Dynamical phase transitions in supercooled liquids: Interpreting measurements of dynamical activity

Christopher J. Fullerton and Robert L. Jack
Department of Physics, University of Bath, Bath BA2 7AY, United Kingdom

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We study dynamical phase transitions in a model supercooled liquid. These transitions occur in ensembles of trajectories that are biased towards low (or high) dynamical activity. We compare two different measures of activity that were introduced in recent papers and we find that they are anti-correlated with each other. To interpret this result, we show that the two measures couple to motion on different length and time scales. We find that “inactive” states with very slow structural relaxation nonetheless have increased molecular motion on very short scales. We discuss these results in terms of the potential energy landscape of the system and in terms of the liquid structure in active/inactive states. © 2013 AIP Publishing LLC.

I. INTRODUCTION

As liquids are cooled towards their glass transitions, their relaxation times increase dramatically, and the motion of their constituent particles becomes increasingly co-operative and heterogeneous. There are several competing theories that aim to describe these phenomena, but neither simulation nor experimental data have so far proven sufficient to establish which (if any) can fully describe the supercooled liquid state. Recently, novel dynamical phase transitions have been discovered in glassy systems: these are new results that can be used to test existing theories. These phase transitions take place in ensembles of trajectories (sometimes called s-ensembles), where the dynamical evolution of the glassy system is biased towards low-activity states. Since these phase transitions are dynamical in nature, they fit naturally with theories of the glass transition where dynamical motion takes a central role, but they can also be interpreted in terms of random first order transition theory, and are linked with properties of the energy landscape and its normal modes.

In this article, we discuss these dynamical phase transitions and their associated ensembles of trajectories. We are motivated primarily by two previous studies, which provided evidence for such transitions in a model glass-former, composed of Lennard-Jones particles. In the first study, Hedges et al. measured the activity in this model through the mean square displacement of its particles. Biasing the dynamics with respect to this parameter, they found evidence for a first-order phase transition between active (equilibrium fluid) and inactive (glass) states. In the second study, Pitard et al. used an alternative measure of activity, based on the steepness and curvature of the energy landscape, integrated over time. Using this activity measure to bias the system, they again found evidence for a dynamical phase transition, but the properties of the dynamical phases were different to those found in Ref. 20, including apparently non-extensive behaviour of the activity in one of the phases.

In this study, we combine measurements of the different measures of activity used in Refs. 20 and 21. We find that these measures couple to different kinds of molecular motion. Further, the two measures are anti-correlated in the system that we consider. Physically, the structural relaxation of the system ceases almost completely in the inactive state, but particle motion on short length and time scales is actually enhanced, due to subtle differences in structure between active and inactive states. Based on this observation, we are able to resolve some of the apparent differences between the results of Refs. 20 and 21. We also gain insight into the nature of the inactive (glassy) states, and how these relate to properties of the underlying energy landscape, and the normal modes associated with motion on this landscape.

Section II of this paper introduces the model and the ensembles that we will use; in Sec. III, we compare the two measures of the activity used in Refs. 20 and 21, showing that they are anti-correlated. In Sec. IV, we investigate the activity of Pitard et al. in more detail, and discuss the relationship of this activity measurement to other properties of the fluid and glassy states in the system. We summarise our main conclusions in Sec. V.

II. BACKGROUND

A. Model

We consider the Kob-Andersen mixture of Lennard-Jones particles, which is a well-studied model glass former. There are N particles in the system and a configuration \( r^N \) has potential energy \( E(r^N) = \sum_{i<j} V(r_{ij}), \) where \( r_{ij} \) is the distance between particles \( i \) and \( j, \) and

\[
V_{ij}(r_{ij}) = 4\epsilon_{ij} \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6.
\]

There are two species of particle, A (large) and B (small) and the parameters \( \epsilon_i \) and \( \sigma_i \) depend on the species of particles \( i \) and \( j, \) as \( \sigma_{AA} = \sigma = 1, \) \( \sigma_{BB} = 0.88\sigma, \) \( \sigma_{AB} = 0.8\sigma, \) \( \epsilon_{AA} = \epsilon = 1, \) \( \epsilon_{BB} = 0.5\epsilon, \) and \( \epsilon_{AB} = 1.5\epsilon.\) For numerical efficiency,
$V_{ij}(r_{ij})$ is truncated at $r_{ij}^{\text{min}} = 2.5\sigma_{ij}$ and shifted so that the energy of a pair of particles separated by $r_{ij}^{\text{min}}$ is zero. For a system of $N$ particles, there are $N_A = (4N/5)$ particles of type A and $N_B = (N/5)$ of type B. The density is fixed at $\rho = 1.2\sigma^{-3}$ as in Ref. 20; note that $\rho = 1000/(9.4\sigma^3) \approx 1.204\sigma^{-3}$ was used in Refs. 22 and 23, and in some other studies. This small difference has no qualitative effect on the behaviour shown here.

The system evolves by Monte Carlo (MC) dynamics: as discussed by Berthier and Kob,24 this dynamical scheme results in structural relaxation that is in quantitative agreement with molecular dynamics, up to a rescaling of time. It was also shown in Ref. 20 that MC dynamics and constant-temperature molecular dynamics give very similar results in the $s$-ensemble. The MC dynamical scheme corresponds to a system evolving with overdamped Langevin dynamics,

$$\frac{d\mathbf{r}_i}{dt} = -\beta \nabla_i E + \eta_i(t),$$

where $D_0$ is the (bare) diffusion constant of a single particle, $\beta = 1/T$ is the inverse temperature (we take Boltzmann’s constant $k_B = 1$), and $\eta_i(t)$ is white noise with zero mean, and covariances

$$\langle \eta^\mu_i(t) \eta^\nu_j(t') \rangle = 2D_0\delta_{ij}\delta^{\mu\nu}\delta(t-t'),$$

in which $\mu$ and $\nu$ label Cartesian components of the vector $\eta(t)$. The natural units in the system are the length $\sigma$ (the diameter of a large particle); the energy $\epsilon$ (interaction strength between large particles); and the time scale $\Delta t = \sigma^2/D_0$ (of the order of the Brownian time for a free particle). When discussing our numerical results in Secs. II B–IV, we take ($\sigma$, $\epsilon$, $\Delta t$) all equal to unity, for compactness.

The MC dynamical scheme that we use is equivalent to the Langevin equation (2) in the limit when all MC steps are small (see, for example, Ref. 25). As in Ref. 24, we draw trial MC displacements from a cube of side $\delta = 0.15\sigma$, centred on the origin. This choice of step size leads to efficient simulations which accurately capture the nature of the structural relaxation. The mean square displacement for a trial MC move is $\delta^2/4$: the requirement that the diffusion constant be $D_0 = \sigma^2/\Delta t$ means that $\Delta t$ corresponds to $24(\sigma/\delta)^2 \approx 1070$ MC sweeps.

We emphasise that overdamped dynamics as studied here were used by Hedges et al.,20 who also considered molecular dynamics with a strong coupling to a thermostat. In that study it was found that both types of dynamics captured the same behaviour, including the dynamical transition of interest here. We expect that all results presented here would be very similar if we had used molecular dynamics with a thermostat—the relevant inactive states are the same in each case. However, the results of Pitard et al.,21 were obtained using molecular dynamics at constant energy. Fixing the energy instead of the temperature affects the inactive states that can be sampled by the system, so this difference in ensemble may account for some of the differences between their results and those that we present here.

**B. Ensembles of trajectories and measures of activity**

We consider dynamical transitions that occur in ensembles of trajectories. These trajectories have duration $t_{\text{obs}}$, and each trajectory is divided into $M$ “slices,” each of duration $\Delta t$. Following Hedges et al.,20 the activity of a trajectory $r^N(t)$ is defined as

$$K[r^N(t)] = \Delta t \sum_{i=1}^{N_A} \sum_{j=0}^{M-1} |r_i(t_j) - r_i(t_{j+1})|^2,$$

where the index $i$ runs over all particles of type A, and the $t_j$ are the times that separate the slices: $t_j = j\Delta t$. We also define the intensive “activity density” $k = K/(N_At_{\text{obs}})$, which we sometimes refer to simply as the activity.

From (4), it follows that $k$ measures the mean square displacement of a type-A particle during a time interval $\Delta t$. This time scale is comparable with the time taken for a free particle to diffuse over its own diameter; in the supercooled state then $\Delta t$ is long enough for a particle to explore its local environment (part of the $\beta$-relaxation process), but $\Delta t$ is shorter than the typical time for the fluid structure to relax (the $\alpha$-process). Our interpretation is that $k$ measures motion on length scales comparable to the particle diameter.

The dynamical phase transitions that we will consider occur when the equilibrium ensemble of trajectories is biased to low activity. We define a biased ensemble (or “$s$-ensemble”) through its probability distribution over trajectories:

$$P_s[r^N(t)] \propto P_0[r^N(t)]e^{-sK[r^N(t)]},$$

where $P_0[r^N(t)]$ is the equilibrium probability of trajectory $r^N(t)$. (In defining the probability distributions over trajectories, it is sufficient for our purposes to represent a trajectory as the set of $M+1$ configurations at the times $t_i$ that separate the slices. However, a finer-grained representation in time is also possible.)

Within the $s$-ensemble the average of any trajectory-dependent observable $A$ may be calculated using

$$\langle A \rangle_s = \frac{\langle A e^{-sK} \rangle_0}{\langle e^{-sK} \rangle_0},$$

where $\langle \cdot \rangle_s$ denotes an average over trajectories of length $t_{\text{obs}}$ in the $s$-ensemble and $\langle \cdot \rangle_0$ means an average of trajectories of length $t_{\text{obs}}$ at equilibrium (which corresponds to $s = 0$).

An alternative measure of the activity was proposed by Pitard et al.,21 as the time integral (between $t = 0$ and $t = t_{\text{obs}}$) of an “effective potential”:

$$V_{\text{eff}} = \frac{\beta}{4} \sum_i |F_i|^2 + \frac{1}{2} \sum_i \nabla_i \cdot F_i,$$

where the index $i$ runs over all particles and $F_i = -\nabla_i E$ is the force on particle $i$.

In this study, we define

$$K_{\text{alt}}[r^N(t)] = \frac{\Delta t}{2} \sum_{j=1}^{M} [V_{\text{eff}}(t_{j-1}) + V_{\text{eff}}(t_j)],$$

which is an estimate of the integral of $V_{\text{eff}}$ using a trapezium rule (we take $t_j = j\Delta t$ as above). The notation $K_{\text{alt}}$ indicates that this is an “alternative” activity. We also define $k_{\text{alt}}$...
time scales. Following Pitard et al., we therefore define an "$s_{\text{alt}}$-ensemble" through a bias on $K_{\text{alt}}$:  

$$P_s[r^N(t)] \propto P_{0}[r^N(t)]e^{-s_{\text{alt}}K_{\text{alt}}[r^N(t)]}.$$  

(10)

This definition is analogous to (5): continuing the analogy for averages of an observable $A$, we have  

$$\langle A \rangle_{s_{\text{alt}}} = \langle A e^{-s_{\text{alt}}K_{\text{alt}}} \rangle_0 \langle e^{-s_{\text{alt}}K_{\text{alt}}} \rangle_0.$$  

(11)

by analogy with (6). Equations (5) and (10) define the ensembles of trajectories that we will consider in the following.

III. MEASUREMENTS OF ACTIVITIES IN BIASED ENSEMBLES

We use transition path sampling (TPS) to sample biased ensembles of trajectories, as discussed in Appendix A. Pitard et al. use a different method: the differences between the two are discussed in Appendix A. We show numerical results obtained by TPS in Figs. 1 and 2, which summarise the behaviour of $K$ and $K_{\text{alt}}$, as $s$ and $s_{\text{alt}}$ are varied. We concentrate
on the behaviour of a system of $N = 150$ particles at temperature $T = 0.6$, as in Ref. 20. [Recall we have fixed units such that $(\epsilon, \sigma, \Delta t)$ are all equal to unity.] In Figs. 1(a) and 1(d), we show scatter plots of $K$ and $K_{alt}$, combining data sampled from equilibrium and for several values of $s$ and $s_{alt}$. We find that $k$ is always positive and $k_{alt}$ is always negative. (For the sake of clarity we will refer to the absolute value of $k_{alt}$ when talking about its size.) Perhaps surprisingly, we also find that while $k$ and $k_{alt}$ were both proposed as measures of dynamical activity, they are anti-correlated with one another. This observation will be crucial in the following discussion.

We see that the distributions have a peak at $s = 0$, and that on increasing the system size to 300 particles, there is no significant change either in the equilibrium state or in its derivative with respect to $s$. The differences between our results and those of Ref. 21 in this regime remain a subject for future study: here we concentrate on the crossover that we do find for $s_{alt} < 0$, and its relationship to the active/inactive phase existence phenomena found in Ref. 20.

IV. INTERPRETATION OF ACTIVITY MEASUREMENTS

The interpretation of the activity $k$ is transparent in that it measures particle motion on a timescale $\Delta t$. As discussed in Ref. 20, the low-$k$ phase found on increasing $s$ is characterised by an absence of structural relaxation (at least for small systems of 150 particles, on time scales up to 40 times the equilibrium relaxation time). The relation between $k_{alt}$ and particle motion is somewhat indirect, operating via expression (9) which gives the probability that a particle deviates significantly from its initial position, on short time scales.

In the following, we focus on the activity $k_{alt}$, aiming in particular to understand why the activity measurement increases during the transition to the inactive state of Ref. 20.

FIG. 2. (a) and (b) Averaged activities in biased ensembles. Note that panel (b) shows the negatives of the field and the activity, $-s_{alt}$ and $-k_{alt}$. All data are for $N = 150$ and $T = 0.6$, except for the red-dashed lines, where $N = 300$ and we show the linear response behaviour about equilibrium: $\langle K \rangle = \langle K \rangle_0 + (\delta K)^2 + O(s^2)$, and similarly for $s_{alt}$. These linear response results do not capture the non-trivial crossovers, but they do show that the mean and variance of $K$ and $K_{alt}$ are approximately extensive in $N$, for $s = 0$ (there is a weak finite-size correction to $\langle k \rangle_0$; particle motion in smaller systems is known to be slightly slower for this system, compared to the bulk).
A. Two contributions to $V_{\text{eff}}$ and a quasi-equilibrium/two-temperature scenario

From (7), we see that $V_{\text{eff}}$ (and hence also $k_{\text{ah}}$) has two contributions, one from the interparticle forces and the other from the divergence of the force. At equilibrium, these contributions are related:

$$
\langle |\beta F_i|^2 \rangle_0 = Z^{-1} \int d^N r |\beta \nabla_i E(r^N)|^2 e^{-\beta E(r^N)} = Z^{-1} \int d^N r \beta \nabla_i^2 E(r^N) e^{-\beta E(r^N)} = -\langle \nabla_i \cdot F_i \rangle_0,
$$

where $Z = \int d^N r e^{-\beta E(r^N)}$ is the equilibrium partition function. The first and third equalities in (12) follow trivially from the definition of the equilibrium average, while the second relies on an integral by parts. This result is well known and has been exploited to determine the temperature of a system directly from its configurations.\(^{31, 32}\) At equilibrium, we conclude that $\langle V_{\text{eff}} \rangle_0 = -\frac{1}{2} \sum_i \langle |F_i|^2 \rangle_0$.

Data for the two terms in $V_{\text{eff}}$ are shown in Fig. 3. Despite (12), we note a small difference between the two terms, even at equilibrium. This effect arises because of the truncated and shifted Lennard-Jones potential that we use in simulation, which has a discontinuity in its first derivative at the cutoff radius $r_{ij}^{\text{cut}} = 2.5 \sigma_{ij}$.

We discuss this effect in Appendix B (see also Ref. 32) where we define a regularised average $\langle \nabla \cdot F_i \rangle_{\text{sim}}$, and discuss how (12) is modified to account for this regularisation. Consistent with Fig. 3, we find that the effect of this regularisation is small throughout, so we use $\langle \nabla \cdot F_i \rangle_{\text{sim}}$ interchangeably with $\langle \nabla \cdot F_i \rangle$ in what follows.

Having accounted for the small systematic deviation between the two quantities plotted in Fig. (3), the most important feature of that figure is that the two contributions to $V_{\text{eff}}$ remain almost equal, as $s$ increases. That is, for the range of $s$ considered, our numerical results indicate that

$$
\langle k_{\text{ah}} \rangle_s \approx -\frac{\beta}{4} \sum_i \langle |F_i|^2 \rangle_s \approx \frac{1}{4} \sum_i \langle \nabla_i \cdot F_i \rangle_s.
$$

Since (12) applies only at equilibrium, this is a non-trivial result. Our interpretation is that the “slow” (structural) degrees of freedom respond strongly to the bias $s$, while “fast” degrees of freedom respond much more weakly. In other words biasing moves the system to a region of the energy landscape not typical of equilibrium, but the system explores the region captured by the potential. In a similar way, one may expect the quasi-equilibrium hypothesis of (14) to hold much more weakly. In other words biasing moves the system to a region of the energy landscape not typical of equilibrium, but the system explores the region captured by the potential. In a similar way, one may expect the quasi-equilibrium hypothesis of (14) to hold much more weakly. In other words biasing moves the system to a region of the energy landscape not typical of equilibrium, but the system explores the region captured by the potential. In a similar way, one may expect the quasi-equilibrium hypothesis of (14) to hold much more weakly. In other words biasing moves the system to a region of the energy landscape not typical of equilibrium, but the system explores the region captured by the potential. In a similar way, one may expect the quasi-equilibrium hypothesis of (14) to hold much more weakly. In other words biasing moves the system to a region of the energy landscape not typical of equilibrium, but the system explores the region captured by the potential. In a similar way, one may expect the quasi-equilibrium hypothesis of (14) to hold much more weakly. In other words biasing moves the system to a region of the energy landscape not typical of equilibrium, but the system explores the region captured by the potential. In a similar way, one may expect the quasi-equilibrium hypothesis of (14) to hold much more weakly. In other words biasing moves the system to a region of the energy landscape not typical of equilibrium, but the system explores the region captured by the potential. In a similar way, one may expect the quasi-equilibrium hypothesis of (14) to hold much more weakly. In other words biasing moves the system to a region of the energy landscape not typical of equilibrium, but the system explores the region captured by the potential. In a similar way, one may expect the quasi-equilibrium hypothesis of (14) to hold much more weakly. In other words biasing moves the system to a region of the energy landscape not typical of equilibrium, but the system explores the region captured by the potential. In a similar way, one may expect the quasi-equilibrium hypothesis of (14) to hold much more weakly.
seems to hold quite accurately. This is the sense in which the slow fluctuations (between states) respond strongly to the field $s$ (via the $w_s$), while the fast (intra-state) fluctuations respond much more weakly.

### B. Normal modes of the fluid in biased ensembles

The relationship between $k_{ab}$ and the properties of equilibrium and inactive states can also be analysed through the distribution of eigenvalues of the dynamical matrix (or Hessian) $H$. This distribution, together with the vibrational normal modes of supercooled liquids, has been connected with their dynamical properties in a variety of studies.\textsuperscript{17–19, 37, 38} For the overdamped (MC) dynamics used here, there is no true vibrational motion on short time scales, but motion on short length and time scales depends strongly on $H$, since it gives the curvatures of the underlying potential energy surface. Here we exploit the connection between the matrix $H$ and the contribution of $\sum_i \nabla_i \cdot F_i$ to $k_{ab}$. The Hessian is a $3N \times 3N$ matrix with elements $H_{ij\mu\nu} = \frac{\partial^2 E(r)}{\partial r_i \partial r_j}$, where the indices $i$ and $j$ run over all particles and $\mu$ and $\nu$ run over the Cartesian components of the position vectors $r_i$.

The matrix $H$ has $3N$ eigenvalues, which we denote by $\omega_1^2, \omega_2^2, \ldots$. For a system evolving with molecular dynamics, each $\omega_\mu$ can be interpreted as a natural frequency for vibrational motion on the energy landscape, along a particular eigenvector. However, we note that since typical configurations of the system are not located at minima of the energy landscape, some eigenvalues of $H$ will be negative, $\omega_\mu^2 < 0$. In this case the interpretation of $\omega_\mu$ is less clear, but the relevant directions on the energy landscape are unstable, indicating that the system is close to a saddle point of the landscape, and not a stable minimum. The $\nabla \cdot F$ term in $V_{\text{eff}}$ is related to the eigenvalues as

$$\sum_i \nabla_i \cdot F_i = -\text{Tr}(H) = -\sum_{\alpha=1}^{3N} \omega_\alpha^2,$$  \hspace{1cm} (15)

We identify the right-hand side as $-3N\omega_{\text{E}}^2$ where $\omega_{\text{E}}$ is the (generalised) Einstein frequency.\textsuperscript{39} Hence, at equilibrium, one has $(-k_{ab})_0 = \frac{3}{4} \omega_{\text{E}}^2$.

Defining the distribution of eigenvalues, $D(\omega^2)$, the trace can be expressed as

$$\langle \text{Tr}(H) \rangle = 3N \int_{-\infty}^{\infty} d(\omega^2) \omega^2 D(\omega^2).$$ \hspace{1cm} (16)

[We use $D(\omega^2)$ in this article for the number density of eigenvalues of $H$, along the real line. This is different from the number density of normal mode frequencies, sometimes denoted by $D(\omega)$. We use $D_1(\omega)$ for this latter quantity, to avoid confusion.]

Combining 13, 15, and 16, we see that $k_{ab} \approx -\frac{1}{3} \int_{-\infty}^{\infty} d(\omega^2) \omega^2 D(\omega^2)$, allowing us to relate the difference in $k_{ab}$ between active and inactive (small-$k$) states to the distributions $D(\omega^2)$ in these states. Results are shown in Fig. 4. Comparing equilibrium ($s = 0$) and inactive ($s > 0$) data, the differences in $D(\omega^2)$ are subtle, but the dominant effect is that the main peak in $D(\omega^2)$ is slightly sharper in the inactive state. That is, the inactive state has not only fewer modes with small or negative $\omega^2$, but also fewer modes with large positive $\omega^2$. Hence, it has more modes with intermediate $\omega^2$. When evaluating the change in $\text{Tr}(H)$ between states, the dominant effect comes from large eigenvalues, which correspond to “stiff” (strongly-curving) directions on the potential energy landscape. Figure 4 shows that there are fewer stiff directions in the inactive state, and this results in the absolute value of $k_{ab}$ being smaller for that state. The difference is more pronounced when plotting $D_1(\omega)$, the distribution of $\omega$ among modes where $\omega^2 > 0$.

In Fig. 5, we show the distributions of $\omega^2$ and of $\omega$ that we obtained by using conjugate gradient minimisation on configurations from the $s$-ensemble, and then constructing the matrix $H$ at the resulting energy minimum [inherent structure (IS)]. In this case, all eigenvalues of $H$ are positive. The differences in $D(\omega^2)$ between active and inactive states are more pronounced at the IS level, but the main conclusion is the same: the peak in $D(\omega^2)$ is narrower in the inactive state, and this pushes the mean value of $\omega^2$ to a smaller value. However, these data also emphasise that the inactive state has fewer “soft” modes (with small $\omega$), compared to equilibrium. This effect was noted in Ref. 35: it indicates that part of the stability of the inactive state can be accounted for by the paucity of soft-directions on the energy landscape.

These differences in $D(\omega^2)$ between the active and inactive state are similar to the changes that are found on reducing...
the temperature.\textsuperscript{37} That is, in terms of its normal modes, the inactive state resembles a state at a temperature lower than that of the thermal bath. This is consistent with the hypothesis of Ref.\textsuperscript{35}, that configurations from the inactive state occupy regions of the energy landscape typical of lower temperatures, while exploring these regions as if they were at equilibrium. The reduced absolute value of $k_{alt}$ in the inactive state is then consistent with the known tendency of $\omega_{E}^{2}$ to decrease as fluids are cooled.\textsuperscript{39}

The resulting physical picture is summarised in Fig. 6. The potential energy surface (or “landscape”) is divided into basins, each associated with a single inherent structure (local minimum). Moving away from the inherent structure, most of the directions are quite “stiff,” with large $\omega$, but a few are “soft,” with small $\omega$. Comparing the equilibrium state with the inactive (small-$k$) state, Figs. 4 and 5 show that the stiff directions in the inactive state are (on average) less stiff than at equilibrium; on the other hand, the soft directions in the inactive state are also less soft than at equilibrium. The activity parameter $k_{alt}$ of Pitard et al.\textsuperscript{21} is most sensitive to the stiff directions: the stiffer these are, the less particles are free to move (on short scales), and the larger is the absolute value of $k_{alt}$. On the other hand, the activity parameter $k$ of Hedges et al.\textsuperscript{20} is most sensitive to structural relaxation, which couples more strongly to the soft modes: these are less soft in the inactive state, suppressing large-scale particle motion, and reducing $k$. This difference in sensitivity to fast and slow motion explains the anticorrelation between $k$ and $k_{alt}$ in Fig. 1, and it also explains why the active/inactive transition of Ref. 20 appears only in $s_{alt}$-ensembles with $s_{alt}<0$. We argue that it should be borne in mind in any future studies that use $V_{eff}$ to measure activity.

To end this discussion of normal modes, we return to the role of the low-frequency modes considered recently.\textsuperscript{18,19} It is useful to expand the energy of the system to second order around the inherent structure: if $\delta r_{i}$ is the deviation of particle $i$ from its position in the inherent structure then one may calculate the size of fluctuations at equilibrium in the resulting harmonic system as

$$\Delta^{2} = \frac{1}{N} \sum_{i} \langle |\delta r_{i}|^{2} \rangle = \frac{T}{N} \sum_{\alpha} \frac{1}{\omega_{a}^{2}}.$$ \hspace{1cm} (17)

The factor of $\omega_{a}^{2}$ in the denominator means that $\Delta^{2}$ is dominated by low-frequency “soft” modes, in contrast to the Einstein frequency and $k_{alt}$ which are dominated by high-frequency (“stiff”) modes. For active and inactive states, $s = (0, 0.04)$, respectively, we find $(\Delta^{2}) = (0.007, 0.016)\omega^{2}$. The larger value in the active state arises because of the extra soft modes in that state. This behaviour is reminiscent of results for dynamically heterogeneous systems.\textsuperscript{18,19,40} In those contexts, particles with larger $\Delta^{2}$ have increased propensity for motion on long time scales—here we find similarly that $\Delta^{2}$ is larger in the active state. This result emphasises the subtleties of measuring activities in these systems: the stiffer high-frequency modes in the active state reduce motion on very short time scales (reduced $k_{alt}$), but the softer low-frequency modes tend to increase longer time scale motion, so both $\Delta^{2}$ and $k$ are larger.

C. Liquid structure in biased ensembles

We now turn to the structure of the active and inactive states that we have found, and the connection of this structure to $k_{alt}$. It is notable from Fig. 2 that typical values of $k_{alt}$ are around $-380(\epsilon/\sigma^{2})$, while the difference in $k_{alt}$ between active and inactive states is much smaller, around $30(\epsilon/\sigma^{2})$. (We

FIG. 5. (a) Distribution of eigenvalues of the Hessian for inherent structures of both phases. (b) Distribution of $\omega$ for inherent structures of both phases. [(b), inset] Dividing $D_{1}(\omega)$ by $\omega^{2}$ emphasises the lack of low-frequency modes associated with the inactive phase.

FIG. 6. A schematic representation of the differences in the energy landscape between the active and inactive phases. In the inactive phase, the barriers between basins (inherent structures) are smaller making rearrangements on large length scales less likely. These correspond to small values of $\omega^{2}$. The strongly curving directions around basins are less steep in the inactive phase, allowing more motion on short length scales. These correspond to large values of $\omega^{2}$.
give the units of $k_{\text{alt}}$ explicitly in this discussion: recall that numerical data are shown after fixing $(\epsilon, \sigma)$ to unity.

To interpret these results, it is useful to write
\[ \left\langle \nabla \cdot \mathbf{F}_i \right\rangle_s = -\sum_{i \neq j} 4\pi r^2 \delta_{ij}(r) \nabla^2 V_{ij}(r), \tag{18} \]
where $\delta_{ij}(r) = (\delta(r - r_{ij}))$, is proportional to a radial distribution function (in the $s$-ensemble). Since $V_{ij}(r)$ and $\delta_{ij}(r)$ depend on the particle indices $i$ and $j$ only through their types, it is convenient to use a shorthand notation for the non-trivial part of the integrand in (18)
\[ G^{AA}(r) = -\nabla^2 V_{ij}(r) \delta_{ij}(r) \bigg|_{i,j \text{ of type } A}, \tag{19} \]
where the right-hand side is evaluated with $i$ and $j$ both being particles of type A. Similarly, we define $G^{AB}(r)$ and $G^{BB}(r)$ for particles of other types. (Note that these functions depend implicitly on the biasing parameter $s$, through $\delta_{ij}(r).$

By comparing $4\pi r^2 G^{AA}(r)$ and $g_{AA}(r)$ (the radial distribution function for particles of species A), we can see how the liquid structure on different length scales contributes to $\left\langle \nabla \cdot \mathbf{F}_i \right\rangle_s.$ We focus only on the function for the large particles as these are the most numerous species. Figure 7(a) shows $g_{AA}(r)$ for the active phase (at $s = 0.00$) and the inactive phase (at $s = 0.04$). There are some subtle changes: the first and second peaks and the first trough are enhanced in the inactive phase. Panel (b) shows $4\pi r^2 G^{AA}(r)$ for the same values of $s$. Only a small range of $r$ contributes significantly to $\left\langle \nabla \cdot \mathbf{F}_i \right\rangle_s$—the width is less than that of the first peak in $g_{AA}(r).$ This further emphasises that $k_{\text{alt}}$ is dominated by behaviour on short length scales. Again, the differences between the phases are subtle. This is in line with the observation that the size of the change in $k_{\text{alt}}$ between phases is much smaller than the size of $k_{\text{alt}}$ itself.

To emphasise the change, we consider the difference $\Delta G^{AA}(r) = [G^{AA}(r)]_{s = 0.04} - [G^{AA}(r)]_{s = 0.00}.$ This is shown in the inset to Figure 7(b). It is clear that the change in $k_{\text{alt}}$ is largely due to changes in the liquid structure at very small length scales; the dashed line in the plot indicates where $G^{AA}(r)$ is largest in magnitude, which corresponds to the maximum of the first peak in $g_{AA}(r).$ These changes are subtle enough that they are not apparent when comparing radial distribution functions, but since $\nabla^2 V_{ij}(r)$ is very large for small $r$ they are ultimately what is important when considering $k_{\text{alt}}.$

In addition to the results in Fig. 7, we have obtained similar data for $G^{AB}(r)$ and $G^{BB}(r)$: the main picture is the same but the smaller numbers of B particles in the system mean that these functions contribute less strongly to $V_{\text{eff}},$ and also that the numerical uncertainties in our results are larger. As shown by Speck and co-workers, 41,42 the radial distribution function $g_{BB}(r)$ shows the largest relative changes between active and inactive states. However, the small number of B-particles means that this gives a relatively small contribution to the changes in $k_{\text{alt}}$ shown in Fig. 2.

**D. The dynamical action**

Finally, we discuss one other context in which the activity $K_{\text{alt}}$ appears. For overdamped dynamics as in (2), at equilibrium, the probability of a trajectory $r^N(t)$ can be written as
\[ P_0[r^N(t)] = \frac{1}{Z} P_{\text{free}}[r^N(t)] \cdot e^{\frac{1}{\beta D_0} \left[ E(0) - E(t_{\text{obs}}) \right]} \]
\[ \times e^{-\beta D_0 k_{\text{alt}}[r^N(t)]}, \tag{20} \]
where $P_{\text{free}}[r^N(t)]$ is the probability of the trajectory in the absence of any forces, and $Z$ is a normalisation constant.

Hence if we consider the equilibrium distribution of $k_{\text{alt}}$ for this model, we have
\[ P_{\text{alt}}(k_{\text{alt}}) = \frac{1}{Z} e^{N_{\text{obs}}[S(k_{\text{alt}}) - \beta D_0 k_{\text{alt}}]}, \tag{21} \]
where $e^{N_{\text{obs}}[S(k_{\text{alt}})]}$ is the marginal distribution of $k_{\text{alt}}$ associated with the distribution $P_{\text{free}}[r^N(t)] e^{\frac{1}{\beta D_0} \left[ E(0) - E(t_{\text{obs}}) \right]}.$ (We emphasise that the function $S(k_{\text{alt}})$ depends on the parameter $\beta$ via the definition of $k_{\text{alt}},$ and it also depends on $D_0.$) Further, the distribution of $k_{\text{alt}}$ within the $s_{\text{alt}}$-ensemble is
\[ P_s(k_{\text{alt}}) \propto e^{N_{\text{obs}}[S(k_{\text{alt}})] - \beta (D_0 + s_{\text{alt}}) k_{\text{alt}}}, \tag{22} \]
There is a relevant analogy here: compare the distribution of the energy density $\epsilon = E/N$ in a thermal system at equilibrium,
\[ P_\beta(\epsilon) \propto e^{N[S(\epsilon) - \beta \epsilon]}, \tag{23} \]
where $S(e)$ is the entropy per particle. This analogy between ensembles of trajectories such as (22) and ensembles of configurations such as (22) was a key starting point for studies of the dynamical transitions and biased ensembles that we consider here.\(^{9,12-14}\)

Extending this analogy, the interpretation of $k_{alt}$ and $s_{alt}$ is as follows. Within the distribution $P_0[p^{alt}(t)]$, there are many trajectories with large values of $k_{alt}$, each of which is individually rare because of the factor of $e^{-\beta D_{0}k_{alt}}$. There are fewer trajectories with smaller $k_{alt}$, but these are individually more probable because they are less strongly suppressed by the factor $e^{-\beta D_{0}k_{alt}}$. The most likely value of $k_{alt}$ occurs when the “entropic” term $S(k_{alt})$ balances the “energetic” term $\beta D_{0}k_{alt}$. [Here we are using the labels “entropic”/“energetic” to emphasise the analogy with (23); these terms have no simple relation to thermodynamic energy or entropy.]

If we introduce a negative value of $s_{alt}$, the system is biased towards the more numerous (“entropically favourable”) trajectories in the system, which have smaller absolute values of $k_{alt}$. As shown in Fig. 2, even a small negative $s_{alt}$ is sufficient to drive the system into an “inactive” state in which structural relaxation is arrested. The unexpected anticorrelation between $k$ and $k_{alt}$ that we found in this study arises because the inactive state has the higher “entropy” $S$ in trajectory space. The reason for this is that the inactive state consists of configurations in which most directions on the energy landscape are not too “stiff”: despite the slow structural relaxation, the particles have greater freedom to move on small length scales, compared with equilibrium. And the more free the particles are to move, the more trajectories are available, and the larger is $S$. As before, the conclusion is that propensity for motion on small scales is anti-correlated with propensity on scales of the order of the particle diameter.

V. CONCLUSIONS AND OUTLOOK

This study has two central conclusions. First, the transition found by Hedges et al.\(^{20}\) for $s > 0$ corresponds to a transition for $s_{alt} < 0$ within the ensembles defined by Pitard et al.\(^{21}\) Second, the activity parameter $k_{alt}$ defined in Ref. 21 couples to dynamical motion on very small scales, which is anticorrelated with the structural relaxation of the fluid. This anticorrelation arises from properties of the energy landscape of the inactive state. In addition to these main points, we have also discussed the structure of the inactive states and the connection of $k_{alt}$ to the liquid structure; and also the extent to which the inactive states have the quasi-equilibrium property given in (14).

We hope that this work clarifies the role of the activity measurement introduced by Pitard et al.\(^{21}\) which we have denoted by $K_{alt}$. Equation (22) shows that $K_{alt}$ is intimately connected with dynamical motion in overdamped Langevin systems, and it is also strongly connected to the energy landscape of the fluid. These facts present a strong argument in favour of $K_{alt}$ as an activity measure that arises naturally from the dynamics of the system, without any prejudice as to the nature of its dynamical relaxation. However, the results of Fig. 1 show that $K_{alt}$ must be interpreted carefully, since the extent of short-scale motion may not be correlated with the effectiveness of structural relaxation. Also, this study did not find evidence for singular behaviour in $(k_{alt})_{s_{alt}}$ for the range of positive $s_{alt}$ that we considered: the physical interpretation of the behaviour found in Ref. 21 for larger positive $s_{alt}$ remains unexplained (although it seems unrelated to the active/inactive crossover discussed in Ref. 20).

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APPENDIX A: SAMPLING BIASED ENSEMBLES

We sample trajectories from the $s$-ensemble and $s_{alt}$-ensemble by using transition path sampling (TPS). This method samples trajectories in a similar way to the sampling of configurations by standard Metropolis Monte Carlo methods. Its operation is reviewed in Ref. 29 and the “shifting moves” used in this study are discussed in Ref. 43. We give a brief overview here: Starting with an initial trajectory $r_{0}^{alt}(t)$, a new trajectory $r_{0}^{alt}(t)$ is generated by a “shifting move.” In “forward shifting,” one chooses a random number $p$ between 1 and $M$, and slices 1, 2, …, $p$ of $r_{0}^{alt}(t)$ are discarded. The remaining slices $(p + 1, …, M)$ of $r_{0}^{alt}(t)$ form the initial slices $(1, …, M - p)$ of the new trajectory $r_{1}^{alt}(t)$. Slices $M - p + 1, …, M$ are then generated by unbiased dynamical evolution from slice $M - p$. Finally, this new trajectory $r_{1}^{alt}(t)$ is accepted with probability

$$P_{acc} = \min\{1, e^{-\Delta K[r_{1}^{alt}(t)] + \Delta K[r_{0}^{alt}(t)]}\}.$$  \hspace{1cm} (A1)

Otherwise one rejects the new trajectory and retains the original one, $r_{0}^{alt}(t)$. This procedure is used in conjunction with “backwards shifting” moves where slices 1, 2, …, $p$ of $r_{0}^{alt}(t)$ are used to form slices $M - p + 1, …, M$ of $r_{1}^{alt}(t)$, and then slices 1, …, $M - p$ of $r_{1}^{alt}(t)$ are generated by unbiased time evolution, backwards in time from slice $M - p + 1$ (use of this scheme requires the time-reversal symmetry property of the equilibrium state of the model). This combination of moves ensures detailed balance within the ensemble of trajectories (5), so after sufficiently many moves, the procedure converges in a stationary regime which generates representative samples of the ensemble. Further, since the system is stochastic and the ensemble of trajectories being sampled is (approximately) time-translationally invariant, these shifting moves are effective in sampling the ensemble, and it is not necessary to supplement them with “shooting” moves. (A combination of shooting and shifting is the conventional choice in rare event sampling problems dominated by barrier crossing, but we do not use this procedure here.)

The results shown here were obtained from TPS simulations as follows. We used a weighted histogram analysis (WHAM)\(^{44}\) to combine data obtained using different values of $s$ and $s_{alt}$. For trajectories of length $t_{obs} = 200\Delta t$ we used data from $s = -0.025$ to $s = 0.03$ in the $s$-ensemble and from $s_{alt} = -3.0 \times 10^{-5}$ to $s_{alt} = 5.0 \times 10^{-5}$ in the $s_{alt}$-ensemble. For trajectories of length $t_{obs} = 400\Delta t$ we used data from $s = 0.00$ to $s = 0.020$ for the $s$-ensemble and from $s_{alt} = -1.75 \times 10^{-5}$
to $s_{\text{alt}} = 0.00$ for the $s_{\text{alt}}$-ensemble. These choices ensure that we concentrate our numerical effort in the crossover regime between active and inactive states: as we bias further into the inactive regime, the slow structural dynamics of the inactive state limit the effectiveness of sampling. We, therefore, access the inactive regime by histogram reweighting from the crossover regime, using the results from WHAM.

Large values of $s$ (and $-s_{\text{alt}}$) bias the system towards inactive states, and this can lead to crystallisation within trajectories. This happens rarely and we exclude trajectories with a high degree of crystalline order from our analysis. We measure crystalline order using the common neighbour analysis scheme described in the supplementary material of Ref. 20. We note that the values given for the maximum separation of bonded pairs of particles in Ref. 20 are incorrect, and we use the correct values: $\lambda_{AA} = 1.45$, $\lambda_{AB} = 1.25$, and $\lambda_{BB} = 1.07$.

We note that Pitard et al. used a different method to sample biased ensembles of trajectories. In contrast to transformation sampling, which operates on trajectories of fixed duration $t_{\text{obs}}$, that method provides direct estimates of observables in the limit where $t_{\text{obs}} \to \infty$. On the other hand, the algorithm requires that many copies (or clones) of the system evolve in parallel, and there are systematic errors associated with the method, which vanish only when the number of clones is taken to infinity. In this sense, the TPS method results in controlled sampling of ensembles with finite $t_{\text{obs}}$, requiring an extrapolation to reach the large-$t_{\text{obs}}$ limit; on the other hand, the method of Ref. 30 gives direct access to a limit of large $t_{\text{obs}}$, but at the expense of an extrapolation in the number of clones.

**APPENDIX B: REGULARISATION OF $\nabla \cdot \mathbf{F}_i$**

The results in Fig. 3 indicate that Eq. (12) is not satisfied exactly at equilibrium, for the model system used here. As discussed in Ref. 32, this behaviour is generic for systems where interaction potentials are truncated. To analyse this behaviour quantitatively, we imagine modifying the potential $V_{ij}(r_{ij})$ in a region of width $\varepsilon$ around $r_{ij}^{\text{cut}}$ so that its second derivative exists everywhere, and then taking the limit of small $\varepsilon$. In this case,

$$\nabla_i \cdot \mathbf{F}_i = \sum_{j \neq i} [q_{ij} + \tilde{q}_{ij} \delta(r_{ij} - r_{ij}^{\text{cut}})],$$  \hspace{1cm} (B1)

where

$$q_{ij} = \begin{cases} -\nabla^2 V_{ij}(r_{ij}), & r_{ij} < r_{ij}^{\text{cut}} \\ 0, & \text{otherwise} \end{cases}$$  \hspace{1cm} (B2)

and

$$\tilde{q}_{ij} = \frac{dV_{ij}(r_{ij}^{\text{cut}})}{dr_{ij}}$$

is the discontinuity in the force at the potential cutoff. If one uses (B1) as the definition of $\nabla \cdot \mathbf{F}_i$, then (12) will hold exactly at equilibrium.

However, the $\delta$-function in (B1) makes it problematic in simulation. We, therefore, define instead

$$\left\langle \sum_i \nabla \cdot \mathbf{F}_i \right\rangle = \left\langle \sum_i q_{ij} \right\rangle$$  \hspace{1cm} (B3)

and note that

$$\left\langle \sum_i \nabla \cdot \mathbf{F}_i \right\rangle = \left\langle \sum_i \nabla \cdot \mathbf{F}_i \right\rangle + N_A \rho_A \Delta_{AA} + N_A \rho_A \Delta_{AB} + N_A \rho_A \Delta_{BB},$$  \hspace{1cm} (B4)

where $\left\langle \sum_i \nabla \cdot \mathbf{F}_i \right\rangle$ on the left-hand side uses the definition from (B1), while $\Delta_{AA} = 4\pi \rho_A^2 \bar{q}^{AA} \delta(r_{AA}^{\text{cut}})$, with similar expressions for $\Delta_{AB}, \Delta_{BB}$. Here $\rho_A = N_A/V$ is the number density of A-particles, $g^{AA}(r)$ is the radial distribution function between A-particles, and $\bar{g}^{AA}$ is the value of $\bar{q}_{ij}$ if particles $i,j$ are both of type A. We used the fact that if particles $i,j$ are of type A then $(\delta(r - r_{ij})) = 4\pi r^2 \rho_A g^{AA}(r)$.

We have evaluated the $\Delta$-terms in (B4) at equilibrium, and verified that the data in Fig. 3 are then consistent with (12). However, since these $\Delta$-terms are small, we use $\left\langle \sum_i \nabla \cdot \mathbf{F}_i \right\rangle$ throughout this work as our numerical estimator for $\left\langle \sum_i \nabla \cdot \mathbf{F}_i \right\rangle$.