Does the Adam-Gibbs relation hold in simulated supercooled liquids?

Misaki Ozawa,1 Camille Scalliet,1 Andrea Ninarello,2 and Ludovic Berthier1

1Laboratoire Charles Coulomb (L2C), Université de Montpellier, CNRS, Montpellier, France
2CNR-ISC Uos Sapienza, Piazzale A. Moro 2, IT-00185 Roma, Italy

Dated: May 21, 2019

We perform stringent tests of thermodynamic theories of the glass transition over the experimentally relevant temperature regime for several simulated glass-formers. The swap Monte Carlo algorithm is used to estimate the configurational entropy and static point-to-set lengthscales, and careful extrapolations are used for the relaxation times. We first quantify the relation between configurational entropy and the point-to-set lengthscales in two and three dimensions. We then show that the Adam-Gibbs relation is generally violated in simulated models for the experimentally relevant temperature regime. Collecting experimental data for several supercooled molecular liquids, we show that the same trends are observed experimentally. Deviations from the Adam-Gibbs relation remain compatible with random first order transition theory, and may account for the reported discrepancies between Kauzmann and Vogel-Fulcher-Tammann temperatures. Alternatively, they may also indicate that even near \( T_g \) thermodynamics is not the only driving force for slow dynamics.

I. INTRODUCTION

Since its first derivation in 1965 [1], the Adam-Gibbs relation has played a central role in glass transition studies [2], since it is at the core of thermodynamic approaches to the glass problem [1–9]. The Adam-Gibbs relation captures in a simple mathematical form the physical idea that the decrease of the configurational entropy \( S_{\text{conf}} \) controls the growth of the relaxation time \( \tau_\alpha \) as the experimental glass transition temperature \( T_g \) is approached:

\[
\log(\tau_\alpha/\tau_0) \propto \frac{1}{T S_{\text{conf}}}, \tag{1}
\]

where \( \tau_0 \) is a microscopic timescale. Testing the Adam-Gibbs relation has almost become synonymous to testing the thermodynamic nature of glass formation [10–13].

Since computational methods have become available in the early 2000’s to measure the configurational entropy in numerical simulations [14–16], the Adam-Gibbs relation has been tested in a large number of studies using many different models of glass-forming materials [12, 17–24]. Importantly, these simulations are all restricted to a high temperature regime (typically above the mode-coupling crossover temperature \( T_{\text{mct}} \)) that barely overlaps with the corresponding experimental studies. In addition simulations typically cover a dynamic window of at most 3-4 decades, much narrower than in experimental studies. Despite these caveats, the general consensus is that the Adam-Gibbs relation is generally valid in the regime accessed by the simulations. In experiments, which typically analyse temperatures close to \( T_g \), the Adam-Gibbs relation seems again to be well obeyed for a range of materials [10, 11, 26–32]. Yet, experiments indicate as well that the Adam-Gibbs relation does not hold anymore above a temperature scale close to \( T_{\text{mct}} \) [11, 28], in stark contrast with the numerical results. Systematic deviations from the Adam-Gibbs relation were also reported below \( T_{\text{mct}} \) for some systems [28, 30], but imprecise entropy measurements or inappropriate timescale determinations have been invoked to rationalise them.

In the last three decades, the random first order transition (RFOT) theory of the glass transition [3, 5] has revisited the Adam-Gibbs relation in greater depth [4–7] to provide an increasingly precise description of the connection between thermodynamics and dynamics in supercooled liquids. This connection can be decomposed in two steps. First, the decrease of the configurational entropy is shown, by a purely thermodynamic reasoning [4], to give rise to a growing ‘point-to-set’ static correlation lengthscale:

\[
\xi_{\text{pts}} \propto S_{\text{conf}}^{−1/(d−\theta)}, \tag{2}
\]

where an interface exponent \( \theta \) is introduced. In the simplest approximation, one has \( \theta = d−1 \) which corresponds to a (hyper-)surface in a space of dimension \( d \). The value \( \theta = d/2 \) was also proposed [3, 7], to take into account finite dimensional surface fluctuations due to the disordered nature of the amorphous phase. More generally, the inequality \( \theta \leq d−1 \) is expected to hold. Second, the connection to dynamics is made via the assumption that relaxation in the liquid for \( T < T_{\text{mct}} \) proceeds via thermally activated events correlated over a lengthscale \( \xi_{\text{pts}} \), resulting in the general relation [3, 4],

\[
\log(\tau_\alpha/\tau_0) \propto \xi_{\text{pts}}^\psi/T, \tag{3}
\]

where \( \psi \) is a dynamical exponent. Various theoretical and numerical estimates of \( \psi \) have been proposed [4, 33–36]. In the original paper by Kirkpatrick et al. [3], \( \psi = \theta = d/2 \) was assumed and so only one exponent had been introduced.

Using Eqs. (2, 3), one finds a generalised version of the Adam-Gibbs relation,

\[
\log(\tau_\alpha/\tau_0) \propto \frac{1}{T S_{\text{conf}}} \tag{4}
\]

with a non-trivial exponent

\[
\alpha = \frac{\psi}{d−\theta}. \tag{5}
\]
This shows that $\alpha$ may or may not be equal to unity, depending on the relative values of the two independent exponents $\psi$ and $\theta$. As a consequence, Eq. (4) may or may not be equivalent to Eq. (1).

To our knowledge, a direct test of Eqs. (3, 4, 5) in the theoretically-motivated temperature regime, employing appropriate observables, has never been performed. Most previous simulations have considered a temperature regime $T \gtrsim T_{\text{mct}}$ [12, 17, 21, 37] where the physics is expected to be non-activated and the configurational entropy and point-to-set lengthscales are not well-defined. This is of course valuable work, but theory itself suggests that the tested scaling relations have no reason to hold in this temperature regime. Experiments instead access the correct temperature regime, but cannot easily measure the point-to-set correlation lengthscale. As a proxy, Refs. [38, 39] replaced $\xi_{\text{pats}}$ by the lengthscales of dynamic heterogeneities that can be more easily estimated experimentally [40]. Many other experimental studies study Eq. (1) directly near $T_g$ [11, 30].

In this work, we take advantage of the progress allowed by the swap Monte Carlo algorithm [41, 42] to measure directly in several numerical models the temperature dependence of the configurational entropy and point-to-set lengthscales down to $T_g$. For the dynamics, we build on previous work [42] and provide additional experimental support showing that one can safely estimate the temperature dependence of the relaxation time also down to $T_g$, using a careful fitting procedure. We collect data from earlier works [43-45] that we extend where needed, and perform new simulations for one additional model.

As a result, we are in a position to provide for the first time stringent tests of the Adam-Gibbs relation and of RFOT theory for computer models simulated in the same regime as in experiments. Our results suggest that the Adam-Gibbs relation is generally not valid in computer models in the experimental regime $T_g < T < T_{\text{mct}}$. To test our findings against experiments, we collect high-quality thermodynamic and dynamic data for several supercooled liquids (most of which are obtained by state-of-the-art thermodynamic measurements [46]), and reach similar conclusions. Overall, we find that Eq. (1) is not obeyed for most systems, while Eq. (4) is obeyed with an exponent $\alpha$ that fluctuates weakly from system to system, with typically $\alpha < 1$. Our findings can be taken either as a confirmation that RFOT theory works well, with a non-trivial set of critical exponents, or that a small $\alpha < 1$ exponent indicates that thermodynamics is not the only driving force for the dynamic slowdown near $T_g$.

This paper is organised as follows. In Sec. II we present the numerical methods used to obtain the configurational entropy, the point-to-set lengthscales, and the relaxation time. We also describe our choice of experimental data to reliably test the Adam-Gibbs relation over a broad range of temperatures. In Sec. III we present the results of our analysis of the exponents $\theta$ and $\alpha$ in simulations, then in experiments. We discuss the physical meaning of our results in Sec. IV.

II. DESCRIPTION OF THE DATA

In order to analyse quantitatively the connection between dynamic and thermodynamic properties, we collect and extend data from previous numerical works. We also collect data from selected published experimental works, and motivate our selection.

A. Numerical models

The recent development of the swap Monte Carlo algorithm allows us to access very low-temperature equilibrium configurations in computer simulations. In particular, the temperature regime $T_g < T < T_{\text{mct}}$ can be comfortably accessed. This temperature regime is the correct one to test thermodynamic theories, as it is precisely where they should apply, and it corresponds to the regime explored experimentally.

We gather simulation data for polydisperse systems using a continuous size distribution [42]. The particle diameters $\sigma$ are distributed between $\sigma_{\text{min}}$ and $\sigma_{\text{max}}$ from $f(\sigma) = c\sigma^{-3}$, where $c$ is a normalization constant and $\sigma_{\text{min}}/\sigma_{\text{max}} = 0.45$. We use the average diameter $\bar{\sigma}$ as the unit length.

We study four numerical models: three-dimensional additive hard spheres (HS3D) [41], two and three dimensional non-additive soft disks (SSV2D) [43] and spheres (SSV3D) [42] under an isochoric path. We also perform new simulations of three-dimensional non-additive soft spheres (SSP3D), under an isobaric path. To thermalize the last model, we use an hybrid molecular dynamics/swap Monte Carlo scheme [47].

We use the following pairwise potential for the polydisperse soft sphere/disk models [42],

$$v_{ij}(r) = v_0 \left( \frac{\sigma_{ij}}{r} \right)^{12} + c_0 + c_1 \left( \frac{r}{\sigma_{ij}} \right)^2 + c_2 \left( \frac{r}{\sigma_{ij}} \right)^4,$$

$$\sigma_{ij} = \frac{(\sigma_i + \sigma_j)}{2} (1 - \epsilon|\sigma_i - \sigma_j|),$$

where $v_0$ is the energy unit, and $\epsilon$ quantifies the degree of non-additivity of the system. We set $\epsilon = 0.2$ for SSP3D and SSV2D, and $\epsilon = 0.1$ for SSP3D. The constants, $c_0$, $c_1$ and $c_2$, are chosen to smooth $v_{ij}(r)$ up to its second derivative at the cut-off distance $r_{\text{cut}} = 1.25\sigma_{ij}$. We set the number density $\rho = N/L^3 = 1.02$ with $N = 1500$ for SSV3D, and $\rho = N/L^2 = 1.01$ with $N = 1000$ for SSV2D. For SSP3D, the pressure on the isobaric path is $P = 30.0$. For HS3D [41], the pair interaction is zero for non-overlapping particles and infinite otherwise. The relevant control parameter for hard spheres is the reduced pressure $p = P/(\rho T)$. For hard spheres, $1/p$ plays precisely the same role as temperature $T$ for a dense liquid [48], and there is no distinction between isochoric and isobaric paths.

Relaxation times for HS3D, SSV3D, and SSV2D are measured in units of MC sweeps, which comprise $N$
Monte Carlo trial moves. For SSP3D, the relaxation time is expressed in units of \( \sqrt{v_0/m} \), where \( m \) is the mass of the particles.

### B. Configurational entropy and point-to-set length

The configurational entropy \( S_{\text{conf}} \) is measured from configurations generated with swap Monte Carlo simulations. It is defined as \( S_{\text{conf}} = S_{\text{tot}} - S_{\text{glass}} \), where \( S_{\text{tot}} \) and \( S_{\text{glass}} \) are the total and glass entropies, respectively [16]. \( S_{\text{tot}} \) and \( S_{\text{glass}} \) are computed using thermodynamic integration schemes, as explained in Ref. [45]. In Appendix A we describe how to measure \( S_{\text{conf}} \) along an isobaric path using constant pressure simulations for SSP3D, as this was not documented before.

Figure 1 shows the configurational entropy that we use for latter analysis. The data for \( S_{\text{conf}}(T) \) are normalized by the values at the mode coupling crossover \( T_{\text{mct}} \), whose value is determined by a power law fit to the dynamic relaxation time data [25]. The actual values are \( T_{\text{mct}} = 0.0426, 0.104, 0.556, \) and 0.123 for HS3D, SSV3D, SSP3D, and SSV2D, respectively.

In order to increase the accuracy of the analysis, we employ empirical fitting functions. For the three-dimensional models, we use a conventional fitting function \( T S_{\text{conf}} = A(T - T_K) + B(T - T_K)^2 \) [11, 49]. For the two-dimensional model, we use \( 1/S_{\text{conf}} = A/T + B \) [43]. The fitting parameters are presented in Table I.

We also collect the point-to-set lengthscale \( \xi_{\text{pts}} \) data for SSV2D [43] and HS3D [44], obtained from recently developed computational methods [50, 51]. Together with \( S_{\text{conf}} \), the data for \( \xi_{\text{pts}} \) will allow us to estimate the exponent \( \theta \) using Eq. (2).

### C. Relaxation times

Dynamical information is obtained using either standard Monte Carlo (for HS3D, SSV3D, SSV2D) or molecular dynamics (for SSP3D). The equivalence between the two types of dynamics is well documented [52]. Both Monte Carlo and molecular dynamics simulations are run starting from initial configurations that are obtained using the swap Monte Carlo algorithm. This procedure allows us to cover about 5 orders of magnitude of relevant slow dynamics.

The relaxation time \( \tau_\alpha \) is measured by the self-intermediate scattering function in three dimensional models. For the two-dimensional model, we use the autocorrelation function of the bond-orientational order parameter, which is insensitive to the long-range Mermin-Wagner fluctuations that are specific to \( d = 2 \) [53].

The relaxation time \( \tau_\alpha \) for HS3D [44], SSV3D [42], SSP3D (new to this work), and SSV2D [43] is shown in Figure 2. The data are normalized using an onset temperature \( T_o \) for the emergence of slow dynamics, determined from the fitting procedure described below, and define \( \tau_\alpha = \tau_\alpha(T = T_o) \). Clearly, all simulation data show a non-Arrhenius temperature dependence of the relaxation time, which demonstrates that our models describe fragile glass-formers.

The swap numerical schemes allow us to prepare equilibrated configurations at very low temperatures. Because they involve non-physical particle dynamics, one cannot use them to measure the relaxation time of the physical dynamics in this low-temperature regime. Therefore, we need to extrapolate the relaxation time from the regime where \( \tau_\alpha \) can be measured to the experimental regime, where this is unachievable.

We start by employing the Vogel-Fulcher-Tammann (VFT) law:

\[
\log(\tau_\alpha/\tau_0) \propto (T - T_{\text{VFT}})^{-1}.
\]

where \( \tau_0 \) and \( T_{\text{VFT}} \) are fitting parameters. We fitted this function on our numerical data over the accessible time window and we concluded that it performs very badly when extrapolated at lower temperatures. We found for instance that the swap Monte Carlo algorithm easily

| Model  | A     | B     | \( T_K \) | \( \log_{10}(\tau_\alpha) \) | \( T_o \) | C    | m    |
|--------|-------|-------|----------|------------------|--------|------|------|
| HS3D   | 3.208 | -37.33| 0.0251   | 3.88             | 0.063  | 22.72| 45.5 |
| SSV3D  | 1.495 | -1.92 | 0.0386   | 3.02             | 0.266  | 3.15 | 32.0 |
| SSP3D  | 2.082 | -1.74 | 0.2902   | 0.41             | 0.961  | 16.77| 42.4 |
| SSV2D  | 0.453 | 1.89  | -        | 2.40             | 1.006  | 0.25 | 31.2 |

TABLE I. Fitting parameters for the configurational entropy \( A, B, \) and \( T_K \), for the relaxation time \( \tau_\alpha \), and \( C \) and kinetic fragility index \( m \) for the simulated models. Note that Monte Carlo dynamics (HS3D, SSV3D, SSV2D) and molecular dynamics (SSP3D) have different time units.
thermalises at temperatures below the extrapolated VFT critical temperature $T_{\text{VFT}}$, which invalidates directly its use to describe numerical data [42]. The inability of the VFT law to describe experimental data over a wide range of temperature was discussed in detail in Refs. [54, 55].

It has been found in previous experimental studies that the parabolic law

$$
\tau_{\alpha}^\text{para} = \tau_0 \exp[C(T_\alpha/T - 1)^2]
$$

fits accurately the data over a very large temperature range [56, 57]. Its fitting parameters are $\tau_0$, $C$, and $T_\alpha$.

In addition to the VFT and parabolic laws, we consider two other functional forms, shown in Fig. 2. One is a double exponential equation (MEYGEA) discussed in Refs. [56, 57]:

$$
\tau_\alpha = \tau_0 \exp \left[ \frac{K}{T} \exp[C/T] \right],
$$

where $\tau_0$, $K$, and $C$ are the fitting parameters. The other one is the Avramov and Milchev (AM) equation [58] given by

$$
\tau_\alpha = \tau_0 \exp[A/T^n],
$$

where $\tau_0$, $A$, and $n$ (real exponent) are the fitting parameters. All the fitting functions considered in this paper have three free-fitting parameters which is the minimal number to mathematically characterize non-Arrhenius behavior. Given the small variation of the apparent activation energy over the dynamic range studied experimentally, it is not surprising that several smooth functions of temperature can describe the evolution of $\log(\tau_\alpha)$. Figure 2 shows that different fitting functions produce slight variations in the extrapolated value for $T_g$. The key issue is therefore to choose the best fitting function, i.e., the one from which the low temperature data can be inferred accurately from the high temperature one.

To find the best fitting procedure, we train on experimental data with kinetic fragility indexes similar to our numerical models (see Appendix II). We fit the above four equations to the data, restricting ourselves to a modest dynamic range, comparable to numerical timescales. We then extrapolate to temperatures close to $T_g$, and compare the extrapolation to the actual data. We find excellent agreement when using the parabolic law, which validates further our procedure. Thus, we empirically find that fitting the parabolic law to the numerical time window provides an excellent description of the data close to $T_g$, as reported previously [56, 57]. This is a purely practical choice, and we make no assumption about the physical mechanism which could lead to such a law.

By using the fitting parameter $\tau_0$ obtained from the parabolic law, we define two time windows. First we define the simulation window by $\tau_0/\tau_0 \in [10^4, 10^5]$. The upper bound of this timescale corresponds to recent simulation studies with very long timescales [44, 59]. The experimental window is defined by $\tau_0/\tau_0 \in [10^4, 10^{12}]$. The lower bound corresponds to a timescale around the mode-coupling crossover $T_{\text{mct}}$ ($\tau_0 \approx 10^{-7} \text{ s}$ [60]), and the upper bound corresponds to the timescale at the experimental glass transition $T_g$ ($\tau_0 \approx 100 \text{ s}$). The experimental window is therefore the appropriate regime to test the predictions made by the RFO theory. Notice that in this paper, we neither try to go below $T_g$, nor to examine the fate of supercooled liquids at even lower temperature [61].

For numerical models, we determine the experimental glass transition temperature $T_g$ as $\tau_\alpha^\text{para}(T_g)/\tau_0 = 10^{12}$. The kinetic fragility index $m$ is determined by $m = \partial \log_{10} \tau_\alpha^\text{para}/\partial(T_g/T)|_{T=T_g}$. The fitting parameters and fragility indexes are given in Table I.

D. Experimental data

We select materials for which high-quality data for the configurational entropy and relaxation time over a broad temperature range is available in the literature. This allows for a comparison with computer simulations and an accurate determination of the exponent $\alpha$ in Eq. (4).

We select 2-methyl tetrahydrofuran (2MTHF), ethylbenzene (ETB), ethanol, glycerol, o-terphenyl (OTP), 1-propanol, propylene carbonate (PC), salol, and toluene. The configurational entropy data for 2MTHF, ETB, OTP, PC, salol, and toluene were recently obtained from accurate experiments by Tatsumi, Aso and Yamamuro. Some of the data is presented in Ref. [46]. The data for 1-propanol is taken from Ref. [62]. In these data for all the above materials, $S_{\text{conf}}$ is measured by thermo-
dynamic integration of the heat capacity difference between supercooled liquids and non-equilibrium glasses. This treatment should be conceptually better than using the crystal entropy [11], but this is still a rather crude approximation [63], whose accuracy is expected to be material-dependent [64]. For ethanol [65, 66] and glycerol [65, 67], $S_{\text{conf}}$ is obtained using the crystal entropy $S_{\text{cry}}$, i.e., $S_{\text{conf}} = S_{\text{liq}} - S_{\text{cry}}$.

The relaxation time data are mainly obtained from dielectric measurements, but some data are combined with other methods, such as viscosity measurements. The corresponding references are: 2MTHF [11], ETB [68–70], ethanol [46], glycerol [71–73], OTP [74], 1-propanol [11, 75], PC [72, 73, 76], salol [77], and toluene [74].

For the experimental data, we set $\tau_0 = 10^{-10}$ s. Therefore the simulation and experimental time windows correspond to $\tau_\alpha \in [10^{-10}$ s, $10^{-5}$ s] and $\tau_\alpha \in [10^{-7}$ s, $10^{2}$ s], respectively. In particular, $T_g$ corresponds to the standard relaxation time $\tau_\alpha = 100$ s.

The configurational entropy and relaxation time data for the materials presented above are gathered in Fig. 3, together with empirical quadratic fits to the configurational entropy.

III. RESULTS

In this section, we perform a test of Eqs. (1, 2, 3, 4, 5) using the experimental and numerical data presented in Sec. II. We first study Eq. (2) using numerical data for $\xi_{\text{pts}}$ and $S_{\text{conf}}$ to estimate $\theta$. Then, we estimate $\alpha$ in Eq. (4) by comparing $\tau_\alpha$ and $S_{\text{conf}}$ using both computer simulations and experiments to investigate the validity of the Adam-Gibbs relation in Eq. (1). Finally, the values of $\theta$ and $\alpha$ allow us to discuss that taken by $\psi = (d-\theta)\alpha$, deduced from Eq. (5).

A. The static exponent $\theta$

First we estimate the exponent $\theta$ in Eq. (2) combining independent data obtained for $S_{\text{conf}}$ and $\xi_{\text{pts}}$.

Figure 4 shows a log-log plot of $S_{\text{conf}}$ versus $\xi_{\text{pts}}$ for three dimensional polydisperse hard spheres (HS3D) (a) and two dimensional soft disks (SSV2D) (b). We emphasize that while temperature is a running parameter in this plot, the data point in Fig. 4 correspond to the regime of interest $T < T_{\text{met}}$. Such results have never been achieved, as earlier numerical work were all performed for $T > T_{\text{met}}$, or only slightly below $T_{\text{met}}$ [33].

For HS3D, we report two estimates for $S_{\text{conf}}$, obtained from different schemes. One is a generalized Frenkel-Ladd (GFL) method [45, 80], and the other is the Franz-Parisi (FP) free energy method proposed earlier [44, 81, 82]. The exponent $\theta$ is extracted by fits to straight lines, whose slope gives $\theta = d$, see Eq. (2). We obtain $\theta \approx 1.35$ for GFL and $\theta \approx 1.84$ for FP. These values are compatible with either the theoretical prediction $\theta = d/2$ by Kirkpatrick et al. [3], or with that of Franz $\theta = d - 1$ [83].

We obtain $\theta = 1.12$ for SSV2D. This value is close to both theoretical predictions, $\theta = d/2$ and $\theta = d - 1$, which coincide in $d = 2$, giving $\theta = 1$. Obviously, one cannot discriminate between the two predictions.

Overall, we find that for $d = 3$ the value measured for $\theta$ conforms with the two available predictions, which is an encouraging result from the viewpoint of RFOT theory. Unfortunately, the obtained values fall in-between the two predictions, which are too close to be discriminated. We suggest that performing point-to-set and configurational entropy measurements in $d = 4$, combining recently developed tools [45, 51, 84], would be very useful to conclude on this point. Indeed, when $d = 4$, the two predictions yield $\theta = d/2 = 2$ and $\theta = d - 1 = 3$, which are further apart than in $d = 3$. 

FIG. 3. (a) Configurational entropy data for 2MTHF [46], ETB [46], ethanol [66], glycerol [67], OTP [78], 1-propanol [62], PC [46], salol [78], and toluene [46]. The solid curves are quadratic fitting functions, as used for the $d = 3$ numerical models. (b) Relaxation time data for 2MTHF [11], ETB [68–70], Ethanol [79], glycerol [71–73], OTP [74], 1-propanol [11, 75], PC [72, 73, 76], salol [77], and toluene [74]. The horizontal dashed line indicates the timescale of the experimental glass transition, $\tau_\alpha = 100$ s.
FIG. 4. $S_{\text{conf}}$ vs. $\xi_{\text{pts}}$ plot in $d = 3$ hard spheres (HS3D) (a) and $d = 2$ soft disks (SSV2D) (b). The straight lines are power law fits. For HS3D, we show two independent estimates of $S_{\text{conf}}$ obtained from: the generalized Frenkel-Ladd (GFL) method and the Franz-Parisi (FP) free energy approach.

B. Breakdown of the Adam-Gibbs relation and numerical estimation of $\alpha$

We next examine the validity of Eq. (4) by connecting $\tau_\alpha$ and $S_{\text{conf}}$, and estimating the exponent $\alpha$. When $\alpha = 1$, the Adam-Gibbs relation in Eq. (1) is recovered.

In Fig. 5(a,c,e,g) we show conventional Adam-Gibbs plots where the evolution of $\log_{10}(\tau_\alpha/\tau_0)$ is represented as a function of $1/(T s_{\text{conf}})$, where $s_{\text{conf}} = S_{\text{conf}}/N$, for hard spheres (HS3D) (a), soft spheres along the isochoric path (SSV3D) (c), along the isobaric path (SSP3D) (e), and the soft disks (SSV2D) (g). We combine the dynamic and thermodynamic data described in Sec. II, restricted to the experimental time window ($\tau_\alpha/\tau_0 \in [10^3 - 10^{12}]$). To our knowledge, this is the first time that the Adam-Gibbs relation is tested for computer models over the time window where it is actually supposed to apply.

For all three-dimensional models, we find that $\log_{10}(\tau_\alpha/\tau_0)$ is a concave function of $1/T s_{\text{conf}}$, whereas it is convex for the two-dimensional model. If tested over a narrow time window close to $T_{\text{mct}}$, an acceptable linear behaviour could possibly be observed, that would suggest the validity of the Adam-Gibbs relation, in agreement with many earlier findings [12, 17–24]. The trend that we report here appears to contrast with recent results obtained in the Kob-Andersen model, where slight convexity and concavity are respectively observed in $d = 3$ [23] and $d = 2$ [21]. These results were however obtained in the numerical time window, above $T_{\text{mct}}$. Our results demonstrate that when observed over a much broader range, and closer to $T_g$, the Adam-Gibbs relation is actually not obeyed for any of the numerical models studied here.

The clear violations of the standard Adam-Gibbs relation that we find over the experimental time window imply that the exponent $\alpha$ must deviate from the value $\alpha = 1$. We varied its value around unity and used it as a free parameter to obtain generalised Adam-Gibbs plots, which are shown in Fig. 5(b,d,f,h) for the same numerical estimation of $\alpha$. 

FIG. 5. Left panels: Standard Adam-Gibbs plot for the $d = 3$ hard spheres (HS3D) (a), $d = 3$ soft spheres along the isochoric path (SSV3D) (b), the isobaric path (SSP3D) (c), and $d = 2$ soft disks (SSV2D) (d). Right panels: Generalized Adam Gibbs plots with the fitted $\alpha$ value for each model. The horizontal dashed lines correspond to the timescale for the experimental glass transition $T_g$. 

...
ical models. All plots now show a perfect straight line, suggesting that the introduction of the parameter $\alpha$ is sufficient to describe the data. We obtain $\alpha = 0.24, 0.49, 0.72$, and 1.89, for HS3D, SSP3D, SSV3D, and SSV2D, respectively, so that $\alpha < 1$ for the three dimensional models, whereas $\alpha > 1$ for the two dimensional model.

Since the four models we have simulated all display violations of the Adam-Gibbs relation, we conclude that Eq. (1) does not describe well the physics of simulated supercooled liquids when analysed over the experimental time window. Additional models should be studied and analysed before concluding about the possible universality of the exponent $\alpha$, but our initial results do not point towards a constant value. Once more, it would be very valuable to obtain data in $d = 4$ to see if a different value for $\alpha$ is found in larger spatial dimensions.

C. Breakdown of the Adam-Gibbs relation and experimental estimation of $\alpha$

Before starting this study, we felt that there was a general consensus in the community that the Adam-Gibbs relation is well-obeyed in real materials analysed near the experimental glass transition $T_g$. Thus, the outcome of the computer simulations showing deviations from Eq. (1) appeared as a worrying disagreement between simulations and experiments.

Therefore, we decided to collect data sets for several molecular liquids, where high-precision dynamic and thermodynamic data would be available over both simulation and experimental time windows, in order to perform a direct comparison with computer models.

We present the results of our data collection in Fig. 6 using again the representation where the standard Adam-Gibbs relation would yield a straight line. When analysed over the entire experimental time window, defined above, we again observe a clear concavity for most materials. The Adam-Gibbs relation in Eq. (1) is violated over this regime, although of course it holds if observed over a restricted time window close to $T_g$ [11] (almost by definition—the data is continuous!).

As for the simulations, we fit the experimental data using the exponent $\alpha$ as an additional free parameter. From the experimental data, we determine two distinct values for $\alpha$, obtained by fitting either over the simulation or the experimental time window. The typical trend that we observe is that $\alpha > 1$ over the simulation time window, but $\alpha < 1$ over the experimental time window. The latter fits are included in Fig. 6, and they describe well the data over the entire experimental time window.

We notice that the concavity in the Adam-Gibbs plot in the experimental time window was already reported [28, 30]. However, the concavity would be overlooked as it is less pronounced than the convexity found at much higher temperature, close to $T_{mef}$ and above [28]. Moreover, Ref. [30] concluded that the observed concavity was attributed to an imprecise estimate of the configurational entropy. Our results obtained from simulation data with accurate configurational entropy measurements and recent high-quality experimental data suggest instead that the observed concavity is a generic physical phenomenon reflecting the nature of glassy dynamics over the experimental time window.

IV. DISCUSSION

Our central conclusion from both simulations and experiments considered over a broad time regime $\tau_{o}/\tau_{o} \in [10^3, 10^7]$ (defined to be both experimentally accessible and theoretically relevant) is that the conventional Adam-Gibbs relation in Eq. (1) is not obeyed. Instead, the general form predicted by RFOT theory in Eq. (4) describes numerical and experimental data well. This is maybe not so surprising, from an empirical viewpoint, given that the generalised relation has one more free fitting parameter.

We compile all our results for the values of $\alpha$ from simulations (empty points) and experiments (filled points) in Fig. 7. To organise the data, we use the kinetic fragility index $m$ as the horizontal axis. This is simply a matter of convenience (as a matter of fact, no strong trend is observed). Note that, somewhat paradoxically, we do not have values for $\alpha$ in the computer models over the simulation time window because our computational schemes to measure $S_{conf}$ only become applicable for low enough temperatures, typically $T \lesssim T_{mef}$ [45, 82].

The experimental data in Fig. 7 obtained by considering the simulation time window are dispersed, $\alpha = 0.61 - 2.34$, and tend to be characterised by rather large values $\alpha > 1$. By contrast, considering a broader and physically better justified experimental time window, data for both simulations and experiments are much less
scattered, $\alpha \simeq 0.25 - 1.28$, with a preferred average value $\alpha \simeq 0.5 - 0.6$, except for ethanol. We notice that the deviation for ethanol might be due to a poor estimation of $S_{\text{conf}}$. The data was measured using the crystal entropy, and the approximation $S_{\text{glass}} \simeq S_{\text{cryt}}$ may not be good for this material.

Before concluding, we make a further caveat regarding the above analysis of the RFOT theory predictions. In principle, we could have introduced additional subdominant physical prefactors into the scaling relations in Eqs. (2, 3) that could also be temperature dependent quantities. In particular, a surface tension could enter the relation between $S_{\text{conf}}$ and $\xi_{\text{pairs}}$ [6, 85], and an energy scale could enter the activated scaling relation in Eq. (3). In the absence of strong theoretical insights into these quantities, we decided to ignore them. They could of course very well affect the measured values of the reported exponents. Thus, a better determination of these quantities is an important research goal [33, 86, 87], in particular in the experimental time window.

To summarize our results in terms of numerical values for the critical exponents introduced within RFOT theory, we observe in $d = 3$ that the combination $\theta \simeq 3/2$ and $\alpha \simeq 0.5 - 0.6$ works well, which would then result in $\psi$ falling in the range $\psi \simeq 0.75 - 0.90$. If we use instead the value $\theta = 2$, we would obtain a somewhat larger value for the dynamic exponent $\psi \simeq 1.0 - 1.2$, which agrees well with earlier indirect analysis [38, 39]. Both values violate the general bound $\psi \geq \theta$ discussed in the context of spin glasses [88], the equality $\psi = \theta$ found for the random field Ising model [89], and the prediction $\psi = \theta = d/2$ in Ref. [3]. In the absence of stronger theoretical constraints, we tentatively conclude that the measured $\psi$ value that we observe appears somewhat small, i.e., smaller than all known theoretical predictions. In $d = 2$, we get $\theta \simeq 1.1$ and $\alpha \simeq 1.9$, which in turns implies that $\psi \simeq 1.7$, which appears somewhat large, by contrast with $d = 3$.

Our conclusion that $\alpha < 1$ is favored by the data over the experimental time window sheds some new light on an old debate in the glass literature [5, 56, 90, 91]. Assuming the existence of an ideal glass transition at equilibrium where $S_{\text{conf}} \rightarrow 0$ and $\tau_{\text{r}} \rightarrow \infty$, one is naturally led to the determination of two critical temperatures: the Kauzmann temperature $T_{\text{K}}$ where $S_{\text{conf}}$ vanishes, and the critical temperature $T_0$ where the relaxation time diverges (not to be confused with onset temperature $T_o$ used above). Typically, the latter is obtained from a Vogel-Fulcher-Tammann fit ($T_0 = T_{\text{VFT}}$ in Eq. (8)) to the relaxation time. The possible equality $T_0 = T_{\text{K}}$ would provide a strong empirical sign for the existence of an ideal glass transition underlying glass formation [5]. A large data set collected by Tanaka suggests the existence of systematic differences between the two temperatures [90], with the tendency that $T_{\text{K}} > T_0$, and an apparent correlation with kinetic fragility. In our analysis using Eq. (4) to describe the data, the connection between thermodynamics and dynamics becomes automatically satisfied, and thus by construction thermodynamic and dynamic singularities necessarily coincide. Assuming that the determination of $T_{\text{K}}$ is the most robust one, we conclude that it is the experimental determination of $T_0$ which should be questioned. In particular, using $\alpha < 1$ in Eqs. (4) and assuming an asymptotically linear vanishing of $S_{\text{conf}}$, one would predict that $\log(\tau_0/\tau_o) \propto (T_{\text{K}} - T_0)^{-\alpha}$, which is distinct from the standard Vogel-Fulcher-Tamman fit and would automatically produce the equality $T_{\text{K}} = T_0$.

From a broader perspective, we conclude that the Adam-Gibbs relation, which is an important milestone in the field of glass transition studies, is generally violated in both computer models and real materials when tested over a broad, experimentally-relevant temperature range. We nevertheless argued that the failure of Eq. (1) cannot be taken as evidence that thermodynamic theories of the glass transition are incorrect. The RFOT theory prediction of a connexion between statics and dynamics in Eq. (4) is obeyed by all materials, with exponent values that are reasonable, but remain to be predicted from first principles. A larger concern, perhaps, is the apparent lack of universality in the data shown in Fig. 7 which clearly display variations from one system to another. This may still be rationalised by invoking the fact that $\alpha$ is obtained from the analysis of a finite time window where additional preasymptotic effects and temperature dependent prefactors may influence the reported results.

Taking an orthogonal perspective, we finally ask: Do our results validate or invalidate some theories of the glass transition? After all, we just established that a slightly generalised version of the Adam-Gibbs relation with $\alpha \simeq 0.5 - 0.6$ describes simulations and experiments.
over 9 orders of magnitude in the experimentally relevant regime. This is not a small accomplishment. One can take the alternative view that the deviations from the canonical exponent values should be taken as an indirect sign that thermodynamics only contributes some part of the slowing down, in addition to other physical factors [92–97]. This view is sometimes also invoked to rationalise the “modest” growth of static correlation length-scale observed numerically and experimentally [98, 99]. Our finding that \( \alpha < 1 \) suggests instead that it is the growth of the relaxation time that is actually too modest! It is therefore difficult to rationalise how another physical factor working in addition to the entropy could be invoked to explain our findings. The most radical view is in fact that thermodynamics is just a spectator to the glassy dynamics [100], in which case our findings should be interpreted as purely coincidental since entropy plays in fact no role. We have no strong argument to oppose to this view, which remains perfectly admissible.

ACKNOWLEDGMENTS

We thank D. Coslovich and F. Zamponi for insightful discussions. We also thank S. Tatsumi and O. Yamamuro for sharing their high-quality experimental data for the configurational entropy. The research leading to these results has received funding from the Simons Foundation (#454933, Ludovic Berthier).

Appendix A: Configurational entropy along an isobaric path

We wish to measure the configurational entropy \( S_{\text{conf}}(T, P) \) along an isobaric (constant pressure) path. It is computed as \( S_{\text{conf}}(T, P) = S_{\text{tot}}(T, P) - S_{\text{glass}}(T, P) \), where \( S_{\text{tot}}(T, P) \) and \( S_{\text{glass}}(T, P) \) are the total and glass entropies at the temperature \( T \) and pressure \( P \). We explain how to get \( S_{\text{conf}}(T, P) \) from NPT simulation trajectories.

1. Notations

We consider the Helmholtz free energy \(-\beta F(T, V) = \ln Z(T, V)\), where \( \beta = 1/T \) and \( Z(T, V) \) is the partition function of the NVT ensemble. We also consider the Gibbs free energy \(-\beta G(T,P) = \ln Y(T,P)\), where \( Y(T,P) \) is the partition function of the NPT ensemble, given by

\[
Y(T,P) = \int_0^{\infty} \text{d}V e^{-\beta(PV+F(T,V))}.
\]

We introduce the probability distribution of the volume \( V \) for a given \( T \) and \( P \),

\[
\rho(V|T,P) = \frac{e^{-\beta(PV+F(T,V))}}{Y(T,P)}.
\]

In equilibrium, \( \rho(V|T,P) \) is given by Gaussian distribution,

\[
\rho(V|T,P) = \frac{1}{\sqrt{2\pi \sigma_V^2}} \exp \left[ -\frac{(V-V_*)^2}{2\sigma_V^2} \right], \tag{A3}
\]

where \( V_* \) and \( \sigma_V^2 \) are the mean and variance of the volume, respectively. We define \( \langle \cdots \rangle_{T,P} = \int_0^\infty \text{d}V \rho(V|T,P) \langle \cdots \rangle \). Using this average, we can write \( V_* = (V)_{T,P} \) and \( \sigma_V^2 = \langle (V - V_*)^2 \rangle_{T,P} \).

2. Total entropy

The total entropy \( S_{\text{tot}}(T, P) \) is obtained by a thermodynamic integration of the isobaric heat capacity from a reference temperature \( T_{\text{ref}} = 1/\beta_{\text{ref}} \), to the target temperature \( T = 1/\beta \),

\[
S_{\text{tot}}(T, P) = S_{\text{tot}}(T_{\text{ref}}, P) - \frac{Nd}{2} \left( \ln \beta - \ln \beta_{\text{ref}} \right) + \beta U_s(T, P) - \beta_{\text{ref}} U_s(T_{\text{ref}}, P)
\]

\[
- \int_{\beta_{\text{ref}}}^{\beta} \text{d}\beta' U_s(T', P) + P \left( \beta V_s(T, P) - \beta_{\text{ref}} V_s(T_{\text{ref}}, P) \right)
\]

\[-P \int_{\beta_{\text{ref}}}^{\beta} \text{d}\beta' V_s(T', P), \tag{A4}\]

where \( U_s(T, P) \) is the mean potential energy, and \( V_s(T, P) \) is the mean volume; \( U_s(T, P) \) and \( V_s(T, P) \) are measured by constant pressure simulations. The entropy at the reference state is obtained by \( S_{\text{tot}}(T_{\text{ref}}, P) = \langle S_{\text{tot}}(T_{\text{ref}}, P) \rangle_{T,P} \) using the NVT ensemble scheme [44]. This treatment for the reference state will be justified below.

3. Glass entropy

To get the glass entropy, we use the generalised Frenkel-Ladd method which relies on the NVT ensemble [45]. In general, one can smoothly connect NVT and NPT ensembles in terms of mean values. For example, thermodynamics guarantees that \( S(T, P) = \langle S(T, V|T,P) \rangle \). However, special attention should be paid if one uses the NVT ensemble scheme with trajectories generated by the NPT ensemble for finite system size [101]. A related issue is discussed in Ref. [102]. Indeed, what we can compute is \( \langle S(T, V) \rangle_{T,P} \). In general,

\[
S(T, P) = \langle S(T, V) \rangle_{T,P} - \langle \ln \rho(V|T,P) \rangle_{T,P}. \tag{A5}\]

Therefore, we need to consider the second term in Eq. (A5) as a correction term. We can evaluate this term with Eq. (A3):

\[
- \frac{1}{N} \langle \ln \rho(V|T,P) \rangle_{T,P} = \frac{1}{N} \ln \sqrt{2\pi e \sigma_V^2}. \tag{A6}\]
shows various fits of the data performed over respectively.
m values, takes comparable to the simulation models employed in this paper. 
m = 53, 48, 35 for glycerol, propylene glycol, and 1-propanol, respectively.

Since $\sigma^2_s \sim N$, this term vanishes in the thermodynamic limit, as expected. Indeed, for $N = 1500$ systems, we get negligible values, $\frac{1}{N} \ln \sqrt{2\pi e \sigma^2_s} \simeq 0.0026$ and 0.0013 at $T_{ref} = 7.0$ and $T = 0.37$, respectively. These values are small compared to the absolute value of $S_{conf}/N \simeq 0.36–0.80$. Thus we can safely use $S(T,P) = (S(T,V))_{T,P}$. Especially we use the following equation, $S_{glass}(T,P) = (S_{glass}(T,V))_{T,P}$.

II. EXTRAPOLATION TIMES TOWARDS $T_g$

Here we test the validity of the extrapolation of relaxation time from the numerical to the experimental timescale using various fitting functions. The experimental data on which this is done have kinetic fragility indexes similar to the simulation models.

Figure 8 shows various fits of the data performed over the simulation time window, $\tau_\alpha \leq 10^{-5}$ sec. and then extrapolated to lower temperatures down to $T_g$ where $\tau_\alpha = 100$ s. In all three cases shown in Fig. 8, the parabolic law is the best functional form that correctly predicts the actual data over the experimental time window. All other functional forms, when fitted over the simulation time window, tend to deviate from the actual data at low temperatures. Notice that the uncertainty on the determination of $T_g$ using the numerical time window and a parabolic fit is very small. This is the strategy we have used in previous numerical studies [42–44].

[1] Gerold Adam and Julian H Gibbs, “On the temperature dependence of cooperative relaxation properties in glass-forming liquids,” J. Chem. Phys. 43, 139 (1965).
[2] Ludovic Berthier and Giulio Biroli, “Theoretical perspective on the glass transition and amorphous materials,” Rev. Mod. Phys. 83, 587 (2011).
[3] T. R. Kirkpatrick, D. Thirumalai, and P. G. Wolynes, “Scaling concepts for the dynamics of viscous liquids near an ideal glassy state,” Phys. Rev. A 40, 1045–1054 (1989).
[4] Jean-Philippe Bouchaud and Giulio Biroli, “On the adam-gibbs-kirkpatrick-thirumalai-wolynes scenario for the viscosity increase in glasses,” J. Chem. Phys. 121, 7347–7354 (2004).
[5] Vassiliy Lubchenko and Peter G. Wolynes, “Theory of structural glasses and supercooled liquids,” Annual Review of Physical Chemistry 58, 235–266 (2007).
[6] G. Biroli and J.P. Bouchaud, “The Random First-Order Transition Theory of Glasses: a critical assessment,” in Structural Glasses and Supercooled Liquids: Theory, Experiment and Applications, edited by P.G.Wolynes and V.Lubchenko (Wiley & Sons, 2012) arXiv:0912.2542.
[7] Vassiliy Lubchenko, “Theory of the structural glass transition: a pedagogical review,” Advances in Physics 64, 283–443 (2015).
[8] Patrick Charbonneau, Jorge Kurchan, Giorgio Parisi, Pierfrancesco Urbani, and Francesco Zamponi, “Glass and jamming transitions: From
exact results to finite-dimensional descriptions,” Annual Review of Condensed Matter Physics 8, 265–288 (2017).

[9] Jacek Dudowicz, Karl F. Freed, and Jack F. Douglas, “Generalized entropy theory of polymer glass formation,” Advances in Chemical Physics, 125–222 (2008).

[10] CA Angell, “Entropy and fragility in supercooking liquids,” Journal of the American Chemical Society 138, 12A541 (2006).

[11] R. Richert and C. A. Angell, “Dynamics of glass-forming liquids. v. on the link between molecular dynamics and configurational entropy,” The Journal of Chemical Physics 108, 9016–9026 (1998).

[12] Srikanth Sastry, “The relationship between fragility, configurational entropy and the potential energy landscape of glass-forming liquids,” Nature 409, 164 (2001).

[13] Jeppe C Dyre, Tina Hechsher, and Kristine Niss, “A brief critique of the adam–gibbs entropy model,” Journal of Non-Crystalline Solids 355, 624–627 (2009).

[14] F. Sciortino, W. Kob, and P. Tartaglia, “Inherent structure entropy of supercooled liquids,” Phys. Rev. Lett. 83, 3214–3217 (1999).

[15] Srikanth Sastry, “Evaluation of the configurational entropy of a model liquid from computer simulations,” Journal of Physics: Condensed Matter 12, 6515–6523 (2000).

[16] Ludovic Berthier, Misaki Ozawa, and Camille Scaliet, “Configurational entropy of glass-forming liquids,” The Journal of Chemical Physics 150, 160902 (2019).

[17] S. Mossa, E. La Nave, H. E. Stanley, C. Donati, F. Sciortino, and P. Tartaglia, “Dynamics and configurational entropy in the lewis-wahnström model for supercooled orthoterpheylen,” Phys. Rev. E 65, 041205 (2002).

[18] Francesco Sciortino, “Potential energy landscape description of supercooled liquids and glasses,” Journal of Statistical Mechanics: Theory and Experiment 2005, 038086 (2005).

[19] Ivan Saika-Voivod, Peter H Poole, and Francesco Sciortino, “ Fragile-to-strong transition and polymorphism in the energy landscape of liquid silica,” Nature 412, 514 (2001).

[20] Luca Angelani, Giuseppe Foffi, Francesco Sciortino, and Piero Tartaglia, “Diffusivity and configurational entropy maxima in short range attractive colloids,” Journal of Physics: Condensed Matter 17, L113–L119 (2005).

[21] Shiladitya Sengupta, Smarajit Karmakar, Chandan Dasgupta, and Srikanth Sastry, “Adam-gibbs relation for glass-forming liquids in two, three, and four dimensions,” Phys. Rev. Lett. 109, 095701 (2012).

[22] Francis W Starr, Jack F Douglas, and Srikanth Sastry, “The relationship of dynamical heterogeneity to the adam-gibbs and random first-order transition theories of glass formation,” The Journal of chemical physics 138, 12A541 (2013).

[23] Anshul DS Parmar, Shiladitya Sengupta, and Srikanth Sastry, “Length-scale dependence of the stokes-einstein and adam-gibbs relations in model glass formers,” Physical review letters 119, 056601 (2017).

[24] Philip H Handle and Francesco Sciortino, “The adam-gibbs relation and the tip4p/2005 model of water,” Molecular physics 116, 3366–3371 (2018).

[25] Wolfgang Götze, Complex dynamics of glass-forming liquids: A mode-coupling theory, Vol. 143 (Oxford University Press, Oxford, 2008).

[26] JH Magill, “Physical properties of aromatic hydrocarbons. iii. a test of the adam–gibbs relaxation model for glass formers based on the heat-capacity data of 1, 3, 5-tri-naphthylbenzene,” The Journal of chemical physics 47, 2802–2807 (1967).

[27] Shuichi Takahara, Osamu Yamamuro, and Takasuke Matsuo, “Calorimetric study of 3-bromopentane: correlation between structural relaxation time and configurational entropy,” The Journal of Physical Chemistry 99, 9589–9592 (1995).

[28] KL Ngai, “Modification of the adam–gibbs model of glass transition for consistency with experimental data,” The Journal of Physical Chemistry B 103, 5895–5902 (1999).

[29] C Alba-Simionesco, “Saltent properties of glass-forming liquids close to the glass transition,” Comptes Rendus de l’Académie des Sciences-Series IV-Physics-Astronomy 30, 1556–1559 (2004).

[30] CM Roland, Simone Capaccioli, Mauro Lucchesi, and R Casalini, “Adam-gibbs model for the supercooled dynamics in the ortho-terphenyl ortho-phenylphenol mixture,” The Journal of chemical physics 120, 10640–10646 (2004).

[31] D Cangialosi, A Alegria, and J Colmenaro, “Relationship between dynamics and thermodynamics in glass-forming polymers,” EPL (Europhysics Letters) 70, 614 (2005).

[32] Elżbieta Masiewicz, Andrzej Grzybowski, Katarzyna Grzybowska, Sebastian Pawlus, Jürgen Piontek, and Marian Paluch, “Adam-gibbs model in the density scaling regime and its implications for the configurational entropy scaling,” Scientific reports 5, 13998 (2015).

[33] Chiara Cammarota, Andrea Cavagna, Giacomo Gradenigo, Tomas Grigera, and Paolo Verrocchio, “Numerical determination of the exponents controlling the relationship between time, length, and temperature in glass-forming liquids,” The Journal of Chemical Physics 131, 194901 (2009).

[34] Takasuke Matsuo, “Calorimetric study of 3-naphthylbenzene,” Phys. Rev. Lett. 80, 225506 (2012).

[35] R. Gutiérez, S. Karmakar, Y. G. Pollack, and I. Procaccia, “The static lengthscale characterizing the glass transition at lower temperatures,” EPL (Europhysics Letters) 111, 56009 (2015).

[36] Andrea Cavagna, Tomas S. Grigera, and Paolo Verrocchio, “Dynamic relaxation of a liquid cavity under amorphous boundary conditions,” The Journal of Chemical Physics 136, 204502 (2012).

[37] Simone Capaccioli, Giancarlo Ruocco, and Francesco Zamponi, “Dynamically correlated regions and configurational entropy in supercooled liquids,” The Journal of Physical Chemistry B 112, 10652–10658 (2008).

[38] C Brun, F. Ladié, D L'Hôte, G Biroli, and J. Pouchaut, “Evidence of growing spatial correlations during the aging of glassy glycerol,” Physical review letters 109, 175702 (2012).

[39] L. Berthier, G. Biroli, J.-P. Bouchaud, L. Cipelletti, D. El Masri, D. L'Hôte, F. Ladieu, and M. Pernot, “Direct experimental evidence of a growing length scale accompanying the glass transition,” Science 310, 1797–1800 (2005).
and Misaki Ozawa, “Equilibrium sampling of hard spheres up to the jamming density and beyond,” Phys. Rev. Lett. 116, 238002 (2016).

42 Andrea Ninarello, Ludovic Berthier, and Daniele Coslovich, “Models and algorithms for the next generation of glass transition studies,” Phys. Rev. X 7, 021039 (2017).

43 Ludovic Berthier, Patrick Charbonneau, Andrea Ninarello, Misaki Ozawa, and Sho Yaida, “Zero-temperature glass transition in two dimensions,” Nature Communications 10, 1508 (2019).

44 Ludovic Berthier, Patrick Charbonneau, Daniele Coslovich, Andrea Ninarello, Misaki Ozawa, and Sho Yaida, “Configurational entropy measurements in extremely supercooled liquids that break the glass ceiling,” Proceedings of the National Academy of Sciences 114, 11356–11361 (2017).

45 Misaki Ozawa, Giorgio Parisi, and Ludovic Berthier, “Configurational entropy of polydisperse supercooled liquids,” The Journal of Chemical Physics 149, 154501 (2018).

46 Soichi Tatsumi, Shintaro Aso, and Osamu Yamamoto, “Thermodynamic study of simple molecular glasses: Universal features in their heat capacity and the size of the cooperatively rearranging regions,” Phys. Rev. Lett. 109, 045701 (2012).

47 Ludovic Berthier, Elijah Flenner, Christopher J. Fullerton, Camille Scalliet, and Murari Singh, “Efficient swap algorithms for molecular dynamics simulations of equilibrium supercooled liquids,” arXiv preprint arXiv:1811.12837 (2018).

48 Ludovic Berthier and Thomas A. Witten, “Glass transition of dense fluids of hard and compressible spheres,” Phys. Rev. E 80, 012102 (2009).

49 Atreyee Banerjee, Shiladitya Sengupta, Srikanth Sastri, and Sarika Maitra Bhattacharyya, “Role of structure and entropy in determining differences in dynamics for glass formers with different interaction potentials,” Phys. Rev. Lett. 113, 225701 (2014).

50 G. Biroli, J.P. Bouchaud, A. Cavagna, TS Grigera, and P. Verrochio, “Thermodynamic signature of growing amorphous order in glass-forming liquids,” Nature Physics 4, 771–775 (2008).

51 Ludovic Berthier, Patrick Charbonneau, and Sho Yaida, “Efficient measurement of point-to-set correlations and overlap fluctuations in glass-forming liquids,” The Journal of Chemical Physics 144, 024501 (2016).

52 Ludovic Berthier and Walter Kob, “The monte carlo dynamics of a binary lennard-jones glass-forming mixture,” J. Phys.: Condens. Matter 19, 205130 (2007).

53 Elijah Flenner and Grzegorz Szamel, “Fundamental differences between glassy dynamics in two and three dimensions,” Nature communications 6, 7392 (2015).

54 F. Stickel, E. W. Fischer, and R. Richert, “Dynamics of glass-forming liquids. I. Temperature-derivative analysis of dielectric relaxation data,” J. Chem. Phys. 102, 6251–6257 (1995).

55 ME Blodgett, Takeshi Egami, Z Nussinov, and KF Kelton, “Proposal for universality in the viscosity of metallic liquids,” Scientific reports 5, 13837 (2015).

56 Yael S. Elmataz, David Chandler, and Juan P. Garrahan, “Corresponding states of structural glass formers. ii,” The Journal of Physical Chemistry B 114, 17113–17119 (2010).

57 John C. Mauro, Yuanzheng Yue, Adam J. Ellison, Prabhat K. Gupta, and Douglas C. Allan, “Viscosity of glass-forming liquids,” Proceedings of the National Academy of Sciences 106, 19780–19784 (2009).

58 I Avramov and A Milchev, “Effect of disorder on diffusion and viscosity in condensed systems,” Journal of non-crystalline solids 104, 253–260 (1988).

59 Daniele Coslovich, Misaki Ozawa, and Walter Kob, “Dynamic and thermodynamic crossover scenarios in the kob-andersen mixture: Insights from multi-cpu and multi-gpu simulations,” The European Physical Journal E 41, 62 (2018).

60 V. N. Novikov and A. P. Sokolov, “Universality of the dynamic crossover in glass-forming liquids: A “magic” relaxation time,” Phys. Rev. E 67, 031507 (2003).

61 C Patrick Royall, Francesco Turci, Soichi Tatsumi, Kiyoshi Takeda, Osamu Yamamoto, and Hiroshi Suga, “Heat capacities and glass transitions of 1-propanol and 3-methylpentane under pressure. new evidence for the entropy theory,” Journal of non-crystalline solids 171, 259–270 (1994).

62 Akira Yoshimori and Takashi Odagaki, “Configurational entropy and heat capacity in supercooled liquids,” Journal of the Physical Society of Japan 80, 064601 (2011).

63 Hillary L Smith, Chen W Li, Andrew Hoff, Glenn R Garrett, Dennis S Kim, Fred C Yang, Matthew S Lucas, Tabitha Swan-Wood, Jiao YW Lin, Matthew B Stone, et al., “Separating the configurational and vibrational entropy contributions in metallic glasses,” Nature Physics 13, 900 (2017).

64 Kiyoshi Takeda, Osamu Yamamoto, Itaru Tsukushi, Takasuke Matsuo, and Hiroshi Suga, “Calorimetric study of ethylene glycol and 1, 3-propanediol: configurational entropy in supercooled polyalcohols,” Journal of molecular structure 479, 227–235 (1999).

65 Osamu Haida, Hiroshi Suga, and SuyuSuki Seki, “Calorimetric study of the glassy state xii. plural glass-transition phenomena of ethanol,” The Journal of Chemical Thermodynamics 9, 1133–1148 (1977).

66 G. E. Gibson and W. F. Giauque, “The third law of thermodynamics. evidence from the specific heats of glycerol that the entropy of a glass exceeds that of a crystal at the absolute zero,” Journal of the American Chemical Society 45, 93–104 (1923).

67 Zhen Chen and Ranko Richert, “Dynamics of glass-forming liquids. xv. dynamical features of molecular liquids that form ultra-stable glasses by vapor deposition,” The Journal of chemical physics 135, 124515 (2011).

68 AJ Barlow, J Lamb, and AJ Matheson, “Viscous behaviour of supercooled liquids,” Proceedings of the Royal Society of London. Series A: Mathematical and Physical Sciences 459, 2821–2838 (2003).

69 Frederick Dominic Rossi, Selected values of physical and thermodynamic properties of hydrocarbons and related compounds: comprising the tables of the American Petroleum Institute Research Project 44 extant as of December 31, 1952, Vol. 44 (American Petroleum Institute, 1953).

70 Ulrich Schneider, P Lunkenheimer, R Brand, and A Loidl, “Dielectric and far-infrared spectroscopy of glycerol,” Journal of non-crystalline solids 235, 173–179 (1998).
[72] P. Lunkenheimer, U. Schneider, R. Brand, and A. Loidl, “Glassy dynamics,” Contemporary Physics 41, 15–36 (2000).

[73] P. Lunkenheimer, R. Wehn, U. Schneider, and A. Loidl, “Glassy aging dynamics,” Phys. Rev. Lett. 95, 055702 (2005).

[74] B. Schmidtke, N. Petzold, R. Kahlauf, M. Hofmann, and E.A. Rössler, “From boiling point to glass transition temperature: Transport coefficients in molecular liquids follow three-parameter scaling,” Physical Review E 86, 041507 (2012).

[75] Per Sillrén, Aleksandar Matic, Mathis Karlsson, M. Koza, M. Maccarini, P. Fouquet, M. Götz, Th Bauer, R. Gulich, P. Lunkenheimer et al., “Liquid 1-propanol studied by neutron scattering, near-infrared, and dielectric spectroscopy,” The Journal of Chemical Physics 140, 124501 (2014).

[76] U. Schneider, P. Lunkenheimer, R. Brand, and A. Loidl, “Broadband dielectric spectroscopy on glass-forming polypropylene carbonate,” Phys. Rev. B 59, 6924–6936 (1999).

[77] F. Stickel, Erhard W. Fischer, and Ranko Richter, “Dynamics of glass-forming liquids. ii. detailed comparison of dielectric relaxation, dc-conductivity, and viscosity data,” The Journal of chemical physics 104, 2043–2055 (1996).

[78] Soichi Tatsumi and Osamu Yamamuro, “Unpublished data.”

[79] R. Brand, P. Lunkenheimer, U. Schneider, and A. Loidl, “Excess wing in the dielectric loss of glass-forming ethanol: A relaxation process,” Phys. Rev. B 62, 8878–8883 (2000).

[80] Daan Frenkel and Berend Smit, eds., Understanding Molecular Simulation (Second Edition), second edition ed. (Academic Press, San Diego, 2002).

[81] Silvio Franz and Giorgio Parisi, “Phase diagram of coupled glassy systems: A mean-field study,” Phys. Rev. Lett. 79, 2486–2489 (1997).

[82] Ludovic Berthier and Daniele Coslovich, “Novel approach to numerical measurements of the configurational entropy in supercooled liquids,” Proceedings of the National Academy of Sciences 111, 11668–11672 (2014).

[83] Silvio Franz, “First steps of a nucleation theory in disordered systems,” Journal of Statistical Mechanics: Theory and Experiment 2005, L12002 (2009).

[84] Ludovic Berthier, Patrick Charbonneau, and Joyjit Kundu, “Bypassing sluggishness: Swap algorithm and glassiness in high dimensions,” Phys. Rev. E 99, 031301 (2019).

[85] Vassily Lubchenko and Pyotr Rabochiy, “On the mechanism of activated transport in glassy liquids,” The Journal of Physical Chemistry B 118, 13744–13759 (2014).

[86] C. Cammarota, A Cavagna, G. Gradenedi, T.S. Grigera, and P. Verrocchio, “Evidence for a spinodal limit of amorphous excitations in glassy systems,” Journal of Statistical Mechanics: Theory and Experiment 2009, P05015 (2009).

[87] Divya Ganapathy, K. Hima Nagamanasa, AK. Sood, and Rajesh Ganapathy, “Measurements of growing surface tension of amorphous–amorphous inter-