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Anomalous slowing down in the metastable liquid of hard spheres

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It is demonstrated that a straightforward extension of the Arrhenius law accurately describes diffusion in the thermodynamically stable liquid of hard spheres. A sharp negative deviation from this behavior is observed as the liquid is compressed beyond its stability limit. This dynamical anomaly can be compared with the nonlinear slowing down characteristic of the supercooled dynamics regime in liquids with continuous interaction. It is suggested that the observed dynamical transition is caused by long-time decomposition of the configuration space. This interpretation is corroborated by the observation of characteristic anomalies in the geometry of a particle trajectory in the metastable domain.

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Computer simulations of liquids using hard spheres (HS) remain a key source of information about the most fundamental aspects of the liquid state. The main intellectual attraction of these models is in their purely geometric nature: all the observable properties of a HS liquid can be reduced to a single thermodynamic quantity—entropy, a measure of finite-range structural correlations [1,2]. Thus, mapping a phenomenon exhibited by liquids with continuous interactions on a HS model yields its interpretation in terms of the statistical geometry of sphere packing.

An important aspect of liquid behavior addressed using HS models is supercooled liquid dynamics [3–6]. This notion refers to the complex of dynamical anomalies observed in a liquid that remains in a metastable equilibrium below its melting point. For the one-component HS system, the stable liquid domain is bounded by the critical value of the packing fraction $\eta_c = 0.493$ [6] ($\eta = \pi\rho\sigma^3/6$, where ρ is the density and σ is the HS diameter). Having been compressed beyond $\eta = 0.54$, the HS liquid inevitably crystallizes [6].

The most prominent indicator of the supercooled liquid regime, and, in fact, its defining feature [7,8], is the characteristic behavior of the relaxation dynamics that slows down with cooling progressively faster than it can be inferred from the Arrhenius prescription universally describing the temperature variation of the transport coefficients in stable liquids.

In contrast to atomistic models with continuous interaction, the HS systems lack the energy scale. Therefore, in order to compare the non-Arrhenius liquid dynamics as observed in the former with the respective behavior of the metastable HS liquid, we have to resolve the fundamental problem of finding a description of the *stable* HS liquid dynamics that would be an adequate analog of the Arrhenius law. In this capacity, Hildebrant-Batchinski relation [9] connecting the diffusion coefficient with the free volume was suggested [10]. The HS liquid diffusion [10] follows this relation in the stable domain and deviates from it for $\eta > \eta_c$ [11]. However, this deviation is *positive* and, therefore, cannot be regarded as an appropriate analog of the super-Arrhenius slowing down in supercooled liquids.

In this paper, it is demonstrated that an earlier suggested relation between the diffusion coefficient and the thermodynamic entropy [12] can be interpreted as a straightforward extension of the Arrhenius law. Having been tested by molecular dynamics, it is found to accurately describe the diffusion in the stable one-component HS liquid. Moreover, a significant slowing down as compared with this relation is observed in the metastable HS liquid domain that can be compared with the nonlinear slowing down in supercooled liquids with continuous interatomic interactions. This transition in the HS dynamics is interpreted in terms of long-time scale decomposition of the configuration space.

The Arrhenius law asserts that the diffusion coefficient D scales with the temperature T as

$$D = zpD_0 e^{-E_a/k_B T}, \tag{1}$$

where the activation energy E_a is interpreted as the average height of the energy barrier that a particle has to cross in its escape route from the current position, p is the success probability in an attempt to find an escape route, and z is the attempt rate. In the case of HS, $E_a = 0$, and D is controlled by p that essentially quantifies the topological constraints imposed on the local structural rearrangements. In this context, two possible dynamical regimes can be considered.

(i) The available configurations are abundantly connected; the connectivity is facilitated by independent motions of individual particles. An attempt of a particle to move to an adjacent position is always successful if the destination position is allowed by the equilibrium structural constraints. Then the inverse average number of attempts needed for a particle to move from its current position scales as $p = e^s$ where s is the excess entropy per particle—the difference between the system's entropy and that of the perfect gas at the same thermodynamic conditions.

(ii) The configuration-space connectivity is restricted by additional constraints, complementary to the ensemble-averaged structural constraints described above. In this case, the diffusive motions of an individual particle are coupled, in a presumably hierarchical manner, with the respective motions of other particles within a certain range [13]. These constraints give rise to a long-time decomposition of the available configuration space [14]. Therefore, a particle, in its elementary diffusive motion, cannot access all the adjacent positions that are allowed by the ensemble-averaged constraints, which implies that $p < e^s$. It has to be empha-

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sized that the described division of the configuration space exists on a limited time scale and, therefore, is quite distinct from the equilibrium distribution. However, there exists a conjecture [15] relating the cooperativity range to the equilibrium entropy; this conjecture is not discussed here.

It has to be mentioned that almost all points of a confined region of a multidimensional configuration space are close to its surface [16]. Therefore, in the divided configuration space corresponding to situation (ii), almost every point is adjacent to a dividing boundary, with a profound effect on the rate of dynamics. Another remark is that the type (i) dynamics can be compared with the "small world" dynamics of randomly connected multidimensional networks [17].

The central postulate we adopt here is that the configuration-space topology that controls the relaxation dynamics in the stable HS liquid is of type (i). It is also assumed that the attempt frequency z is proportional to the Enskog collision frequency Γ [18]. With this assumption, Arrhenius law (1) can be transformed into the following simple form relating s and D:

$$D=\Gamma D_0 e^s. \tag{2}$$

In this form, the relation becomes equivalent to the earlier suggested scaling law for atomic diffusion [12]. The latter was successfully tested on a number of simple liquids, including the HS liquid using a two-body approximation for s [2]. In the full s version, the scaling law was tested on some metallic liquids [19], but for the HS liquid, such tests have not been done so far. In this context, a conjecture should be mentioned where $D\propto e^{Bs}$ with $B\neq 1$ [20].

In this study, relation (2) was tested using a molecular-dynamics simulation of a HS system comprising 6912 identical particles. This simulation was necessitated by the fact that, although the HS diffusion has been explored in a number of simulations, a considerable uncertainty remains concerning its size dependence at different densities [6,21].

The assumption that the dynamics in a liquid is controlled by the excess entropy, a measure of the structural correlations, implies that the length should be measured in terms of the characteristic length of the structure that manifests itself in the position of the main peak of the structure factor. It is known that the latter scales with the density ρ as $\rho^{1/3}$; therefore, $\rho^{-1/3}$ is a convenient unit of length. This unit of length is also consistent with the equilibrium separation of the nearest neighbors in the Lennard-Jones (LJ) liquid of which the structure factor can be reproduced by that of the HS liquid. The use of σ as the unit of length that was adopted in the earlier test of the scaling law [12] on the HS liquid is apparently inappropriate at lower densities.

The HS excess entropy was calculated here by the thermodynamic integration using Boublik-Nezbeda approximation [23] for the equation of state:

$$P/\rho k_B T=(1+\eta+\eta^2-b_1\eta^3-b_2\eta^4-b_3\eta^5)/(1-\eta)^3 \tag{3}$$

with $b_1=0.764314$, $b_2=0.151532$, and $b_3=0.654551$. A minor correction was introduced for $\eta>0.47$ [6]. Within the range of η explored here, the approximation was found to reproduce the simulation results within 0.2%.

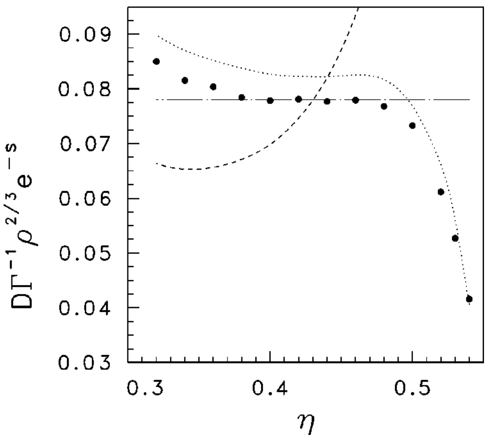

FIG. 1. Diffusion coefficient in the HS liquid as a function of the packing fraction η. Dots, the present molecular-dynamics simulation; dotted line, the extrapolated limit for the infinite system size [21,22]; chain-dashed line, Eq. (2) with $D_0=0.078$; dashed line, the Enskog approximation [18].

The simulation results are shown in Fig. 1. Each value of D was obtained from the mean-square displacement averaged over 10^4 collisions per particle. These results are compared with another set of the HS diffusion data that represent an extrapolation to the infinite system size [21,22]. It is clear that with $D_0=0.079$, relation (2) accurately describes the diffusion in the one-component HS system within the range $0.36<\eta<0.49$ that covers the entire stable liquid domain. D_0 corresponds to the diffusion rate in a hypothetical situation where the discussed liquid diffusion mechanism is still valid but $s=0$. The observed value of D_0 can be rationalized using the following arguments based on a simple toy model in the spirit of the lattice gas models. Consider a tessellation of the space into equal-size cells. Each cell contains one stationary particle that stays within the cell until its status is changed; besides, there is a number of mobile particles distributed in space. At each time step, a mobile particle collides with the stationary particle that is in the same cell. As a result, the former becomes stationary, whereas the latter becomes mobile and traverse the cell boundary into a randomly chosen adjacent cell (if several mobile particles simultaneously occur in one cell, an arbitrary collision sequence is assumed). Thus, each particle performs a random walk with the step size $\approx\rho^{-1/3}$. Assuming that the number of mobile particles is small, and keeping in mind that there is one particle jump per two collisions, the diffusion coefficient can be estimated as $D\approx\Gamma\rho^{-2/3}/12$, which is in a good agreement with the above value of D_0. The results presented in Fig. 1 demonstrate that in the metastable liquid domain $\eta>\eta_c$, the HS diffusion exhibits a rapidly increasing slowing down as compared with the stable liquid behavior conjectured by relation (2). The apparent nonlinearity of the dynamical slowing down of HS liquid under supercompression revealed in Fig. 1 can be compared with respective behavior of the supercooled liquids with continuous interactions. Using the above arguments, the onset of this new dynamical regime

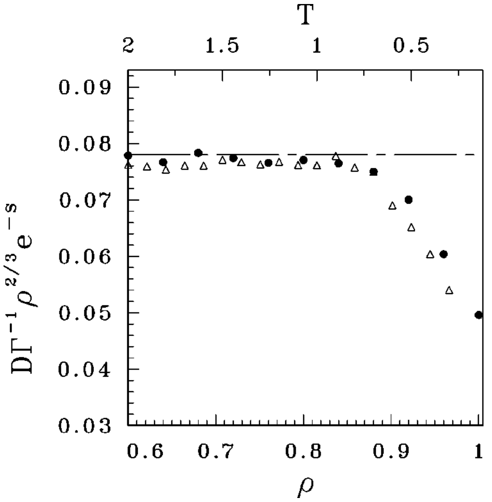

FIG. 2. Diffusion coefficient of the liquid simulated using the truncated LJ potential. Dots and the lower scale correspond to the density variation at constant temperature $T=0.7$. Open triangles and the upper scale correspond to the temperature variation at constant density $\rho=0.88$. The chain-dashed line marks the same value as in Fig. 1.

can be interpreted as a clear evidence that the type (i) configuration-space dynamics controlled by the equilibrium distribution, transforms into type (ii) dynamics dominated by the extra dynamical constraints and long-time configuration-space decomposition.

Figure 2 shows D, as a function of temperature and density, in a liquid simulated by molecular dynamics using the LJ potential truncated at its minimum (the truncation was done to avoid a phase decomposition at low densities). D is scaled using s obtained by thermodynamic integration and Γ estimated as [18]

$$\Gamma=4\rho\sigma^2 g(\sigma)(\pi k_B T/m)^{1/2}. \tag{4}$$

Here, σ is interpreted as the position of the main maximum of $g(r)$ [1,12]. The results agree with Eq. (2) in the stable liquid domain, whereas both supercooling and supercompression result in a sharp negative deviation.

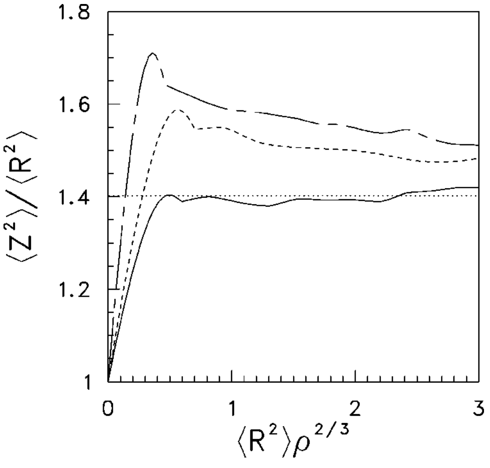

FIG. 3. The ratio of the mean-square maximum displacement $\langle Z^2(t)\rangle$ to the mean-square displacement $\langle R^2(t)\rangle$. Solid line, $\eta=0.48$; dashed line, $\eta=0.52$; chain-dashed line, $\eta=0.53$. The dotted line indicates the random-walk limit $\langle Z^2(t)\rangle/\langle R^2(t)\rangle=1.4024\ldots$ [24].

The long-time configuration-space decomposition conjectured to dominate the HS liquid dynamics in the metastable domain can be detected from its impact on a particle trajectory. The latter represents a three-dimensional (3D) real space projection of the multidimensional trajectory of the system in its configuration space. The relaxation dynamics that unfolds in type (i) regime represents a random walk in the configuration space, which must also be true for a single particle trajectory. The long-time decomposition of the configuration space caused by the development of extra constraints characteristic of the type (ii) regime give rise to distinct anomalies in the geometry of a particle trajectory. A quantity that can be conveniently employed as an indicator of a possible deviation from the random-walk geometry in a particle trajectory is the maximum absolute value of the displacement from the original position within the time interval $(0,t)$:

$$Z(t)\equiv\max\{R(\tau),\ 0<\tau<t\}. \tag{5}$$

The ratio of its second moment $\langle Z^2(t)\rangle$, the mean square maximum displacement, to the mean square displacement $\langle R^2(t)\rangle$ for a random walk in 3D space is equal to $1.4024\ldots$ [24]. The evolution of this ratio as a function of $\langle R^2(t)\rangle$ for various values of η is presented in Fig. 3. For $\eta=0.48$, in the stable liquid domain, the random-walk limit is attained after a short initial period of ballistic behavior, as soon as a particle leaves the cage of its nearest neighbors. The geometry of a particle trajectory changes significantly as the HS liquid is compressed beyond its stability limit: a new regime of diffusion develops where $\langle Z^2(t)\rangle/\langle R^2(t)\rangle$ exceeds the random-walk value. This indicates that a particle trajectory has a higher chance than random to return to an earlier covered region. The extent of this apparent confinement effect in a particle trajectory amounts to the diffusive displacement of several particle diameters, and it increases rapidly, as well as the magnitude of the effect, with the increase of η.

According to the arguments presented above, the characteristic time of a transition between two configuration-space regions can be regarded as a measure of the real-space extent of the local configurational transformation that the system has to perform to cross between the two regions. The long-lived configuration-space decomposition that was presumed to arise in type (ii) regime implies the existence of real-space correlations, both positional and dynamical, that extend beyond the range of the equilibrium correlations. The rapid increase in the (time-limited) correlation length in the metastable HS liquid that has been detected here from the geometry of a particle trajectory represents a generic feature of the supercooled liquid behavior [25]. In that regime, ergodicity restoring relaxation dynamics whereby long-lived metastable states are created and destroyed is facilitated by highly collective activated hopping. This dynamics was discerned in the metastable HS liquid using dynamical density-functional theory analysis [26].

The profound similarity between the pattern of slowing down in the metastable HS liquid and that in conventional supercooled liquids indicates the entropic nature of this phenomenon [27], and suggests a unifying scenario for its development in terms of the configuration-space connectivity. The change in the packing geometry under cooling/compression beyond the liquid phase stability limit, presumably caused by the reduction of free volume [28], leads to the loss of the short time-scale configuration-space connectivity. This results in a fundamental transformation of the relaxation dynamics that can be detected as breaking the relation between between s and D prescribed by the scaling law (2).

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