



## Self-Diffusion of Particles in Complex Fluids: Temporary Cages and Permanent Barriers

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We study self-diffusion in complex fluids within dynamic density functional theory and explicitly account for the coupling to the fluctuating background. Applying the formalism to nematic and smectic liquid crystals, we find the temporary cages formed by neighboring particles to compete with permanent barriers in nonuniform systems, resulting in non-Gaussian diffusive motion that in different directions becomes correlated. Qualitative agreement with recent experiments demonstrates the importance of explicitly dealing with time-dependent self-consistent molecular fields.

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Phenomena such as multisite hopping in microstructures, void diffusion in colloidal crystals, dynamical heterogeneities of colloidal glasses, and the self-assembly of micelles, supramolecular polymers, and viruses are striking examples of the intriguing dynamics of complex fluids, whose understanding remains relatively rudimentary despite intense research spanning many decades. The main reason for this state of affairs presumably is an incomplete understanding of temporal fluctuations of the fluid structure and how these couple to single-particle diffusive motion. To circumvent this problem, self-diffusion of particles in locally or globally inhomogeneous fluids is therefore often studied in a fixed background potential mimicking the actual fluid structure but completely ignoring the inherently fluctuating nature of it [1].

It is the aim of this Letter to theoretically investigate the influence of the local fluid structure and the temporally fluctuating background on the self-diffusion in uniform and nonuniform complex fluids. As a simple yet quite interesting example, we apply our treatment, based on dynamical density functional theory, to dispersions of elongated colloidal particles in uniaxial nematic and smectic liquid-crystalline phases. In the former, the orientational degrees of freedom are frozen out and in the latter also one positional degree of freedom. This allows us to compare our theory with results of a very recent experimental study of the unusual self-diffusion in aqueous dispersions of the filamentous bacteriophage fd [2].

As we shall see, the local fluid structure forms a temporary cage around every test particle that initially hinders its free self-diffusion but that decays at later times. Remarkably, this temporal caging effect of the background particles can produce a coupling between motion in different directions, in particular, if the fluid is symmetry-broken. Both these phenomena influence the self-diffusion in structured fluids and cannot be accounted for by presuming a fixed molecular background field. In fact, even if

a fluctuating molecular field is presumed, its effect can only be predicted beyond the usual linear analysis of density fluctuations; i.e., they are inherently nonlinear.

Focal point of our discussion are the van Hove correlation functions that probe diffusive processes [3]. We generalize the formalism introduced for simple fluids in Ref. [4]. The key idea is to define conditional densities for which equations of motion can be prescribed [4] and which are related to the well-known van Hove correlation functions. The formalism, although applied here to athermal systems, can be generalized readily to, say, thermotropic liquid crystals within Landau-de Gennes theory [5].

Consider an equilibrium fluid of  $N$  particles with arbitrary degrees of freedom  $\mathbf{x}$  and define self ( $s$ ) and distinct ( $d$ ) conditional densities as

$$C_s(\mathbf{x}, t|\mathbf{x}', 0) := \frac{1}{\varrho(\mathbf{x}')} \left\langle \sum_{n=1}^N \delta(\mathbf{x} - \mathbf{X}_n(t)) \delta(\mathbf{x}' - \mathbf{X}_n(0)) \right\rangle,$$

$$C_d(\mathbf{x}, t|\mathbf{x}', 0) := \frac{1}{\varrho(\mathbf{x}')} \left\langle \sum_{\substack{n, n'=1 \\ n \neq n'}}^N \delta(\mathbf{x} - \mathbf{X}_n(t)) \delta(\mathbf{x}' - \mathbf{X}_{n'}(0)) \right\rangle, \quad (1)$$

respectively, where  $\langle \dots \rangle$  is the average taken over all equilibrium trajectories,  $\delta$  the Dirac- $\delta$  in configuration space,  $\mathbf{X}_n(t)$  the configuration of particle  $n$  at time  $t$ , and  $\varrho(\mathbf{x}')$  the one-particle equilibrium density at configuration  $\mathbf{x}'$ . The conditional densities  $C_{s,d}$  and the van Hove self and distinct correlation functions  $G_{s,d}$  [3] are related via

$$G_{s,d}(\Delta\mathbf{x}, t) = \frac{1}{N} \int d\mathbf{x}' C_{s,d}(\mathbf{x}' + \Delta\mathbf{x}, t|\mathbf{x}', 0) \varrho(\mathbf{x}'). \quad (2)$$

According to Eq. (1), the conditional densities at zero time  $t = 0$  read  $C_s(\mathbf{x}, 0|\mathbf{x}', 0) = \delta(\mathbf{x} - \mathbf{x}') =: n_l(\mathbf{x}, 0)$  and  $C_d(\mathbf{x}, 0|\mathbf{x}', 0) = \varrho(\mathbf{x}) g(\mathbf{x}, \mathbf{x}') =: n_u(\mathbf{x}, 0)$  with  $g$  the pair distribution function [3] and  $n_{l,u}$  the one-particle equilib-

rium densities of a fluid of one labeled ( $l$ ) and  $N - 1$  unlabeled ( $u$ ) particles in which the labeled particle is fixed in configuration  $\mathbf{x}'$ . Upon releasing the fixed labeled test particle at time  $t = 0$ , the neighboring host fluid relaxes towards a new equilibrium state, and it is assumed that the time-dependent two-particle correlators  $C_{s,d}(\mathbf{x}, t | \mathbf{x}', 0)$  equal the one-particle densities  $n_{l,u}(\mathbf{x}, t)$  for all times  $t \geq 0$ . This identification is reminiscent of Onsager's regression hypothesis and implies the fluctuation-dissipation theorem to hold, which is strictly proven only within linear response theory [6]. A free energy density functional  $F[n_l, n_u]$  [7] describing the fluid automatically produces the one-particle equilibrium density distribution  $\varrho$  and the pair distribution function  $g$  as well as expressions for the local chemical potentials

$$\mu_{l,u}(\mathbf{x}, t, [n_l, n_u]) := \frac{\delta F}{\delta n_{l,u}(\mathbf{x})} \Big|_{n_l(\cdot,t), n_u(\cdot,t)} \quad (3)$$

that within a generalized Fickian approximation give rise to the equations of motion [8]

$$\frac{\partial}{\partial t} n_{l,u}(\mathbf{x}, t) = \nabla_{\mathbf{x}} \cdot \{n_{l,u}(\mathbf{x}, t) \Gamma(\mathbf{x}, t, [n_l, n_u]) \cdot \nabla_{\mathbf{x}} \mu_{l,u}(\mathbf{x}, t, [n_l, n_u])\} \quad (4)$$

with  $\Gamma$  the mobility matrix. Note that Eq. (4) implies the hypothesis of local equilibrium to hold and neglects hydrodynamic interactions, i.e., the free draining limit to effectively hold. In dense systems, the latter presumption seems reasonable due to screening of hydrodynamics. The mobilities are then to be interpreted as renormalized ones. Integrating this closed set of equations for  $n_{l,u}$  subject to the specified initial conditions and interpreting  $n_{l,u}$  as conditional densities  $C_{s,d}$ , one obtains the van Hove correlation functions  $G_{s,d}$  from Eq. (2). For a uniform, simple fluid, where the particles possess only translational degrees of freedom,  $\mathbf{x} = \mathbf{r}$ , and the one-particle density  $\varrho$  is spatially constant, the conditional densities  $C_{s,d}(\mathbf{r}, t | \mathbf{r}', 0)$  depend only on  $\mathbf{r} - \mathbf{r}'$ , so that  $G_{s,d}(\Delta \mathbf{r}, t) = C_{s,d}(\Delta \mathbf{r}, t | \mathbf{0}, 0) = n_{l,u}(\Delta \mathbf{r}, t)$  and Eqs. (3) and (4) can be interpreted as equations of motion for the van Hove correlation functions  $G_{s,d}$  and avoids having to explicitly deal with kinetic equations for conditional densities that in actual fact are two-point correlators. Note that the quantities called ‘‘van Hove functions’’ in Ref. [4] are actually conditional densities, which, in general, differ from the well-known van Hove correlation functions. The general formalism described here is applicable to any nonuniform or complex fluid and offers a route to analyze the relaxational dynamics of a wide range of interesting structured fluids.

Motivated by the very recent measurements of the van Hove self correlation function of aqueous solutions of the bacteriophage fd [2], a filamentous virus particle of about 900 nm length and 7 nm width, we consider a free energy functional  $F[n_l, n_u]$  describing a lyotropic liquid crystal of

(stiff) hard rods of length  $L$  and diameter  $D$  with  $L \gg D$ . As the root-mean-squared angle between the axis of a rod and the director scales as  $\mathcal{O}(D/L)$  in this limit [9], the orientational degrees of freedom can be ignored, so the rods are assumed to be oriented parallel to the director, which itself is assumed to be fixed. This means that the model particles possess only translational and no orientational or internal conformational degrees of freedom such as arising from a bending flexibility. For the free energy density  $F[n_l, n_u]$ , we for reasons of simplicity invoke the second virial approximation [10]. Although not accurate, it is known to capture the main features of the structure of the smectic phase near the nematic transition point, which suffices for our purposes. Our model of perfectly parallel hard rods is simple but not overly simple, as quantitative precision is not required, and the neglect of features such as particle flexibility, higher virial terms, or (screened) hydrodynamic interaction can in principle be accounted for by renormalization of the model parameters. The bare translational mobilities  $\Gamma_{\parallel}$  and  $\Gamma_{\perp}$  parallel and perpendicular to the director give rise to the parallel translational diffusion time  $\tau := \beta L^2 / \Gamma_{\parallel}$  and the diffusion rate ratio  $\gamma := \frac{\Gamma_{\perp} / D^2}{\Gamma_{\parallel} / L^2}$ .

We calculated the van Hove correlation functions  $G_{s,d}(z, r, t)$  as a function of the parallel displacement  $z$ , the perpendicular displacement  $r$ , and the time  $t$ . Results for the largely arbitrary but definitely representative choice of parameters  $\gamma = 1$  (representing fast radial diffusion) and  $\gamma = 10^{-4}$  (slow radial diffusion) for the three cases of a nematic state  $N$  at a chemical potential  $\beta \Delta \mu = -0.388$  relative to that at the nematic-smectic transition, a weakly smectic state  $S_1$  with  $\beta \Delta \mu = 0.612$ , i.e., at a density just above the smectic transition, and a strongly smectic state  $S_2$  with  $\beta \Delta \mu = 2.612$  are shown in Figs. 1–3. In passing, we note that parallel diffusion becomes independent of the parameter  $\gamma$  if  $\gamma \geq 1$ , because perpendicular relaxation is then much faster than parallel relaxation according to our numerical results. The interlayer distances of the smectic phases within the present model are  $1.4L$  for  $S_1$  and  $1.3L$  for  $S_2$ ; these values would be somewhat smaller had we included particle flexibility [11] and higher virial terms [10].

The radially integrated van Hove self correlation functions  $G_s(z, t) := 2\pi \int_0^{\infty} dr r G_s(z, r, t)$  presented in Fig. 1 exhibit a spatial broadening due to self-diffusion, which is slower the larger the background potential barrier height is. Whereas  $G_s(z, t)$  is a concave function of  $z$  for the nematic state  $N$  for all times  $t$ , shoulder peaks develop in the smectic states  $S_1$  and  $S_2$  located at the centers of the smectic layers in accord with the experimental findings of Ref. [2]. These peaks are the manifestation of the existence of the average self-consistent field due to the equilibrium one-particle density. The curves of the nematic state and the envelopes to the curves of the smectic states are not Gaussians [see Fig. 3(b)] because of the influence of the background fluid that cages the test particle. Upon

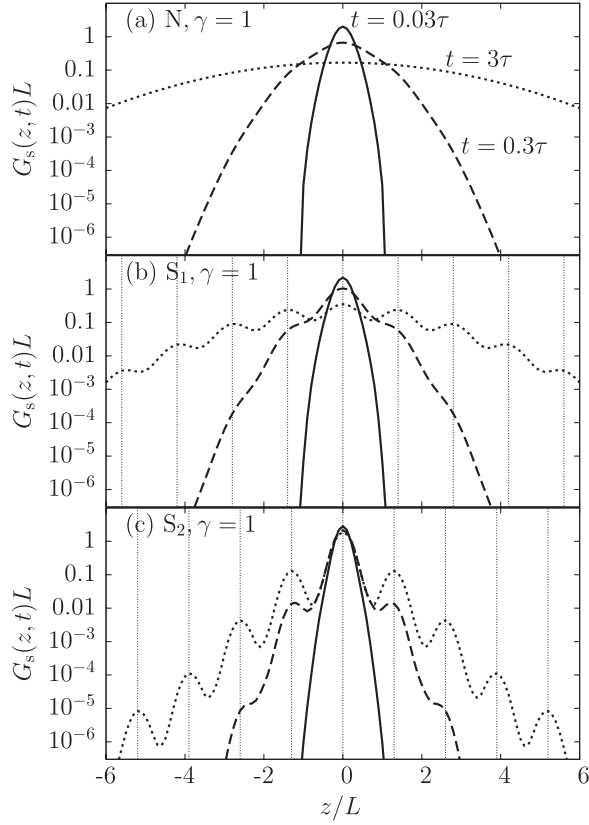


FIG. 1. Radially integrated van Hove self-correlation function  $G_s(z, t)$  as a function of the axial displacement  $z$  in units of the rod length  $L$  and time  $t$  in units of the diffusion time  $\tau$  for diffusion rate ratio  $\gamma = 1$  for (a) the nematic state  $N$ , (b) the weakly smectic state  $S_1$ , and (c) the strongly smectic state  $S_2$ . The thin vertical lines in (b) and (c) indicate the centers of the smectic layers.

approaching the nematic-smectic phase transition from the high-density, smectic side, we found an increase of the time that it takes for the first shoulder peak to appear [see also the curves  $t = 0.3\tau$  in Figs. 1(b) and 1(c)]. This we attribute to influence of the critical slowing down of the collective dynamics of the host fluid when nearing the smectic spinodal. This may well explain the absence of shoulder peaks in Fig. 2b of Ref. [2] presuming that this time exceeds the time of measurement.

Figure 2 shows the time-evolution of the structure of the fluid background for the nematic and the smectic phase in terms of the van Hove distinct correlation function  $G_d(z, r, t)$ . The initial van Hove distinct correlation function  $G_d(z, r, t = 0)$  coincides with the pair distribution function and the nearest-neighbor (solvation) shell in the vicinity of the origin corresponds to a cage around the labeled test particle. This cage initially slows down the self-diffusion of the labeled test particle, but it dissolves with time. Eventually, the labeled particle diffuses effectively only in the permanent background of the unlabeled particles. The presence of the temporary cage that adds to

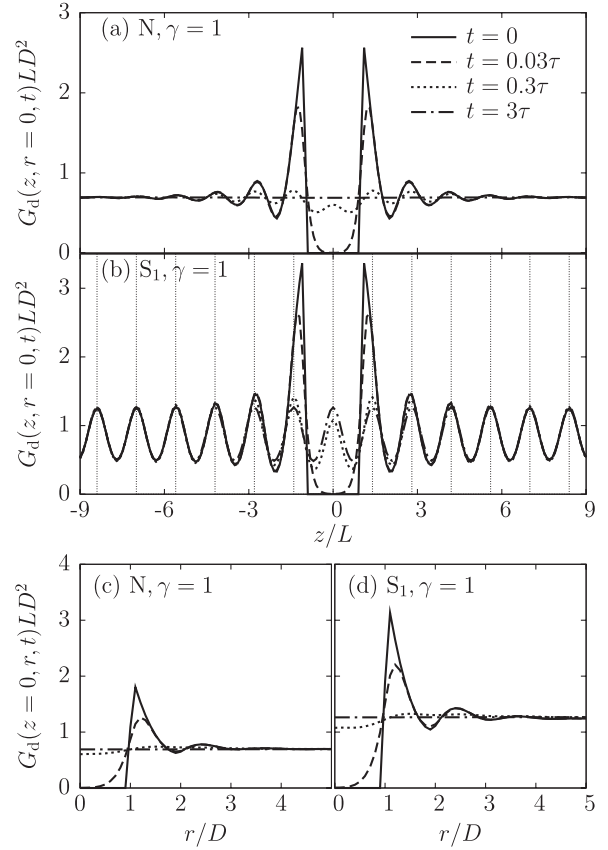


FIG. 2. Cuts of the van Hove distinct correlation function  $G_d(z, r, t)$  as a function of the axial displacement  $z$  in units of the rod length  $L$ , the radial displacement  $r$  in units of the rod diameter  $D$ , and time  $t$  in units of the diffusion time  $\tau$  for diffusion rate ratio  $\gamma = 1$  for (a), (c) the nematic state  $N$  and (b), (d) the weakly smectic state  $S_1$ . The corresponding curves for the strongly smectic state  $S_2$  are similar to those in (b), (d). The thin vertical lines in (b) indicate the centers of the smectic layers.

the permanent equilibrium background barriers between the particle layers is a direct consequence of the local fluid structure, which cannot be accounted for by fixed background models as in Ref. [1]. For  $\gamma = 1$ , the relaxation of  $G_d(z, r, t)$ , i.e., the decay of the temporary cage, takes place on a time scale of the diffusion time  $\tau$ . If the perpendicular diffusion is strongly suppressed, e.g., for  $\gamma = 10^{-4}$ , this relaxation takes place on a larger time scale, indicating that the dissolution of the temporary cage is linked to the perpendicular diffusion. Hence, the time-dependent fluid background mediates a coupling between parallel and perpendicular self-diffusion.

The influence of the fluid structure on the self-diffusion of individual test particles can be inferred from Fig. 3 that shows our results for their mean-squared displacement  $\langle z^2 \rangle$  along the director of the fluids and for the Binder cumulant  $U := \langle z^4 \rangle / (3\langle z^2 \rangle^2) - 1$ , which quantifies deviations from Gaussian behavior [1], where  $\langle z^k \rangle := \int dz z^k G_s(z, t)$ . The

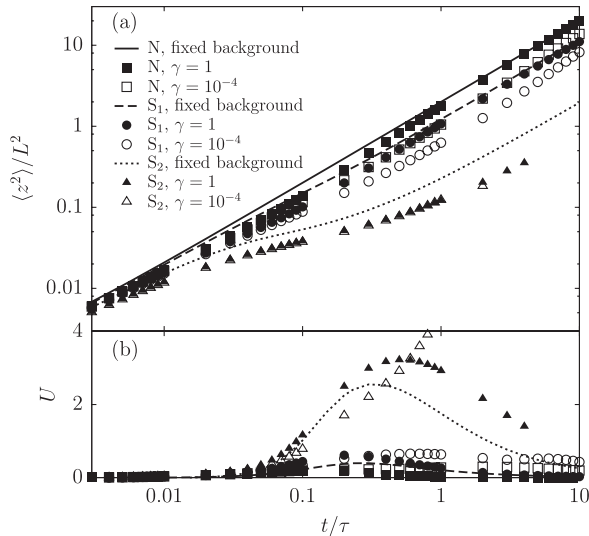


FIG. 3. (a) Parallel mean-squared displacement  $\langle z^2 \rangle$  in units of the squared rod length  $L^2$  and (b) binder cumulant  $U$  (see main text) of the labeled particle as a function of time  $t$  in units of the diffusion time  $\tau$  for the diffusion rate ratios  $\gamma = 1$  and  $\gamma = 10^{-4}$  for the nematic state  $N$ , the weakly smectic state  $S_1$  and the strongly smectic state  $S_2$ . The points represent the results obtained within the present fluid model, whereas the lines describe the one-dimensional self-diffusion in a temporally fixed background potential corresponding to the equilibrium one-particle density.

significant difference between results obtained within fixed background models [1] and our fluid background model highlight the importance of the temporal nature of fluid structure in general and of the sideways diffusion in the intermediate-time regime of uniaxial fluids in particular. For spatially homogeneous as well as spatially inhomogeneous states, caging causes diffusion initially to be slowed down giving rise to a nonvanishing Binder cumulant. The crossover from early- to late-stage diffusive motion of test particles in a congested fluid causes this deviation from Gaussian behavior and can be linked to potential barriers that can be temporary or fixed. In either case, they are due to correlations between particles in the fluid that cannot reasonably be described by a fixed potential. Our calculations show that in the crossover region, subdiffusive behavior may be inferred over a limited time range, as done in Ref. [2]. The slowing down of fd virus particle diffusion in the smectic phase was rationalized in Ref. [2] by considerations involving a fixed periodic molecular field only. In our view, this does not do justice to the complexity of the problem that involves a coupling of between-layer and in-

layer diffusive processes. This can be inferred from a comparison of the cases  $\gamma = 1$  and  $\gamma = 10^{-4}$  for the states  $N$  and  $S_1$  where a reduction of the perpendicular diffusivity gives rise to a slower parallel self-diffusion. On the other hand, the mean-squared displacement for strongly smectic states for which the permanent potential barriers are quite large is virtually independent of  $\gamma$ , as the initial delay of the diffusion is due to the high,  $\gamma$ -independent permanent barriers and not due to the temporal cage.

In summary, we found a remarkable influence of the fluctuating local structure on the self-diffusion of particles in spatially (non-)uniform complex fluids. Diffusion delays initially even in uniform fluids due to a temporary cage formed by neighboring particles. This coupling of the motion of a test particle to its surrounding particles causes motion in different spatial directions to become coupled, in particular, in anisotropic fluids. Fixed molecular background models cannot describe this and have to be replaced by more sophisticated approaches such as the dynamic density functional formalism presented here.

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