Comment on 'Fickian Non-Gaussian Diffusion in Glass-Forming Liquids'.

A recent Letter [1] examined the statistics of individual particles displacements $\Delta x(t)$ over time t in two-dimensional glass-formers and concluded that the corresponding probability distribution $G_s(\Delta x, t)$, called the van-Hove distribution, is non-Gaussian in a time regime where the mean-squared displacement (MSD) is Fickian, $\langle \Delta x^2(t) \rangle \propto D_s t$, where D_s is the self-diffusion constant. If this analysis were correct, glass-formers would be 'Fickian non-Gaussian' materials [2, 3].

Here, we clarify that the multiple lengthscales and timescales reported in [1] have either been characterized before, or are not well-defined. This leads us to dispute the conclusions that glass-formers display Fickian non-Gaussian behaviour and that this analogy fruitfully addresses the central questions regarding the nature of dynamic heterogeneity in these systems.

Let us first recall that the main features of self-diffusion in supercooled liquids are explained by invoking two characteristic timescales [4–7]. The self-diffusion coefficient D_s controls the first one, $\tau_D = \sigma^2/D_s$, where σ is the particle size. The second one is the structural relaxation time τ_α determined from usual time correlations, such as the self-intermediate scattering function. The adimensional ratio $X = \tau_\alpha/\tau_D$ plays a special role. It controls both the amount of decoupling $X(T) \sim D_s \tau_\alpha$ (akin to violations of the Stokes-Einstein relation [8])), and the Fickian lengthscale $\ell_F \propto \sqrt{X}$ [4]. These known results [4–10] paint a picture that is inconsistent with several conclusions reported in [1, 3] as we now show.

Let us start with the van Hove distribution. It was found in [9] that $G_s(\Delta x, t)$ approaches a Gaussian distribution only for times much longer than τ_D, a result rediscovered in [1] with equivalent tools. However, the non-Gaussian parameter $\alpha_2(t)$ used in [1] to reveal Gaussianity decays as a power law at large times. Hence, the gradual emergence of Gaussian behaviour from $\alpha_2(t)$ is a scale-free process and there is no characteristic timescale after which self-diffusion is Gaussian, although of course empirically $\alpha_2(t)$ will be small when $\langle \Delta x^2 \rangle \gg \ell_F^2$. It was found numerically [8] and explained theoretically [4] that it is the lengthscale ℓ_F that controls the crossover in the wavevector dependence of the self-intermediate scattering function, a result ignored in [1].

For times $t < \tau_\alpha$, $G_s(\Delta x, t)$ is characterized by a Gaussian core at small Δx and a nearly exponential tail $G_s \propto \exp(-|\Delta x|/\lambda)$ at large Δx [5]. Refs. [1, 3] discuss the existence and possible universality of a power law description of the time evolution of the exponential tail, $\lambda(t) \sim t^\alpha$. As noticed in [5, 6, 11], the exponential tail is generically explained by a large deviation argument, but asymptotic convergence is so slow that the actual value of λ depends on the fitted range (see [6] for an explicit test and [11] for analytic results suggesting that $\alpha = 0$), which may explain reported discrepancies [1, 3]. More fundamentally $\lambda(t)$ is difficult to measure, and α is not a novel characteristic exponent.

Linear behaviour of the MSD is visually detected [1] in log-log representations after a time τ_D which grows more slowly than τ_α at low temperature, but the approach to linearity is algebraic [12]. This power law approach to Fickian behaviour is again scale free and no characteristic timescale controls the emergence of Fickian behaviour in $\langle \Delta x^2(t) \rangle$; in particular τ_D does not play this role.

Even though glass-formers may appear empirically close to Fickian non-Gaussian materials, there is no characteristic timescales or lengthscales controlling the approach to either Fickian and Gaussian dynamics, and the existence of a Fickian non-Gaussian regime cannot be decided. Instead, the salient features of self-diffusion, including algebraic approach to Fickian and Gaussian behaviours as well as nearly exponential van Hove distributions, are analytically captured by (effective) non-interacting continuous time random walk models [4–7, 10] based on the only two important and well-defined characteristic timescales τ_D and τ_α. The multiple time and length scales determined empirically in [1, 3] are either related to those, or conceptually ill-defined.

The complexity of glass-formers is that the timescales τ_D and τ_α emerge from many-body interactions (disorder is self-induced) and have non-trivial temperature dependencies which are not fully understood, but from which the very rich statistics of single particle displacement naturally follows. The behaviour of supercooled liquids is very different from several Fickian non Gaussian materials, which are described by interesting, but quite different, models [15].

We end by noting that the use of two-dimensional simulations to study the statistics of particle displacements in glass-formers is profoundly influenced at all timescales by Mermin-Wagner fluctuations [13, 14], which presumably adds to the profusion of timescales reported in [1].

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