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Dynamical diagnostics of ergodicity breaking in supercooled liquids

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Abstract. The phenomenon of liquid–glass transition is commonly associated with ergodicity breaking. It is apparent that the structurally arrested glassy phase is non-ergodic. However, finding unambiguous criteria that would allow one to detect the crossover from ergodic to non-ergodic behaviour in a liquid subjected to supercooling remains a problem of profound conceptual interest. Moreover, meaningful criteria of ergodicity must be expressed in terms of finite-time observation of macroscopically measurable quantities. This paper discusses a new diagnostics of non-ergodicity in supercooled liquids based on comparing the entropy and diffusion.

1. Introduction

Some liquids, having been cooled to below the melting point T_m , avoid crystallization and remain in a metastable equilibrium state. Of these liquids, the most interesting are the so-called fragile liquids [1] which under supercooling demonstrate a much stronger temperature dependence of the rate of molecular dynamics than would be expected from the Arrhenius law. Another striking dynamical feature of the supercooled fragile liquids is stretched-exponential relaxation behaviour [2]. When approaching the glass transition point, T_g , the supercooled liquid falls out of equilibrium as the characteristic timescales of some of the relaxation processes exceed the observation timescale.

It is common to describe the onset of structural arrest and apparent solidification observed in a supercooled liquid at T_g as the transition from ergodic to non-ergodic behaviour [3]. Whether or not this interpretation is correct depends on what definition of ergodicity is applied. Although the ergodic hypothesis is a most fundamental concept of statistical mechanics, its formulation still remains an issue of controversy [4]. The ergodic hypothesis asserts that the time average of a dynamical variable $F(\Gamma)$ must converge to its ensemble average:

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt F(t) = \int_{\Omega} d\mu(\Gamma) F(\Gamma) \quad (1)$$

where μ is an invariant measure determined by the macroscopic constraints. Essentially, this invariant measure specifies the region of motion, on the subspace where the ensemble is defined. Thus, ergodicity depends entirely on the choice of the subspace; any system can be regarded as ergodic within a restricted ensemble.

Two major problems have to be addressed in order to apply the above definition to the behaviour of a real liquid under supercooling. First, for a non-equilibrium glassy state below T_g , the concept of ergodicity, to be meaningful, should refer to the underlying equilibrium state. Second, the above definition of ergodicity refers to an ensemble of identical systems

and infinite observation time. In fact, however, we need to assess the ergodicity of a single system within finite time. The original Boltzmann interpretation of ergodicity asserting that the system's phase trajectory covers with sufficient density the whole relevant phase-space region is apparently useless for such a purpose. In the following, we shall discuss possible ways of detecting the non-ergodic behaviour from the finite-time measurements of macroscopically accessible quantities. A novel diagnostics of ergodicity breaking in supercooled liquids is proposed, based on the recently found relation between the static structure and atomic diffusion [5].

2. Ergodicity, mixing and stochasticity

The fact that the entropy S of an equilibrium system of N particles is an extensive quantity: $S \propto O(N)$, implies that there exist a finite correlation length ξ and a finite correlation time τ [4] such that regions separated by distances exceeding ξ evolve independently and produce statistically indistinguishable time averages for time intervals exceeding τ . The properties of the equilibrium liquid state can thus be described in terms of the ensemble of independently evolving regions. The above condition of ergodicity (1) means that the elements of the thus-defined ensemble must produce statistically identical time averages within the observation time.

In dealing with systems of particles, it appears reasonable to consider effective ergodicity based on the concept of mixing [6]. The latter requires that the measure of the points of a region \mathcal{R} of the phase space which happened to be in any other region \mathcal{R}' after a sufficiently long time t must be proportional to the volumes of these regions:

$$\lim_{t \rightarrow \infty} \Gamma[\mathcal{R}(t) \cap \mathcal{R}'] = \Gamma[\mathcal{R}(0)]\Gamma[\mathcal{R}']. \quad (2)$$

If a dynamical system satisfies this condition, its phase trajectory uniformly samples the coarse-grained phase space. Notice that although the property of mixing is sufficient to ensure ergodicity, it is not known whether this is also a necessary condition for ergodic behaviour [4].

The approach to effective ergodicity can be monitored by a measure based on the idea of statistical symmetry. The latter means that time averages of the quantities associated with independently evolving regions of a system (or its constituent particles) must become statistically indistinguishable when approaching ergodic equilibrium; this is an obvious result of the independence principle. If f_i is a quantity associated with particle i , the respective measure of ergodic convergence for a system of N identical particles is defined as [7]

$$R_f(t) = \frac{1}{N} \sum_{i=1}^N \left[\frac{1}{t} \int_0^t f_i(s) ds - \langle f_i \rangle \right]^2 \quad (3)$$

where $\langle f_i \rangle$ is the ensemble average (the average over all of the particles of the system).

It was found that, in a stable liquid state, this measure, defined for a particle energy e , decays with time as $R_e \propto t^{-1}$. By contrast, in the glass transition domain it asymptotically approaches a non-zero limit, thus demonstrating ergodicity breaking. Although ergodic convergence will be eventually attained at a sufficiently long observation time, this result is significant in that it clearly shows separation of the relaxation timescales in strongly supercooled liquid, associated with ergodicity breaking. This analysis, however, requires full information on the phase trajectory that is not available in macroscopic experiments.

The effective ergodicity in the described sense is realized for the systems with the property that two phase trajectories, initially infinitely close, diverge exponentially with time [6, 8]. For each phase-space coordinate x_i , this divergence is quantified by the respective Lyapunov exponent λ_i : $\delta x_i(t) \propto \exp(\lambda_i t)$. The quantity that characterizes the rate at which the state

of an exponentially chaotic system is delocalized in the phase space is the Kolmogorov–Sinai entropy [6]. According to Pesin’s theorem [9], it can be expressed as the sum of all positive Lyapunov exponents:

$$h_{KS} = \sum_{\lambda_i > 0} \lambda_i. \quad (4)$$

Notice that the connection between the exponential chaos and mixing, although intuitively clear, has been rigorously proved only for a few simple cases, like the gas of hard spheres [10]. Numerical simulations appear to be a natural way to extend these results to real systems.

The central conjecture discussed here is that *ergodicity of a dynamical system should be understood as global chaotic connectivity of its region of motion*. If exponential chaos is confined to subregions connected only on sufficiently long timescales, two trajectories, arbitrary close but belonging to different regions of chaotic behaviour, do not diverge exponentially. Obviously, such decomposition of a single chaotic domain results in (i) separation of the relaxation timescales and (ii) slowing down the relaxation dynamics. In the following, we present arguments, supported by evidence from simulation, indicating that the discrepancy between the volume of a single stochasticity region and the total volume of the region of motion can be assessed by exploiting a recently found universal relation between the diffusion coefficient and the entropy [5].

3. Entropy and diffusion in the ergodic domain

The dynamics of dense fluids is dominated by the effect of coupling between the diffusive motions and local structural relaxations [11, 12]. As suggested above, a liquid can be regarded as an ensemble of independently relaxing regions represented by points in the respective configurational space; then the rate of diffusion is determined by the frequency at which these regions are changing their configurations. Each point of the ensemble explores adjacent positions at the rate determined by a characteristic clock frequency. The transition occurs if the destination configuration is open, the probability of which is e^S where S is the entropy. It is convenient to use the excess entropy: $S_{ex} = S - S_{PG}$, where S_{PG} is the entropy of perfect gas under the same conditions [13].

In order to achieve universality in describing the liquid dynamics, the above model can be formulated in terms of the hard spheres. It has been recognized by Enskog [14] that the momentum and energy transfer in a dense hard-sphere fluid is mediated by binary collisions. The collision rate, Γ_{coll} , thus provides a natural timescale for the dynamics. It can be assessed from the value of the radial distribution function, $g(r)$, at the collision distance [11]:

$$\Gamma_{coll} = 4\sigma^2 \rho g(\sigma) \sqrt{\frac{\pi k_B T}{m}} \quad (5)$$

where m is the particle mass, σ is the hard-sphere diameter and T is the temperature. At the same time, the hard-sphere diameter σ is a natural unit of length. In terms of these units, the above conjecture implies that

$$D = A \Gamma_{coll} \sigma^2 e^{S_{ex}}. \quad (6)$$

In order to apply this model to real liquids, it can be assumed that the hard-sphere diameter σ can be replaced by the position of the first peak of $g(r)$, which allows one to calculate Γ_{coll} . In this way, we can express D in different liquids in terms of universal units of time and length. Another approximation concerns the calculation of S_{ex} . The latter can be expressed as an expansion in terms of n -particle correlation functions [15]. In the two-particle approximation,

this gives

$$S_2 = -2\pi\rho \int \{g(r) \ln[g(r)] + [g(r) - 1]\} r^2 dr. \quad (7)$$

It was found [5] that, with the use of these approximations, equation (6) universally describes the relation between S and D in a wide range of simple systems with the value of the scaling constant $A = 0.049$.

Recently, it was found [16] that the Kolmogorov–Sinai entropy, expressed in terms of Γ_{coll} , is uniquely and universally related to the thermodynamic entropy. This implies that: (i) the collision frequency represents a universal timescale for the liquid dynamics; (ii) in liquids, the diffusion rate can be a measure of the rate of exponential chaos.

Equation (6) can be compared with other theories of liquid dynamics involving entropy. The model of Adam and Gibbs [17] postulates the existence of the cooperativity range, the minimum size for regions whose configuration can be changed without interfering with the environment. It conjectures that the relaxation time τ and the configurational entropy S_c are related by

$$\tau = A \exp\left(\frac{C}{S_c k_B T}\right). \quad (8)$$

Another model, suggested by Di Marzio and Yang [18], relates τ and the configurational free energy F_c :

$$\log \tau = B - A F_c / k_B T. \quad (9)$$

An obvious advantage of relation (6) as compared with (8) and (9) is that each of the latter two uses two free fitting parameters. Notice that parameter A in equation (9) is the number of particles participating in a single jump. If that relation is interpreted in terms of hard spheres where $F_c / k_B T = S$, with an additional assumption that $A = 1$, it becomes clearly consistent with (6). In that case, B would be expressed in terms of the collision frequency.

4. Entropy and diffusion in the non-ergodic domain

The dynamics of the supercooled liquid state can be conveniently discussed using the energy landscape paradigm [1]. Any instantaneous liquid configuration can be uniquely mapped onto a local potential energy minimum by the steepest-descent minimization [19]. In this way, the configurational space of a liquid can be uniquely decomposed into a set of basins, each associated with a respective local minimum. It was found that for the stable liquid state above T_m , all of the energy minima are statistically indistinguishable and independent of the temperature. Based on this observation, a concept of ‘inherent liquid structure’ was introduced [19].

In the supercooled domain, however, the average energy of the potential energy minima drops rapidly as the temperature decreases [20]. This indicates that in the supercooled domain, the liquid resides on a different part of the energy landscape to the normal liquid, predominantly staying in deep valleys connected by narrow bottlenecks. These connections are effectively used only on the long timescale, while the short-timescale dynamics of a supercooled liquid unfolds in a limited subregion of the total region of motion.

In order to illustrate the impact of such a strongly profiled landscape on the liquid relaxation dynamics, we consider a simple model sketched in figure 1. The whole set of configurations comprising the region of motion is divided into two components (valleys), depicted by squares and circles. The filled symbols denote the configurations which are energetically forbidden. The components are separated by barriers, indicated by solid lines, and the single

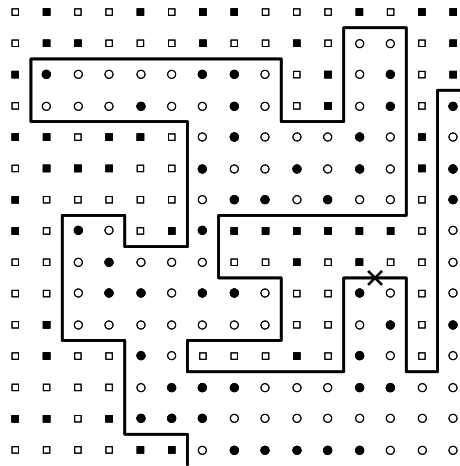


Figure 1. A simple model demonstrating the impact of the valley structure of the phase space on the relaxation dynamics. Energy barriers separating the valleys are depicted by solid lines. Squares and circles denote configurations belonging to different valleys. The point of crossover between the valleys is marked by the cross.

connecting pass is marked by the cross. Consider the probability w_{ij} of transition between the configurations i and j . At high temperature, where the separation of the components is not relevant, the average transition probability is entirely determined by the average probability that the destination configuration is allowed, and, in this way, by the entropy: $\langle w_{ij} \rangle = \langle w_j \rangle = e^S$. Clearly, this leads to the relation (6) for the diffusion rate.

In the case where the dynamics unfolds in the valley landscape, the average probability of transition can be estimated as $\langle w_{ij} \rangle = \langle w_v \rangle \langle w_j \rangle$ where $\langle w_v \rangle$ is the average probability that both i and j belong to the same valley. Obviously, in this case $\langle w_{ij} \rangle < e^S$, and therefore the diffusion rate is expected to show a negative deviation from relation (6). This deviation, indicating that the liquid dynamics is no longer related to the static properties, can be used as a macroscopic diagnostics of the onset for the supercooled (non-ergodic) regime.

5. Evidence from molecular dynamics simulation

In order to test the above conjecture, we investigated a two-component hard-sphere liquid simulated by molecular dynamics. The model consisted of 862 particles. The two species of hard spheres comprising the model (A and B) are characterized by the ratio of diameters $\sigma_A/\sigma_B = 1.69$ and the ratio of the number densities $\rho_A/\rho_B = 0.076$. The liquid phase of this system was found [21] to lose its thermodynamical stability when compressed beyond the critical value of the packing fraction $\phi = 0.5$. At higher densities, its stable phase was identified as the AB_{13} crystal, whose unit cell includes 112 atoms.

Due to the complexity of its crystallization pattern, this system possesses a pronounced glass-forming ability. In this simulation, it was found to remain in a long-living metastable equilibrium liquid state when compressed beyond the indicated critical packing fraction value. The absence of crystalline nucleation was thoroughly verified by monitoring the pressure and the diffusion coefficient, both of which remained constant during the simulation run.

In order to test relation (6) we calculated the diffusion coefficient and the excess entropy, in the pair approximation, S_2 , for the smaller atomic species B, exploring a wide range of

ϕ both below and above the critical value. S_2 was derived using (6) from two partial radial distribution functions, $g_{AB}(r)$ and $g_{BB}(r)$.

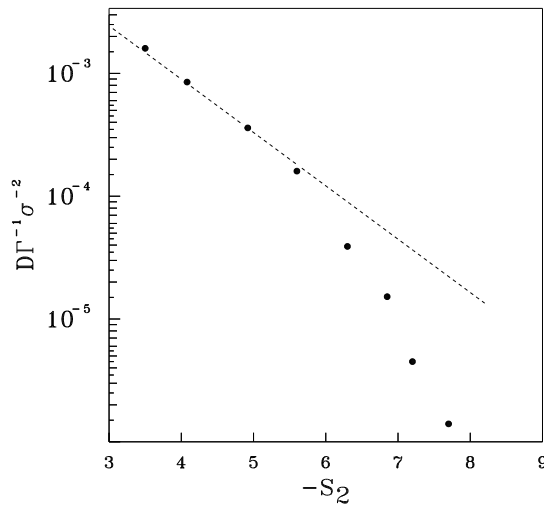


Figure 2. The reduced diffusion coefficient in the binary mixture of hard spheres as a function of the excess entropy, in the pair approximation (equation (6)). The dashed line corresponds to the universal scaling law (6) with $A = 0.049$.

The results of this simulation are presented in figure 2. It is clear that the results agree well with relation (6) for sufficiently small values of S_2 within the stable liquid domain. In the metastable liquid domain, the diffusion coefficient demonstrates a negative deviation from relation (6). An appreciable deviation starts at $S_2 = 6$, which corresponds to $\phi = 0.55$, and increases rapidly with increasing ϕ . The onset of total structural arrest has been observed at $\phi = 0.63$ where $S_2 = 8$.

6. Discussion

The above analysis, supported by the evidence from simulation, shows that the onset of the valley landscape has a dramatic impact on the relaxation dynamics in supercooled liquids. Long-time decomposition of the phase space which is assumed to take place under supercooling breaks any conceivable relation between the diffusion rate and the thermodynamic entropy conjectured for the stable liquid domain. This implies that the relations (6), (8) and (9) become invalid in the supercooled liquid domain. In fact, it has been demonstrated here that the breaking of relation (6) can be used as a diagnostics of the onset for the valley landscape under supercooling. On the other hand, decomposition of the phase space into separate regions of connected stochasticity leads to the separation of the timescales which is commonly associated with non-ergodic behaviour.

The long-time decomposition of the region of motion can be viewed as a reduction of the time-dependent effective entropy which measures the volume of the accessible phase-space region, as compared with the thermodynamic entropy. On the other hand, the entropy, as was pointed out above, can be related to the correlation length. Therefore, on the timescale characterizing the decomposition of the phase space of a supercooled liquid, the relaxation dynamics is expected to be correlated within a range exceeding the range of the static structural

correlations. This consideration suggests the existence in the supercooled liquid of large-scale long-living clusters.

The characteristic length of the above-described cooperative effects can be directly probed by measuring the rate of the liquid dynamics in confined geometries. It has to be emphasized that the time-limited cooperativity is decoupled from the static structure and, therefore, from the thermodynamic entropy. This conclusion was supported by the simulation of lattice-gas models [22]. Attempts to interpret the cooperative dynamics of supercooled liquids in terms of the Adam–Gibbs theory [23] which refers to the (static) configurational entropy, although common, are logically incorrect. In order to detect the existence of time-limited clusters, it is crucial to compare the cooperativity range, as derived from the dynamical measurements, with the range of the static structural correlations which, at least for quasi-simple liquids, can be assessed from the diffraction measurements.

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