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Relation between local diffusivity and local inherent structures in the Kob-Andersen Lennard-Jones model

Emilia La Nave,[1] Srikanth Sastry,[2] and Francesco Sciortino[1]
[1]*Dipartimento di Fisica and CNR-INFM Udr and CRS-SOFT: Complex Dynamics in Structured Systems, Università di Roma "La Sapienza", Piazzale Aldo Moro 2, I-00185 Roma, Italy*
[2]*Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur Campus, Bangalore 500064, India*

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We analyze one thousand independent equilibrium trajectories of a system of 155 Lennard-Jones particles to separate in a model-free approach the role of temperature and the role of the explored potential energy landscape basin depth in the particle dynamics. We show that the diffusion coefficient D can be estimated as a sum over contributions of the sampled basins, establishing a connection between thermodynamics and dynamics in the potential energy landscape framework. We provide evidence that the observed nonlinearity in the relation between local diffusion and basin depth is responsible for the peculiar dynamic behavior observed in supercooled states and provide an interpretation for the presence of dynamic heterogeneities.

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Supercooled liquids are characterized by dynamics that take place on at least two well-separated time scales: a fast microscopic dynamics (associated with atomic or molecular motions at fixed liquid structure) and a slow structural relaxation time τ_α (which requires structural changes and diffusion processes) [1]. If one considers the trajectory of the system in configuration space, such a separation of time scales can be visualized as the exploration (on the microscopic time) of a finite region of the potential energy landscape (a basin), followed at a much slower pace by the exploration of distinct basins [2]. The potential energy landscape (PEL) formalism introduced by Stillinger and Weber [3] provides a thermodynamic description that builds on such a picture. The resulting expression for the liquid free energy requires information on the number of basins, their energy of the local minima (referred to as inherent structures), e_{IS} ('IS' stands for inherent structures) and their shape. Analysis of numerical simulations, recently reviewed in Ref. [4], has provided direct quantification of the statistical properties of the landscape of several models of glass-forming liquids [5–10]. For the case of the Kob-Andersen Lennard-Jones model [11,12], the number $\Omega(e_{IS})de_{IS}$ of distinct basins of energy depth between e_{IS} and $e_{IS}+de_{IS}$ follows a Gaussian distribution [5,6]

$$\Omega(e_{IS})de_{IS}=e^{\alpha N}\frac{e^{-(e_{IS}-E_o)^2/2\sigma^2}}{\sqrt{2\pi\sigma^2}}de_{IS}, \qquad (1)$$

where $e^{\alpha N}$ is the total number of distinct basins for a system of N particles, E_o is the energy scale of the distribution, and σ^2 is the variance; with σ, E_o, and α dependent only on the system number density. Often, it is convenient to define the configurational entropy $S_{\text{conf}}(e_{IS})\equiv k_B \log \Omega(e_{IS})$, which for the Gaussian landscape becomes a quadratic function of e_{IS},

$$\frac{S_{\text{conf}}}{k_b}=\alpha N-\frac{(e_{IS}-E_0)^2}{2\sigma^2}. \qquad (2)$$

When $\Omega(e_{IS})$ is known, the system partition function can be calculated [4] (under the assumption of the e_{IS} independence of the basin anharmonicities) and predictions can be provided for the T dependence of the explored basin depth $\langle e_{IS}(T)\rangle$, the probability $P(e_{IS},T)$ of sampling a basin of depth e_{IS} at temperature T, and the configurational entropy $S_{\text{conf}}(T)$.

The application of the Stillinger-Weber formalism to the analysis of numerical simulations provides an appealing picture of the T-dependent exploration of the landscape and a convenient method to quantify the free energy of supercooled states. Several recent studies attempted, in different ways, to relate landscape properties to dynamics [13–21]. The outcome of these studies strongly supports the reasonable hope that in supercooled states structural properties are strongly connected to dynamic ones and motivate the present detailed and essentially unbiased study of the connection between landscape properties and dynamics.

In this Rapid Communication, we study 1000 independent runs of the well-characterized Kob-Andersen model [11]. We limit ourselves to the smallest system that can be simulated with periodic boundary conditions without changing the model's range of interaction, i.e., 155 particles at number density 1.2 [22]. Due to the small system size, all quantities show large fluctuations, which we exploit to probe wide overlapping regions of e_{IS} values under different T conditions with the aim of disentangling the roles of e_{IS} and T in the dynamics. However, as discussed in previous work [23] and as seen in our unpublished studies, no significant size effects have been found for systems from about 100 particles up to a few thousand particles in the range of temperatures we study.

We simulate six different T between 0.446 and 0.65. In this supercooled T window, the decay of correlation functions clearly shows the presence of two time scales and the diffusion coefficient D varies more than 2 orders of magnitude. For each T, we equilibrate each independent trajectory in the canonical ensemble and estimate $P(e_{IS},T)$, which is found (see Fig. 1) to be described rather well by a Gaussian distribution of T-independent variance $\sigma^2=18\pm2$, for the 155 particles system centered around a T-dependent mean $\langle e_{IS}\rangle\times(T)\sim\sigma^2/T$, in full agreement with the Gaussian landscape model and with previous results [24]. The large σ^2 guarantees a significant overlap of the landscape region sampled at each T.

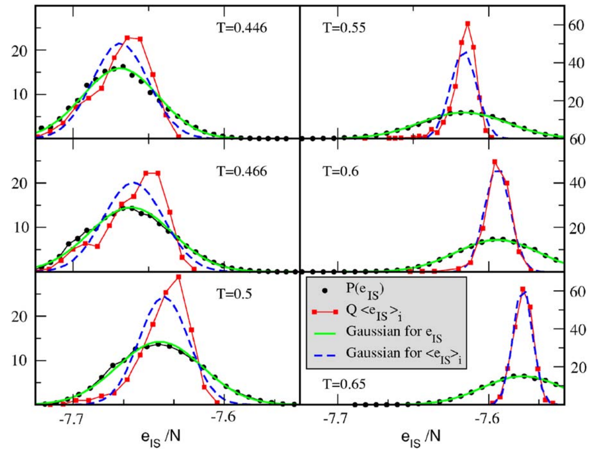

FIG. 1. (Color online) Probability distribution $P(e_{IS},T)$ of exploring an IS of depth e_{IS} at temperature T. Black filled circles: equilibrium data for the $N=155$ system. Green full line: Gaussian distribution of variance $\sigma^2=18/N$. The figure also shows, with red filled squares, the distribution $Q(\langle e_{IS}\rangle_i,T)$ (where $\langle eIS\rangle_i$ is not the instantaneous value but e_{IS} averaged over time $t_{\text{MSD}=1}$ for the trajectory i and with a blue dashed line a Gaussian distribution with the same variance as $Q(\langle e_{IS}\rangle_i,T)$.

Next we attempt to associate each of the 1000 independent runs (indexed by i) an $(e_{IS})_i$ value characterizing the location of the system in the PEL and to a D_i value characterizing its local diffusion coefficient. First we evaluate the time $t_{\langle\text{MSD}\rangle=1}$, defined as the time at which the type-A particles mean square displacement (MSD), averaged over all trajectories i and all A particles of the system, reaches a value of 1. Then we evaluate D_i as $\text{MSD}_i(t_{\langle\text{MSD}\rangle=1})/(6t_{\langle\text{MSD}\rangle=1})$. Different trajectories show very different dynamical properties. As an example, Fig. 2(a) represents the MSD, as a function of t for two different trajectories at the same T. Each trajectory i has a rather well defined diffusion coefficient D_i, which can be extracted from the slope of the MSD vs time. Figure 2(b) shows the t evolution of e_{IS} for the same two trajectories. The more mobile system is characterized by a larger and more fluctuating e_{IS}. Within $t_{\langle\text{MSD}\rangle=1}$, the set of e_{IS} values explored is far from covering the full range of values characteristic of that T. The system retains memory of the starting configurations and this behavior is enhanced at lower T. A quantification of the location of the i configuration on the PEL can thus be provided by $\langle e_{IS}\rangle_i$, defined as the value of e_{IS} averaged over the time interval from zero to $t_{\langle\text{MSD}\rangle=1}$.

Figure 1 also show the probability distribution $Q(\langle e_{IS}\rangle_i,T)$. While $P(e_{IS},T)$ are well approximated by a Gaussian distribution of average $\langle e_{IS}(T)\rangle$ and constant variance [in agreement with Eq. (1)], $Q(\langle e_{IS}\rangle_i)$ are symmetric and well modeled by a Gaussian only at high T. At low T, $Q(\langle e_{IS}\rangle_i,T)$ becomes strongly asymmetric, and its variance increases on cooling. This originates in the different mobility of the system depending on the initial e_{IS}. Indeed, while systems with e_{IS} associated with the high energy tail of $P(e_{IS},T)$ manage to explore different basins, systems in the low energy tail hardly lose memory of the initial configuration within $t_{\langle\text{MSD}\rangle=1}$. In this respect, the observed asymmetry confirms that there is a strong coupling between $\langle e_{IS}\rangle_i$ and D_i, which we now try to quantify.

Figure 3(a) shows D_i as a function of $\langle e_{IS}\rangle_i$ at several T. Data from different T overlap in a wide window of e_{IS} values Data show that the local diffusivity is a function of T not only via the T dependence of e_{IS} but also directly, since for each chosen e_{IS} value, data for higher T always lay above data at lower T. The fact that basins of the same depth are sampled at different T allows us to evaluate the T dependence of D at fixed basin depth and sort out the relative contribution of T and e_{IS} to dynamics. To distinguish between the T and e_{IS} dependence of D we hypothesize that the law relating these two quantities has the form:

$$D(e_{IS},T)=D_\infty e^{-f(e_{IS})/T}, \tag{3}$$

a form compatible both with the idea of activated dynamics as well as with the Adam-Gibbs (AG) hypothesis $\ln(D/D_\infty)=-B/TS_{\text{conf}}$ [in which case $1/f(e_{IS})=S_{\text{conf}}(e_{IS})/B$], with B being a coefficient related to the minimum size of a cooperatively rearranging region. Note that the Adam-Gibbs hypothesis holds for average values, and $S_{\text{conf}}(e_{IS})$ is the configurational entropy evaluated over all the accessed basins at a given temperature. There are no *a priori* reasons for this expression to be valid for subsets of the configuration space accessed by a liquid.

According to Eq. (3), a plot of $T\ln[D(e_{IS},T)/D_\infty]$ should produce a collapse of all data, independently of T, onto a master curve that can be identified as $-f(e_{IS})$. Figure 3(b) confirms that indeed such a procedure generates an impressive scaling of the data. We note that, in this procedure, we use the value of $D_\infty=0.155$ obtained independently from high T simulations. If the resulting $f(e_{IS})$ is interpreted according to activated models, one has to conclude that the height of the barriers increases significantly when the system

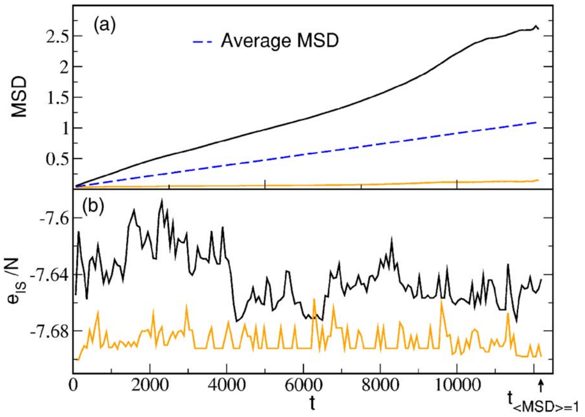

FIG. 2. (Color online) (a) MSD as a function of time for two different equilibrated trajectories at the same thermodynamical state point ($T=0.446$, $\rho=1.2$). The MSD is here averaged over all type-A particles of the system as well as over several starting times within the interval $0<t<t_{\langle\text{MSD}\rangle=1}$. The dashed line represents the MSD averaged over all trajectories and it provides the definition of $t_{\langle\text{MSD}\rangle=1}$. (b) Inherent structure energies as a function of time for the same trajectories shown in (a).

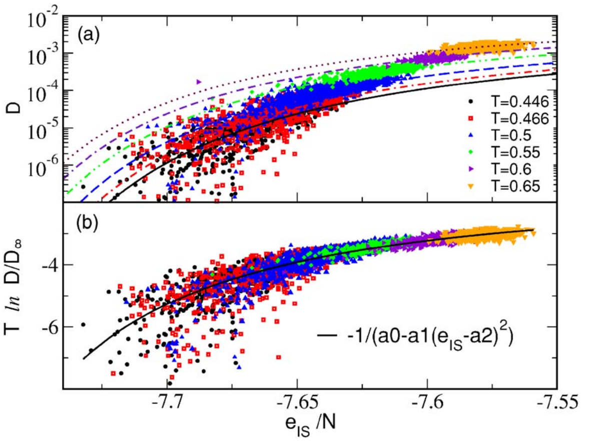

FIG. 3. (Color online) (a) Diffusivity D_i as a function of the corresponding average $\langle e_{IS}\rangle_i$. Different symbols indicate the six different simulated T. The lines are the fitting curves for each set according to Eq. (3). (b) $T\ln(D(e_{IS},T)/D_\infty)$ as a function of e_{IS}. The solid line represents the fitting function $-1/[a_0-a_1(e_{IS}-a_2)^2a]$. All the different fitting curves to individual data sets in panel (a) collapse on to it.

accesses basins with lower e_{IS}. Thus, the extrapolated activation energies for temperatures below the studied range would be different from those arising from the analysis of Doliwa and Heuer [19]. If $f(e_{IS})$ is interpreted according to the AG equation, then $1/f(e_{IS})$ has to be proportional to $S_{\mathrm{conf}}(e_{IS})$, a quantity that has been previously calculated for this model using thermodynamic integration techniques [5,25,26].

The test between the two different estimates of S_{conf} can be made even more stringent, if one realizes that, by fitting $f(e_{IS})$ according to the relation $f(e_{IS})=1/[a_0-a_1(e_{IS}-a_2)^2]$ the fitting coefficients a_0, a_1, and a_2 can be associated, comparing with Eq. (2), to

$$a_0=(\alpha N)/B,$$

$$a_1=1/(2\sigma^2 B),$$

$$a_2=E_0. \tag{4}$$

Interestingly enough, since σ^2 is known independently from the (T-independent) width of $P(e_{IS},T)$, a_1 provides B, a_0, α, and a_2 provide E_0 (yielding, respectively, $B=1.85$, $\alpha=0.78$, $E_0=-1140$). Thus, an estimate of S_{conf} in absolute units is provided by the fit parameters. The comparison between S_{conf} obtained via thermodynamic integration (from Ref. [25]) and S_{conf} obtained here from $f(e_{IS})$ is shown in Fig. 4. The agreement between the two independent estimates of S_{conf} confirms the previously observed possibility of describing the dynamics in this model according to the AG equation [5] and to the interpretation of the landscape basins as states [27].

The combined use of the PEL thermodynamic formalism and of the relation between thermodynamic and dynamics provided by Eq. (3) makes it possible to evaluate the T dependence of D for the present model—independently from the interpretation in terms of activated processes with e_{IS} dependent barrier or in term of AG—according to

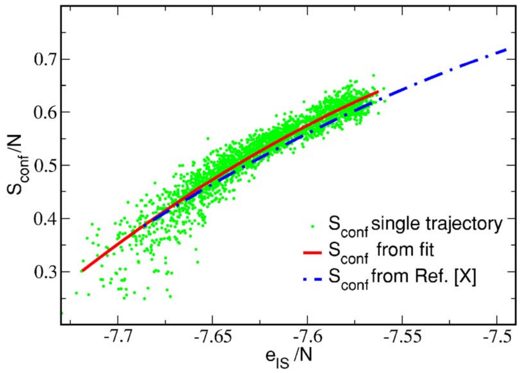

FIG. 4. (Color online) Comparison between S_{conf} evaluated from Eqs. (2) and (4) (solid line) and S_{conf} from Ref. [25] (dot-dashed line). The symbols are the values obtained for each trajectory i.

$$D(T)=\int D(e_{IS},T)P(e_{IS},T)de_{IS}. \tag{5}$$

Note that in our approach we do not consider the possibility of a distribution of D values for basins with the same depth. In this respect $D(e_{IS},T)$ can be considered as the average diffusion coefficient of typical basins of depth e_{IS}. Fig. 5 shows D evaluated directly from the MSD long time limit and from Eq. (3) and (5). The agreement between the two sets of independent data strongly supports the possibility of representing D as a sum over the local diffusivity of different parts of the landscape. This representation is very intriguing and offers an alternative way, within the landscape framework, to look at dynamic heterogeneities, which have been widely studied theoretically in simulations and experiments in recent years [28–41]. Indeed, the nonlinear relation between D and e_{IS} [Eq. (3)] implies that at low T, in equilibrium, the system can be represented by coexisting regions in space with very different local mobility. As seen in Fig. 3, at the lowest investigated T, the D_i values cover about three different orders of magnitude. It is important to stress that

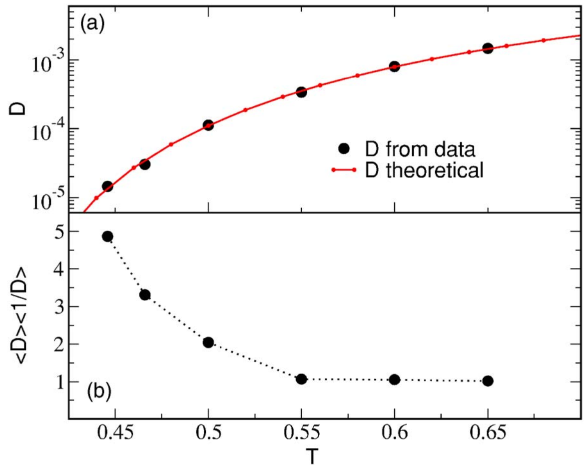

FIG. 5. (Color online) (a) Diffusivity constant as from data compared with the diffusivity constant evaluated from Eq. (5). (b) Product $\langle D\rangle\langle 1/D\rangle$ from data as a function of T. The dashed line is a guide for the eye.

the inhomogeneities in the dynamics are, in the present case, strongly associated with structural properties and in particular to the depth of the IS locally sampled.

This extremely average distribution of D_i values suggests also a possible explanation of the T dependence of the product $D\tau_\alpha$ upon supercooling, analyzed with reference to heterogeneous dynamics in, e.g., Ref. [28,29,32–34], along the lines proposed in Ref. [28]. Indeed, when a distribution is wide, the mean and the inverse of the average of its inverse can be rather different, since they weigh different parts of the distribution. To evaluate this effect in the present case we compare in Fig. 5 the T dependence of the product $\langle D\rangle \times\langle 1/D\rangle$. On cooling, the product starts to deviate from one, consistently with the observations for the model liquid studied here that the product $D\eta/T$ [40] and $D\tau_\alpha$ [41] starts to increase on cooling.

In summary, by considering large numbers of realizations of the trajectory of a small system of particles, we have shown that the dependence of the diffusion coefficients for each such trajectory on the depth of the potential energy minima explored can be extracted in a model-free manner, and that the average diffusion coefficient for the system can be estimated as a sum over contributions of the sampled basins, establishing a connection between thermodynamics and dynamics in the potential energy landscape framework. We provide evidence that the observed nonlinearity in the relation between local diffusion and basin depth is responsible for the peculiar dynamic behavior observed in supercooled states and provide an interpretation within the energy landscape picture for the presence of dynamic heterogeneities.

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