We investigate the origin of the Stokes-Einstein relation in liquids. The hard-sphere dynamics is analyzed using a new measure of structural relaxation - the minimum Euclidean distance between configurations of particles. It is shown that the universal relation between the structural relaxation and diffusion in liquids is caused by the existence of one dominating length scale imposed by the structural correlations and associated with de Gennes narrowing. We demonstrate that this relation can be described by a simple model of independent random walkers confined to single-occupancy cells.

The dynamics of a system of identical particles is commonly described in terms of the van Hove density correlation function $G(r,t)$. Its self-part, $G_s(r,t)$ describes the evolution of the density distribution for a tagged particle. However, because the particles are indistinguishable, the evolution of a tagged particle becomes irrelevant for the structural relaxation as soon as the particle traverses the nearest neighbour distance.

For a system of $N$ identical particles, there exists $N!$ physically indistinguishable permutations of each configuration. Let $r^N(t) = \{r_i(t)\}$ be the system’s configuration at a time moment $t$. We define a correlation function:

$$G_n(r,t) = \frac{1}{N} \left\{ \sum_{i=1}^{N} \delta \left[ r - |r_i(0) - r_{p(i)}(t)| \right] \right\}$$

where $\{p(i)\} = \hat{P}\{i\}$, where $\hat{P}$ is the permutation procedure minimizing the second moment:

$$d(t) = \int_0^\infty r^2 G_n(r,t) 4\pi r^2 dr = \frac{1}{N} \sum_{i=1}^{N} [r_i(0) - r_{p(i)}(t)]^2$$

This quantity, to be referred to as dissimilarity, represents the minimum square Euclidean distance between the two configurations. In general, this minimizing re-labeling procedure ($d$-mapping) can be used to evaluate the dissimilarity between any two configurations:

$$d(a^N, b^N) = \frac{1}{N} \sum_{i=1}^{N} [a_i - b_{p(i)}]^2$$

We use this approach to analyze a molecular dynamics model of 27000 identical HS particles. Throughout this
study, the length is measured in terms of $\rho^{-1/3}$, $\rho$ being the number density.

For high packing fractions and short time intervals where the number of relabellings is negligible, $G_n(r, t)$ would behave as $G_n(r, t)$. Therefore, the former, like the latter, is expected to have a Gaussian form. However, unlike $G_n(r, t)$ the second moment of which - the mean square displacement (MSD) - grows linearly with time, $G_n(r, t)$ converges to a limit distribution with a finite second moment $d(t) \to d_l$ as the two configurations become uncorrelated for $t \to \infty$. The variation of $d_l$ in the HS system is plotted in Fig. 1 as a function of the packing fraction $\varphi$.

For a selected reference configuration, the described permutation $P$ uniquely maps the system’s configuration space onto a compact region possessing the following properties:

(i) For $N \to \infty$ almost all its points are infinitely close to the surface of a sphere of square radius $N d_l$ centered at the reference configuration ($d$-sphere). Therefore, any configuration uncorrelated with the reference configuration is expected to be separated from the latter by $d = d_l$.

(ii) $d_l$ separating two uncorrelated configurations is a static property entirely determined by the density fluctuations in these configurations. In the HS system, it increases monotonously with decreasing packing fraction $\varphi$, see Fig. 1. The impact of the structural fluctuations on $d_l$ can be assessed by using a regular lattice as a reference configuration. It is shown in Fig. 1 that for the entire range of $\varphi$, $d_l$ for the HS system calculated with respect to the fcc lattice is reduced compared with $d_l$ calculated for two uncorrelated HS fluid configurations.

(iii) In the case of the perfect gas (PG), the volume of the $d$-sphere scales as the total number of distinguishable configurations. To test this, we consider a PG model where particles are confined to single-occupancy Wigner-Seitz cells centered at the reference configuration. The arrow indicates $d_l$ for perfect gas constrained to the single-occupancy fcc Wigner-Seitz cells multiplied by $e^{2/3}$.

where $p(i)$ and $q(i)$ are permutations $d$-mapping $r^N(0)$ and $r^N(t)$ onto $c^N$. Covariance of two stochastic variables is a measure of their linear correlation; therefore, (5) implies that $r^N(0)$ and $r^N(t)$ are uncorrelated (notice that $d$-mapping can induce correlation between these configurations if $c^N$ includes any density fluctuations). Fig. 2 shows the evolution of the l.h.s. of Eq. (5) in the HS liquid for $\varphi = 0.48$ as a function of $d(t)/d_l$, the reference configuration $c^N$ being the fcc lattice.

Thus, $d(t) = d_l$ is a necessary and sufficient condition for the two configurations separated by $d(t)$ to be uncorrelated. $d(t)$ can therefore be used as a convenient indicator of the system’s approach to its ergodic equilibrium. We propose to measure the structural relaxation in a system of particles in terms of the following dimensionless quantity:

$$\Phi_d(t) = [d_t - d(t)]/d_l$$

Structural relaxation in liquids is commonly assessed in terms of the intermediate scattering function $F(Q_m, t)$, $Q_m$ being the position of the main maximum of the structure factor $S(Q_m) = F(Q_m, 0)$ multiplied by $e^{2/3}$. For liquid densities, $Q_m$ represents the length scale of the slowest relaxing structural correlation (De Gennes narrowing). This effect, however, disappears at low densities. An important advantage of $\Phi_d(t)$ as a measure of relaxation is that it is not associated with a particular length scale. Also, unlike the energy-based measure of ergodic convergence, its calculation doesn’t require knowledge of the interparticle interaction. Another advantage of $\Phi_d(t)$ is that, being based on a single-particle correlation function, it can provide insight into the link between the individual particle dynamics and the structural relaxation.
the packing fraction, as a function of MSD. For two representative values of \( \varphi \) with the respective evolution of \( \Phi_d \) the liquid domain, the evolution of \( \Phi_{\varphi} \) is evident that for these two values of \( \varphi \) is exponential, and it agrees quite well with the respective 

FIG. 3: Relaxation in the HS system as a function of MSD. Dots, filled boxes and filled stars: \( \Phi_d(t) \) for \( \varphi = 0.48, \varphi = 0.35 \) and \( \varphi = 0.2 \), respectively. Open circles, open boxes and open stars: \( F(Q_m, t)/S(Q_m) \) for \( \varphi = 0.48, \varphi = 0.35 \) and \( \varphi = 0.2 \), respectively. Crossed circles, \( \Phi_d(t) \) for perfect gas. Dashed line, \( \Phi_d(t) \) calculated according to Eq. (7)

In Fig. 3 we analyze the relation between the structural relaxation and diffusion in the HS system. The structural relaxation is measured in terms of \( \Phi_d(t) \) and presented as a function of MSD. For two representative values of the packing fraction, \( \varphi = 0.35 \) and \( \varphi = 0.48 \) which span the liquid domain, the evolution of \( \Phi_d(t) \) is compared with the respective evolution of \( F(Q_m, t)/S(Q_m) \). It is evident that for these two values of \( \varphi \), the decay of \( \Phi_d(t) \) is exponential, and it agrees quite well with the respective behaviour of \( F(Q_m, t)/S(Q_m) \). It is also evident that, within the liquid domain, the rate of structural relaxation relative to the diffusion rate is invariant with respect to the variation of \( \varphi \).

Fig. 4 shows that the universal relation between the structural relaxation and diffusion observed within the liquid domain breaks for lower densities. At \( \varphi = 0.2 \), we find a distinctly different regime. The structural relaxation relative to the diffusion as measured by \( \Phi_d(t) \) becomes retarded as compared with the universal pattern observed for the liquid. Notice that the decay of \( F(Q_m, t)/S(Q_m) \) for \( \varphi = 0.2 \) agrees quite well with the exponential liquid pattern. One can also see that \( \Phi_d(t) \) exhibits a strong stretching as compared with the exponential decay. Both the retardation and the degree of stretching progressively increase with decreasing \( \varphi \). These results can be compared with an earlier simulation study of the HS viscosity [21] where it was found that the Stokes-Einstein relation breaks around \( \varphi = 0.15 \). We note that the Enskog theory [22] predicts violation of the SE relation in the low-density gas limit, with \( D \eta \) diverging as \( \varphi^{-1} \).

These results thus pose us with the following questions: what is the origin of the universality of the liquid relaxation dynamics and why does it break in the low-density domain?

The observation that, within the liquid domain of \( \varphi \), \( \Phi_d(t) \) decays exponentially relative to MSD implies that the liquid relaxation is controlled by a single length scale, and the close agreement between the decay of \( \Phi_d(t) \) and the decay of the respective \( F(Q_m, t)/S(Q_m) \) clearly indicates that this length scale corresponds to the density fluctuation that gives rise to the main peak of \( S(Q) \). This length scale, \( 2\pi/Q_m \), is the size of the first shell of neighbours, the dominant element of the liquid structure. The maximum of the relaxation time of \( F(Q, t) \) at \( Q_m \) (De Gennes narrowing [15]) is caused by the so-called “cage effect” [2, 24] whereby the structural relaxation is facilitated by the diffusive motions of the particles within the
confining cages of the nearest neighbours. The cage size thus controls the relation between the diffusion and the structural relaxation, and its $\varphi$-invariance explains the latter’s universality.

The relaxation time for the $Q$-component of $F(Q, t)$ scales as $\alpha S(Q)/Q^2$ \[ \alpha \] \cite{15,24,25}. Its variation with respect to $Q$ and $\varphi$ is shown in Fig. 4. It features a pronounced maximum at $Q_m$ for $\varphi = 0.35$ where the relaxation and diffusion follow the universal liquid relation, see Fig. 3. For $\varphi = 0.2$, that maximum disappears, and the decay of $F(Q, t)$ is dominated by the density fluctuations with length scales exceeding $2\pi/Q_m$. The respective increase in the range of the diffusive motions dissipating these fluctuations results in the retardation of the relaxation process relative to diffusion as compared with the universal liquid behaviour, see Fig. 3. Moreover, the stretching of $\Phi_d(t)$ beyond a single-exponential behaviour can be interpreted as a superposition of multiple exponential relaxation processes with a wide range of relaxation rates.

We thus conclude that the observed universality of the liquid relaxation behaviour relative to diffusion is explained by the confinement of the relevant density fluctuations to the first coordination shell which manifests itself as the maximum of the $Q$-dependent relaxation time at $Q_m$ (de Gennes narrowing).

We support this picture of liquid dynamics by the following model. Consider a tessellation of space into unit-volume cubic cells. Each cell contains one point particle performing Fickian diffusion with the self-diffusion coefficient $D$. The diffusion starts from the centre of the respective cube, and it is confined to the latter by reflective boundaries. This dynamics relaxes the initial lattice configuration to the equilibrium perfect gas where the density fluctuations are constrained by the single-occupancy confinement. This is supposed to model the confinement of the density fluctuations to the first neighbour shell that was concluded for the liquid dynamics. The relaxation of the initial structure is assessed in terms of $d(t)$. We note that, in this model, reflecting boxes’ boundaries are equivalent to applying the $d$-minimizing permutation, and, for the uniform equilibrium distribution of particles’ density within the cube, $d_l = 1/4$. The solution for $d(t)$ can be obtained as the following serial expansion:

$$d(t) = \frac{1}{4} + \frac{6}{\pi} \sum_{k=1}^{\infty} \frac{1}{k^2} \cos \left( \frac{k\pi}{2} \right) (1 + \cos k\pi) e^{-k^2 \pi^2 D t}$$

The decay of $\Phi_d(t)$ with respect to $\langle r^2(t) \rangle = 6 D t$ shown in Fig. 3 demonstrates good agreement with the liquid relaxation data.

These results highlight two principle aspects of the liquid dynamics representing essential conditions for the universal relation between the relaxation and diffusion, and the Stokes-Einstein relation. First, the relaxation process is dominated by the dissipation of the density fluctuations confined to the first coordination shell. This behaviour, also observed as de Gennes narrowing, can be diagnosed from the structure data as a maximum at $Q_m$ in $S(Q)/Q^2$. Second, the trajectory of a diffusing particle facilitating the relaxation process is expected to be fully randomized within the first-neighbour distance, which implies Gaussianity of the diffusion process. The deviation from the universal pattern of liquid dynamics observed in the low-density domain is evidently caused by the presence of long-range density fluctuations violating the first of the above conditions.

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