, and their underlying inherent states, using computer simulations of 11 different computer-glass-formers. We show that the relative fluctuations of $\delta r^2$ are nonmonotonic in $T$, exhibiting a maximum whose location defines the crossover temperature $T_x$. Therefore, $T_x$ marks the point of maximal heterogeneity during the process of tumbling down the energy landscape, starting from an equilibrium liquid state at temperature $T$, down to its underlying inherent state. We extract $T_x$ for the 11 employed computer glasses, ranging from tetrahedral glasses to packings of soft elastic spheres, and demonstrate its usefulness in putting the elastic properties of different glasses on the same footing. Interestingly, we further show that $T_x$ marks the crossover between two distinct regimes of the mean $(\delta r^2)$: a high temperature regime in which $(\delta r^2) \sim T^{0.5}$, and a deeply-supercooled regime in which $(\delta r^2) \sim T^{1.3}$. Further research directions are discussed.

I. INTRODUCTION

What are the important characteristic temperature scales of equilibrium liquids, that are relevant for glass formation and glass elasticity? This long-lasting question remains debated, as no single definition of a characteristic temperature scale is widely agreed upon. In the context of the dynamics of supercooled liquids [1], the most prevalently discussed temperature scale is the Mode-Coupling Theory [2–4] (MCT) temperature $T_{\text{MCT}}$, conventionally extracted by fitting a the primary relaxation time $\tau_\alpha$ of a liquid to the scaling form $\tau_\alpha \sim (T - T_{\text{MCT}})^{-\gamma}$ [5, 6] over an a priori-undetermined temperature range, where both the exponent $\gamma$ and the critical temperature $T_{\text{MCT}}$ are treated as fitting parameters.

Another important temperature scale of viscous liquid states is traditionally referred to as the ‘onset’ [7–9] or ‘crossover’ [1, 10, 11] temperature $T_{\text{onset}}$. This temperature scale is understood to mark the crossover in the primary mechanism of supercooled liquids’ structural relaxation, from non-activated at high temperatures, to activated over free energy barriers at low temperatures. The crossover at $T_{\text{onset}}$ has been proposed to be related to topological changes occurring between different regions of the energy landscape that are sampled at different equilibrium temperatures [12, 13].

While the primary focus amongst researchers in the field of glass physics has traditionally been devoted to discussing temperature scales extracted from and relevant to supercooled liquids’ dynamics, not much attention has been directed towards understanding which temperature scales are relevant to the elastic properties of the glassy states that underlie equilibrium configurations [14–18]. In this work we propose a scheme to extract a characteristic crossover temperature scale $T_x$ of a liquid by studying the statistics of particles’ squared displacements $\delta r^2$ between equilibrium-liquid states at temperature $T$, and the underlying inherent states obtained by following steepest-descent dynamics from those equilibrium-liquid states [7, 19]. Those statistics reveal a rich picture regarding the relation between equilibrium states and their underlying inherent states, and its variation across different temperature regimes. Using a broad variety of computer glass formers, we show how the extracted crossover temperature scale $T_x$ organizes elastic properties of glasses made by quenching equilibrium liquid states at parent temperature $T_p$. Finally, we discuss further interesting observations regarding the typical behavior of particles’ squared displacements $\delta r^2$ between equilibrium states and their underlying glassy inherent states.

II. MODELS AND METHODS

We employ 11 different computer glass-formers, that vary between each other by their respective attraction strengths, characteristic stiffnesses, and other attributes described at length in Appendix A. For each model, we created large ensembles of equilibrium configurations at various temperatures $T$, ranging from hot liquid states, to deeply supercooled viscous liquids.

In order to measure the squared displacements $\delta r^2$ of individual particles between equilibrium configurations and their underlying inherent states [7, 19], we follow steepest-descent (fully overdamped) dynamics, namely

$$\dot{x} \propto -\frac{\partial U}{\partial x},$$

where $x$ denotes particles’ coordinates, and $U(x)$ is the potential energy. Eq. (1) is integrated forward in time by
a simple Euler scheme [20], until the condition
\[ \left| \frac{\partial U}{\partial x}, \frac{\partial U}{\partial x} \right|_{T_p} \leq 10^{-10} \] (2)
is met, where \( f \) denotes the root-mean-square of interparticle forces. We recorded the squared displacements of at least \( 10^6 \) particles at each temperature, for all models.

At the end of the steepest descent dynamics, we calculate the athermal shear and bulk moduli of the resulting athermal glass-ensembles, following the formalism of [21]. Different glass ensembles belonging to each of the employed models are labeled by the parent equilibrium temperature \( T_p \) from which those glasses were quenched.

III. RELATIVE FLUCTUATIONS OF \( \delta r^2 \) PEAK AT \( T_x \)

Having in hand various data sets for the particle-wise squared displacements \( \delta r^2 \) at temperature \( T \), and their underlying inherent states, we next proceed to analyze the statistics of \( \delta r^2 \) and its temperature- and model-dependence.

In Fig. 1a we show the ratio of the standard deviation (STD) of \( \delta r^2 \) to its mean, referred to in what follows as \( k(T) \). We see that \( k(T) \) is monotonic for all models, and features a peak at some temperature, that we define as \( T_x \), namely
\[ \frac{dk}{dT} \bigg|_{T_x} = 0. \] (3)

In practice we estimate \( T_x \) by fitting a cubic polynomial to the peak regime of \( k(T) \) and finding its maximum. The sharpness of the peak of \( k(T) \) — quantified, e.g., by \( T_x^2 \, d^3k/dT^2 \) evaluated at \( T_x \) — constitutes another attribute of glass-forming models, and appears to be correlated with computer glasses’ thermo-mechanical annealability that was studied extensively in Ref. [18].

IV. \( T_x \) ARRANGES ELASTIC PROPERTIES OF DIFFERENT GLASSES

Is the scale \( T_x \) as defined above relevant for glass physics, and if so, to which observables/phenomena? Here we show that a key dimensionless number in elasticity theory — the ratio \( G/K \) of the shear to bulk elastic moduli — collapses for different glass models, when plotted against \( T_p/T_x \), and rescaled by the high-\( T_p \) plateau \( G_\infty/K_\infty \). We reiterate that \( T_p \) represents the parent equilibrium temperature from which our different glasses were quenched.

The result is shown in Fig. 2: we choose a subset of 7 models that show a good collapse up to \( T_x \), and some small degree of meandering of the different data sets below \( T_x \). Data pertaining to all 11 glass models studied in this work is shown in Appendix B.

V. A CROSSOVER BETWEEN TWO REGIMES

We have shown in Fig. 1a that the relative fluctuations of \( \delta r^2 \) peak at \( T_x \), but how does the mean squared displacement (MSD) \( \langle \delta r^2 \rangle \) behave as a function of \( T \)? To answer this question, we plot \( \langle \delta r^2 \rangle \) vs. \( T \) in Fig. 1b, for...
all models and all equilibrium temperatures $T$; the $y$-axis was rescaled by (the square of) a length $\ell$, plotted in the inset of Fig. 1b in terms of glasses’ typical inter-particle distance $a_0 \equiv V/N$, with $V$ and $N$ denoting the system's volume and number of particles, respectively. The lengths $\ell$ were chosen for each model such that the rescaled MSD $\langle \delta r^2 \rangle/\ell^2$ collapses at high $T$, showing an approximate $\sim T^{0.5}$ scaling, possibly related to the observations of Ref. [22]. We attribute the variability of $\ell$ to the different polydispersities used, which may hinder a direct comparison between lengths expressed in terms of an interparticle distance.

Just below the aforementioned high-$T$ scaling, the rescaled MSD $\langle \delta r^2 \rangle/\ell^2$ enters a crossover regime, that extends over a temperature range corresponding to a factor slightly larger than 2, about $T_\phi$. This is a large range whose lower limit cannot be fully accessible by conventional molecular dynamics simulations (due to very large associated relaxation times), at least for a substantial subset of the glass models studied here [23]. The variability in accessibility to the lower limit of the crossover range indicates that the ratio $T_\phi/T_\phi$ ($T_\phi$ is the glass transition temperature [1]) is expected to vary significantly across different models, indicating that a universal relation between $T_\phi$ and $T_\phi$ does not exist. Within the crossover regime, the rescaled MSD appears to drop by up to a factor of 10, for some models. This drop appears to be again correlated with models' thermo-mechanical anneal-ability, shown in [18] to be controlled by the strength and form of attractive interactions in the glass.

Finally, below the aforementioned crossover regime, some models [23] are seen to enter the deep-supercooling regime at roughly $0.7T_\phi$, in which an approximate $\langle \delta r^2 \rangle/\ell^2 \sim T^{1.3}$ scaling is observed across those models. Interestingly, the prefactor of this scaling shows a large variation across our different computer-glass-forming models, keeping in mind that rescaling $\langle \delta r^2 \rangle$ by $\ell^2$ affects possible interpretations of the prefactor variation.

VI. DISCUSSION

In this short paper we aimed at putting forward a robust, broadly applicable and physically transparent definition of a crossover temperature $T_\phi$ in supercooled liquids, which appears to be relevant to the thermal-annealing-induced variations of glasses’ elastic moduli. The proposed crossover temperature $T_\phi$ represents the temperature at which the relative fluctuations of the particle-wise total squared displacements $\delta r^2$, measured between equilibrium states and their underlying inherent states, is maximal. This maximum indicates that the descent process from equilibrium states to $T = 0$ inherent states becomes inhomogeneous, possibly suggesting that the supercooled liquid’s structure is maximally inhomogeneous too, at $T_\phi$. Following the spatio-mechanical patterns that emerge during the tumbling of a system down its energy landscape might reveal the origin and essence of the observed inhomogeneities in $\delta r^2$. This interesting issue will be addressed in future work.

Apart from demonstrating the potential usefulness of the proposed crossover temperature $T_\phi$, our study also reveals an interesting behavior of the means $\langle \delta r^2 \rangle$, as a function of $T$ (Fig. 1b). In particular, we show that $T_\phi$ is situated in the middle of a crossover regime that separates a high-temperature regime in which $\langle \delta r^2 \rangle \sim T^{0.5}$, and a low-temperature regime in which $\langle \delta r^2 \rangle \sim T^{1.3}$. These observations pose interesting questions regarding the nature of glass formation and its many different faces. They also suggest a possible universality in the behavior of liquids in the deep-supercooling regime $T < 0.7T_\phi$, which is accessible numerically via the Swap Monte Carlo algorithm [24]. We note that while $\langle \delta r^2 \rangle$ appears to feature 3 distinct regimes (as seen in Fig. 1b), the ratio of $G/K$ as seen in Fig. 2 does not show any clear signature of entering the deep-supercooling regime at $T_p \lesssim 0.7T_\phi$.

It is interesting to compare between our estimations for $T_\phi$, and available estimations of the mode-coupling temperature $T_{\text{MCT}}$ and the onset temperature $T_{\text{onset}}$. For instance, the canonical Kob-Andersen Binary Lennard-Jones model [25] — which is also employed in our extensive computational study (see Appendix A) — has been shown to feature $T_{\text{MCT}} \approx 0.435$ [25], in its conventional simulation units. In those same units, we have estimated $T_\phi \approx 0.535$, i.e. over 20% higher. On the other hand, in [8] and in [9] the onset temperature for the same model, expressed in the same simulation-units, was estimated at $T_{\text{onset}} \approx 0.78$ and $T_{\text{onset}} \approx 0.77$, respectively, i.e. much higher than our estimated $T_\phi$. All the aforementioned estimations of the onset or MCT temperatures, however,
were not shown to organize relaxation or elasticity data over various glass models, in any compelling manner.

Finally, the observed scaling $\langle \delta r^2 \rangle \sim T^{1.3}$ in the deep-supercooling regime can be very crudely interpreted as follows: $\langle \delta r^2 \rangle \sim \varepsilon/\kappa$, i.e. it is the ratio of a characteristic energy and a characteristic stiffness. In extreme supercooling conditions, i.e. in the deep-supercooling regime, one expects the energy to follow the harmonic approximation, namely $\varepsilon \sim T$. Under these assumptions, the characteristic stiffnesses $\kappa$ is speculated to grow with decreasing temperature approximately as $\kappa \sim T^{-0.3}$. While characteristic stiffness scales are indeed observed to increase with deeper supercooling of glasses’ parent equilibrium states [14, 17, 26], the precise validation and interpretation of these speculations are left for future work.

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Appendix A: Computer-glass-forming models

We employ 11 models of computer glasses in three dimensions (3D) at fixed volume $V$. In this Appendix we provide brief descriptions of the computer models employed in our work, and refer to relevant literature in which more detailed information about the models can be found. We also report the extracted value of the crossover temperature $T_x$ for each model, expressed in terms of those models’ simulation units.

1. Kob-Andersen binary Lennard Jones

The well-known Kob-Andersen binary Lennard Jones (KABLJ) model [25] is a canonical glass former, which is one of the most thoroughly investigated computer glass models. It consists of an 4:1 binary mixture of type A (‘large’) and type B (‘small’) particles that interact via a radially symmetric Lennard-Jones potential. We have added a polynomial to the Lennard-Jones potential to make it smooth up to the first derivative, as done e.g. in [27]. The system size employed is $N = 3000$. We extracted $T_x = 0.535$ for this model.

2. Stillinger-Weber model

The Stillinger-Weber model [28] is a monocomponent liquid of $N$ particles of mass $m$ whose interaction potential consists of both a short-ranged, two-body interaction and a three-body term that favors triplets of atoms to form an angle $\theta_0 \simeq 109^\circ$. Further details about this model and the employed parameters can be found in [29]. We employed systems of $N = 8000$ particles, and extracted $T_x = 0.025$ for this model.

3. Binary soft spheres

The binary soft spheres model [14] is a 50:50 binary mixture of ‘large’ and ‘small’ particles of equal mass $m$, interacting via an inverse-power-law (IPL) pairwise potential. Details can be found in [14]. We employed systems of $N = 2000$ particles, and extracted $T_x = 0.65$ for this model.

4. Polydisperse soft spheres

The polydisperse soft spheres model considers particles of sizes $\lambda_i$ drawn from a distribution $p(\lambda) \sim \lambda^{-3}$, between $\lambda_{\min} = 1.0\AA$ and $\lambda_{\max} = 2.22\lambda$, where $\lambda$ is the simulation units of length. In the variant of the model we used, pairs of particles interact via the same inverse-power-law interaction potential of the Binary soft spheres model discussed above. Ensembles of equilibrium states were created using the Swap Monte Carlo Method [24], that allows for very deep supercooling. Details about the model and parameters employed here can be found in [15]. We employed systems of $N = 2000$ particles, and extracted $T_x = 0.66$ for this model.

5. Hertzian spheres

The Hertzian spheres model is a 50:50 binary mixture of small and large soft, linear-elastic spheres interacting via the Hertzian interaction law [30]. We use systems with $N = 4000$ particles, and fix the number density at $N/V = 0.9386\lambda$, where $\lambda$ is the diameter of the small-particle species. We employed the same system as described in [29], and extracted $T_x = 0.0023$ for this model.

6. Sticky spheres (binary)

The sticky spheres model consists of a 50:50 binary mixtures of ‘small’ and ‘large’ particles of equal mass $m$ in three dimensions at fixed volume $V$, interacting radially via a piece-wise modified Lennard-Jones potential —
first introduced in [31] — in which the attractive part of the potential can be readily tuned via the cutoff-length \( r_c \), as illustrated in Fig. 4. Further details about the interaction potential, the supercooled liquid dynamics, the elastic properties of the resulting glasses, and the precise parameters used, can be found in [18].

Here we employ four different variants of the model, with cutoff-lengths: \( r_c/r_{\text{min}} = 1.1, 1.2, 1.3, 1.5 \) (see Fig. 4 for the definition of \( r_{\text{min}} \)), with systems of \( N = 3000 \) particles. In the legend of Fig. 1, ‘sticky spheres (binary) 1,2,3,4’ stand for the aforementioned model variants with \( r_c = 1.1, 1.2, 1.3, 1.5 \), and we extracted \( T_x = 2.02, 1.26, 1.06, 0.85 \), respectively, for those models.

### 7. Sticky spheres (polydisperse)

This model is the same as ‘sticky spheres (binary)’ discussed in the preceding subsection, except that instead of binary mixtures we employed the same polydispersity as used for the ‘polydisperse soft spheres’ model discussed above. This means that particle sizes were drawn from the distribution \( p(\lambda) \sim \lambda^{-5} \), between \( \lambda_{\text{min}} = 1.0A \) and \( \lambda_{\text{max}} = 2.22A \), where \( A \) is the simulation units of length. The number density \( N/V \) was fixed at 0.40\( A^{-3} \), such that the high-\( T_p \) pressure to bulk modulus ratio \( p/K \approx 0.05 \). We employed the Swap Monte Carlo algorithm [24] to achieve deeply supercooled equilibrium states. The approach used to reduce possible particle-size induced finite-size effects is the same as employed in Ref. [15]. We employed two variants of this model, referred to as ‘sticky spheres (polydisperse) 1’ using \( r_c/r_{\text{min}} = 1.1 \) and ‘sticky spheres (polydisperse) 2’ using \( r_c/r_{\text{min}} = 1.2 \). The system size used was \( N = 2000 \), and we extracted \( T_x = 1.27 \) and \( T_x = 1.27 \) for the \( r_c/r_{\text{min}} = 1.1 \) and \( r_c/r_{\text{min}} = 1.2 \) variants, respectively.

### Appendix B: \( G/K \) for all glass models

In this Appendix we provide a plot, similar to Fig. 2, but this time including all of the 11 data sets pertaining to all investigated computer-glass-forming models.
[1] A. Cavagna, Supercooled liquids for pedestrians, Phys. Rep. **476**, 51 (2009).

[2] W. Götze, Complex dynamics of glass-forming liquids: A mode-coupling theory, Vol. 143 (OUP Oxford, 2008).

[3] L. M. C. Janssen, Mode-coupling theory of the glass transition: A primer, Front. Phys. **6**, 97 (2018).

[4] D. Coslovich, A. Ninarello, and L. Berthier, A localization transition underlies the mode-coupling crossover of glasses, SciPost Phys. **7**, 77 (2019).

[5] W. Kob and H. C. Andersen, Testing mode-coupling theory for a supercooled binary lennard-jones mixture. ii. intermediate scattering function and dynamic susceptibility, Phys. Rev. E **52**, 4134 (1995).

[6] E. Flenner and G. Szamel, Relaxation in a glassy binary mixture: Comparison of the mode-coupling theory to a brownian dynamics simulation, Phys. Rev. E **72**, 031508 (2005).

[7] S. Sastry, P. G. Debenetti, and F. H. Stillinger, Signatures of distinct dynamical regimes in the energy landscape of a glass-forming liquid, Nature **393**, 554 (1998).

[8] Y. Brumer and D. R. Reichman, Mean-field theory, mode-coupling theory, and the onset temperature in supercooled liquids, Phys. Rev. E **69**, 041202 (2004).

[9] A. Banerjee, M. K. Nandi, S. Sastry, and S. Maitra Bhattacharyya, Determination of onset temperature from the entropy for fragile to strong liquids, J. Chem. Phys. **147**, 024504 (2017).

[10] M. Goldstein, Viscous liquids and the glass transition: A potential energy barrier picture, J. Chem. Phys. **51**, 3728 (1969).

[11] T. B. Schroder, S. Sastry, J. C. Dyre, and S. C. Glotzer, Crossover to potential energy landscape dominated dynamics in a model glass-forming liquid, J. Chem. Phys. **112**, 9834 (2000).

[12] K. Broderix, K. K. Bhattacharyya, A. Cavagna, A. Zippelius, and I. Giardina, Energy landscape of a lennard-jones liquid: Statistics of stationary points, Phys. Rev. Lett. **85**, 5360 (2000).

[13] T. S. Grigera, A. Cavagna, I. Giardina, and G. Parisi, Geometric approach to the dynamic glass transition, Phys. Rev. Lett. **88**, 055502 (2002).

[14] E. Lerner and E. Bouchbinder, A characteristic energy scale in glasses, J. Chem. Phys. **148**, 214502 (2018).

[15] E. Lerner, Mechanical properties of simple computer glasses, J. Non-Cryst. Solids **522**, 119570 (2019).

[16] L. Wang, A. Ninarello, P. Guan, L. Berthier, G. Szamel, and E. Flenner, Low-frequency vibrational modes of stable glasses, Nat. Commun. **10**, 26 (2019).

[17] C. Rainone, E. Bouchbinder, and E. Lerner, Pinching a glass reveals key properties of its soft spots, Proc. Natl. Acad. Sci. U.S.A. **117**, 5228 (2020).

[18] K. González-López, M. Shivam, Y. Zheng, M. Pica Ciamarra, and E. Lerner, Mechanical disorder of sticky-sphere glasses. ii. thermo-mechanical inannealability, arXiv preprint arXiv:2009.08238 (2020).

[19] H. Tong, S. Sengupta, and H. Tanaka, Emergent solidity of amorphous materials as a consequence of mechanical self-organisation, Nat. Commun. **11**, 4863 (2020).

[20] M. P. Allen and D. J. Tildesley, Computer simulation of liquids (Oxford university press, 1989).

[21] J. F. Lutsko, Generalized expressions for the calculation of elastic constants by computer simulation, J. Appl. Phys. **65**, 2991 (1989).

[22] Y. Rosenfeld and P. Tarazona, Density functional theory and the asymptotic high density expansion of the free energy of classical solids and fluids, Mol. Phys. **95**, 141 (1998).

[23] We note that the polydisperse models employed here were equilibrated to very low temperatures using the Swap Monte Carlo algorithm [24].

[24] A. Ninarello, L. Berthier, and D. Coslovich, Models and algorithms for the next generation of glass transition studies, Phys. Rev. X **7**, 021039 (2017).

[25] W. Kob and H. C. Andersen, Testing mode-coupling theory for a supercooled binary lennard-jones mixture i: The van hove correlation function, Phys. Rev. E **51**, 4626 (1995).

[26] C. Rainone, E. Bouchbinder, and E. Lerner, Statistical mechanics of local force dipole responses in computer glasses, J. Chem. Phys. **152**, 104503 (2020).

[27] P. Leishangthem, A. D. S. Parmar, and S. Sastry, The yielding transition in amorphous solids under oscillatory shear deformation, Nat. Commun. **8**, 14653 (2017).

[28] F. H. Stillinger and T. A. Weber, Computer simulation of local order in condensed phases of silicon, Phys. Rev. B **31**, 5262 (1985).

[29] D. Richard, K. González-López, G. Kapteijns, R. Pater, T. Vaknin, E. Bouchbinder, and E. Lerner, Universality of the nonphononic vibrational spectrum across different classes of computer glasses, Phys. Rev. Lett. **125**, 085502 (2020).

[30] L. D. Landau and E. M. Lifshits, Theory of Elasticity (Pergamon Press, 1964).

[31] S. Karmakar, E. Lerner, I. Procaccia, and J. Zylberg, Effect of the interparticle potential on the yield stress of amorphous solids, Phys. Rev. E **83**, 046106 (2011).