Tracer Diffusion in a Dislocated Lamellar System

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Many lamellar systems exhibit strongly anisotropic diffusion. When the diffusion across the lamellae is slow, an alternative mechanism for transverse transport becomes important. A tracer particle can propagate across the lamellae by encircling a screw dislocation. We calculate the statistical properties of this mode of transverse transport. When either positive or negative dislocations are in excess, transport across the lamellae is ballistic. When the average dislocation charge is zero, the mean square of the normal displacement grows like $T \log T$ for large times. To obtain this result, the trajectory of the tracer must be smoothed over distances of order of the dislocation core size.

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Diffusion in layered systems is often strongly anisotropic. The mechanisms and the manifestations of the anisotropy vary. Often diffusion across is significantly slower than along the lamellae. For example, enhanced creep resistance of lamellar alloys, such as industrial TiAl, is probably due to the high barrier for the dislocations crossing from one layer to the next [1,2]. In lamellar phases of diblock copolymers [3], tracer diffusion along the lamellae can be up to forty times faster than across [4]. The fact that water diffusion in lamellar phases of phospholipid bilayers [5] is strongly anisotropic may be relevant to attempts to use multilamellar vesicles for drug delivery [6]. Another example of anisotropic diffusion is the kinetics of electroactive probes in lyotropic liquid crystals [7].

When lateral diffusion is much faster than transverse diffusion, the tracer can still be transported quickly in the direction normal to the lamellae by encircling screw dislocations. Screw dislocations are indeed common in a variety of layered systems [8–10]. A summary of various dislocation properties in lamellar systems is presented in Ref. [11].

By encircling screw dislocations, tracer particles can reach any point while remaining confined to a layer. The trajectory of the tracer projected onto a plane parallel to the layers is a two-dimensional random walk. Upon completing a closed 2D trajectory, the random walker moves up or down the number of layers equal to the dislocation charge enclosed by the trajectory. When a single screw dislocation is present, the layer number of the walker is the winding angle around the dislocation divided by 2π. In general, we consider the sum of the winding angles with the signs given by the dislocation charges. The change in this quantity along an open trajectory depends on the shape of the sample due to the contributions of the winding numbers around distant dislocations. However, when the walker returns to the origin, the change in the total winding number is the dislocation charge enclosed by the trajectory. Thus, we identify the total winding number divided by 2π with the layer number $n(t)$ which for closed trajectories coincides with the normal displacement of the walker.

In this Letter, we study the diffusion of a tracer particle confined to the lamellae. The tracer starts at the origin of layer $n = 0$ at time $t = 0$ and explores the x-y plane with diffusivity D. Let there also be a random distribution of positive and negative screw dislocations with densities f_+ and f_-, respectively. Our goal is to determine the nature of the transport normal to the layers by predicting the result of the following experiment. If some amount of the tracer material is placed at the origin at time $t = 0$, what is the density of the resulting cloud of tracer particles as a function of time?

To accomplish this task, we look at paths which start at the origin O (Fig. 1) at time $t = 0$ and arrive at point E located a distance R from the origin at time T. We seek to define the layer number $n(R, T)$. Since the layer number change is well defined only for closed trajectories, we fix

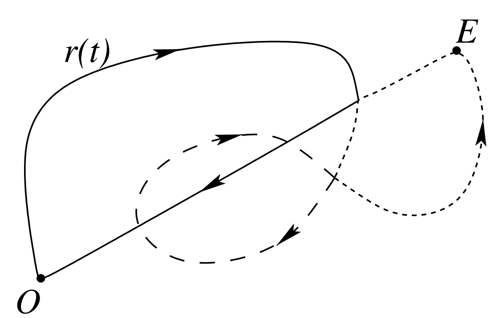

FIG. 1. We complete the path $r(t)$ with a straight segment connecting its beginning O and its end E. The winding angle fluctuation along this closed path can be calculated by decomposing the path into a union of non-self-intersecting loops (denoted by the solid, dashed, and dotted lines).

$n(R,T)$ by completing the path $r(t)$ with a straight segment OE connecting this point to the origin. We define $n(R,T)$ to be the dislocation charge enclosed by this trajectory.

We must compute the powers of n averaged over positions of dislocations and random walks which end at $r = R$ at time $t = T$. We denote the average over positions of dislocations with an overbar and the average over random walks by angular brackets $\langle \cdot \rangle$. Because changing the shape of the completing segment adds a constant to $n(R,T)$, its average $\langle \overline{n}(R,T) \rangle$ has no physical meaning. However, its standard deviation $\sigma(R,T) = \langle \overline{n^2} \rangle - \langle \overline{n} \rangle^2$ is independent of the shape of the completing segment. It gives the shape of the spreading cloud.

We identified two qualitatively different cases. When $f_+ \neq f_-$, the average dislocation charge within a closed trajectory is proportional to its signed area. In this case, we find that the vertical size of the tracer cloud grows linearly in time; i.e., there is superdiffusion across the layers. Moreover, the spreading cloud acquires a biconcave shape, since $\sigma(R,T) \propto D^2T^2 + 2R^2DT$. We must note here that the excess of dislocations of a certain chirality leads in smectics to the breakup of the homogeneous lamellar phase into domains separated by twist grain boundaries [12]. We nevertheless pursue this case since it may be applicable to the Aharonov-Bohm electron phase fluctuations in a type II superconductor and other systems where geometric winding numbers play a role.

When $f_- = f_+$, a more subtle averaging must be performed since the average dislocation charge in a closed loop is now zero. We must compute the variance of the dislocation charge within a closed loop. This variance is proportional to the unsigned area of the loop which has a simple geometrical interpretation.

It turns out that, when the dislocations are thought of as point objects, it is not possible to average the unsigned area over random walks. The variance of the layer number obtained in this fashion is logarithmically divergent. Divergences are common in the statistics of winding numbers of random walks [13–16]. For example, the dispersion of the winding number of a random walker around a point is divergent if the walk is continuous. This divergence arises due to the contributions to the winding number from trajectories that wind tightly around the point. The nature of our divergence is similar. By traversing a short distance around a dislocation, the tracer travels far in the direction normal to the layers. This leads to anomalously fast diffusion in the direction perpendicular to the layers.

We regularize this divergence by noting that the core size a is the distance of closest approach of the tracer to the dislocations. Small loops in the trajectory are therefore irrelevant. Instead we must consider an effective discrete random walk whose steps are of length a taken every a^2/D seconds. The variance of the layer number then grows as $\sigma(R,T) \propto T \log T$. Since $\sigma(R,T)$ is independent of R, the shape of a spreading cloud in this case is an ellipsoid which elongates in the direction normal to the layers. Note also that this divergence is present in the $f_+ \neq f_-$ case. It leads to a correction of order $T \log T$.

We now describe our methods and results in more detail. Let $r_\alpha(t)$ be the Brownian trajectory of the tracer (here α is the two-dimensional vector index). We neglect correlations in the velocity $\dot{r}_\alpha(t)$ on time scales longer than the scattering time of the walker, which is much smaller than all other time scales in our problems, so that

$$\langle \dot{r}_\alpha(t) \dot{r}_\beta(t') \rangle = \delta_{\alpha\beta}\left[\frac{D}{2}\left(\delta(t - t') - \frac{1}{T} \right) + \frac{R_\alpha^2}{T^2} \right]. \tag{1}$$

Equation (1) involves constant terms in addition to the standard $\delta(t - t')$ one. This is because we fix $r(0) = 0$, $r_\alpha(T) = R_\alpha$, to compute the layer number n as a function of position R and time T.

Dislocations of charge q_i are located at x^i_α. q_i takes on values ± 1. The layer number $n(R,T)$ can be expressed in the following way:

$$n(R,T) = \sum_i \frac{q_i}{2\pi} \int dt \, \frac{\epsilon_{\alpha\beta} \dot{r}_\beta (r_\alpha - x^i_\alpha)}{|r - x^i|^2}, \tag{2}$$

where $\epsilon_{\alpha\beta}$ is the antisymmetric tensor of rank 2. Indeed, the integrand in Eq. (2) is the sum over dislocations of the infinitesimal change of the angle between the x axis and the vector connecting the tracer particle and the dislocation. Thus (2) is the cumulative winding number of the tracer around the dislocations. The trajectory $r_\alpha(t)$ in (2) consists of a Brownian walk followed by a straight line from $r_\alpha(T) = R_\alpha$ back to the origin. Equation (2) must be averaged first over dislocation strengths q_i and positions x_i and then over Brownian trajectories $r(t)$. Assuming that positive and negative dislocations are distributed uniformly, the dislocation strength is $q_i = 1$ with probability $f_+/(f_+ + f_-)$, and $q_i = -1$ with probability $f_-/(f_+ + f_-)$.

Averaging (2) over the strengths and positions of the dislocations, we arrive at

$$\overline{n}(R,T) = (f_+ - f_-) \int dt \, \frac{\epsilon_{\alpha\beta}}{2} r_\alpha \dot{r}_\beta . \tag{3}$$

The integral in (3) can be interpreted geometrically as the overall area swept by a vector connecting the tracer to the origin as it moves along its trajectory. The area is computed with the sign, so that when the vector rotates clockwise the area it covers is added, while when it moves counterclockwise it is subtracted from the answer. We refer to the integral in (3) as the signed area. Equation (3) has a simple intuitive interpretation. The signed area is the number of times a dislocation is encircled clockwise minus the number of times it is encircled counterclockwise. Therefore, the signed area times the difference in the densities of + and − dislocations should give $\overline{n}(R,T)$.

At this point, we must clearly distinguish between the $f_- = f_+$ and $f_- \neq f_+$ cases. If the densities are equal,

$\overline{n}(R,T)$ computed in this way vanishes, and we must take into account the fluctuations in the dislocation charge enclosed by a trajectory. Let us first concentrate on the case $f_- \neq f_+$.

We perform averages over random walks with the help of (1). First, $\langle \overline{n} \rangle$ can be shown to vanish, due to the straight shape of the completing segment OE. The standard deviation $\sigma(R,T)$ can then be computed as $\overline{n^2}(R,T)$. Second, we can neglect the difference $\langle \overline{n^2} \rangle - \langle \overline{n}^2 \rangle$ which can be shown to grow slower in time than $\sigma(R,T)$. We obtain

$$\sigma(R,T) \approx \langle \overline{n^2} \rangle = \frac{(f_+ - f_-)^2}{48}(D^2T^2 + 2R^2DT). \tag{4}$$

This is the first of the two main results of this Letter. Noting that $\langle R^2 \rangle = DT$ for a Brownian walker, we conclude that the tracer particle indeed moves superdiffusively in the normal direction. Furthermore, (4) gives us a way to calculate the approximate shape of a tracer cloud shown in Fig. 2.

It is possible to compute the entire probability distribution of $\overline{n}(R,T)$ which gives the density of the cloud. This calculation involves averaging the exponential of (3) over the Brownian walks using Gaussian functional integral techniques. The answer, given in terms of infinite products, is not illuminating. We note here only that the probability distribution $P(\overline{n},T)$ of a simpler quantity $\overline{n}(T)$, which is the average of $\overline{n}(R,T)$ over all positions R, can be calculated in closed form,

$$P(\overline{n},T) = \frac{2}{|f_+ - f_-|DT}\left[\cosh\left(\frac{2\pi\overline{n}}{(f_+ - f_-)DT}\right)\right]^{-1}. \tag{5}$$

The situation becomes more interesting when $f_- = f_+ = f/2$. In this case, to compute $\overline{n^2}$ we need to square (2) first and then average over positions and strengths of dislocations. Assuming that they are uncorrelated, we obtain

$$\overline{n^2}(R,T) = -\frac{f}{4\pi}\int dt \int dt' \times \dot{r}_\alpha(t)\dot{r}_\beta(t')G_{\alpha\beta}\big(r(t) - r(t')\big), \tag{6}$$

where $G_{\alpha\beta}(r) = \delta_{\alpha\beta}\log(r) - (r_\alpha r_\beta)/r^2$ is often referred to as the 2D photon propagator. This formula represents the unsigned area of the loop formed by $r(t)$. It was used in [17] to compute areas of loops in a different context.

To clarify the meaning of the unsigned area, we compute it by decomposing a self-intersecting loop into a union of non-self-intersecting subloops (see Fig. 1). It can be shown that the variance of the dislocation charge enclosed by the loop is equal to the sum of the areas of the subloops plus the sum over all pairs of subloops of the areas of their intersections, with a plus sign if the two subloops are traversed in the same direction, and with the minus sign if they are traversed in opposite directions.

To simplify the task of averaging (6) over Brownian walks, we follow the example of Ref. [17] and rewrite the photon propagator in the following equivalent way:

$$\overline{n^2}(R,T) = -\frac{f}{2}\int dt \int dt' \times \dot{r}_1(t)\dot{r}_1(t')\,\delta(r_1(t) - r_1(t')) \times |r_2(t) - r_2(t')|. \tag{7}$$

The advantage of this formula over (6) is in the fact that r_1 and r_2 coordinates decouple.

It turns out that the average of (7) over random walks is logarithmically divergent at $t \approx t'$. Anticipating that, we need only to average (7) at $t \to t'$. That means we can neglect all the terms in (1) which depend on T and R_α, while keeping only the $\delta(t - t')$ term. We obtain

$$\langle |r_2(t) - r_2(t')| \rangle \approx \sqrt{\frac{2D|t - t'|}{\pi}}, \tag{8}$$

$$\langle \dot{r}_1(t)\dot{r}_1(t')\delta\big(r_1(t) - r_1(t')\big)\rangle \approx \sqrt{\frac{D}{2\pi|t - t'|}} \times \left[\delta(t - t') - \frac{1}{4|t - t'|}\right]. \tag{9}$$

Substituting these into (7), we find the leading term,

$$\sigma(R,T) = \langle \overline{n^2}(R,T) \rangle = \frac{fD}{8\pi}\int dt \int dt' \frac{1}{|t - t'|}. \tag{10}$$

It is clear that the $t = t'$ divergence in (10) should be cut off at some time ϵ. Since the trajectory cannot wind around a given dislocation tighter than the dislocation core size a, the continuous formula (6) breaks down at distances smaller than a. We take $\epsilon = a^2/D$ to be the average time it takes the random walker to diffuse across a dislocation

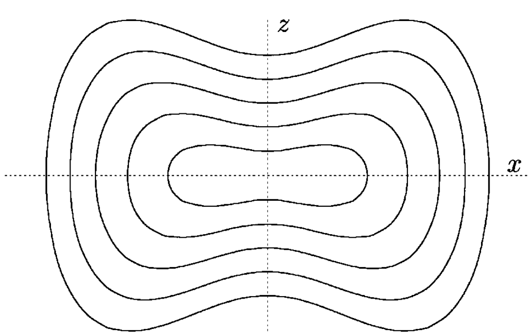

FIG. 2. Five equidistant in time snapshots of the isodensity line of the vertical slice through the expanding tracer cloud when $f_- \neq f_+$. The cloud's shape is a figure of revolution of this slice around the z axis. The lines are drawn at the level where the density is equal to 0.1 of the maximum density in the center of the cloud. Note that that cloud develops into a biconcave shape elongated in the vertical direction (normal to the layers).

core. Thus, we obtain

$$\sigma(R,T) = \frac{fDT}{8\pi} \log\left(\frac{DT}{a^2}\right). \tag{11}$$

This is the second main result of this Letter. Note that $\sigma(R,T)$ does not depend on R, unlike (4) which is valid when $f_+ \neq f_-$.

In summary, we considered tracer diffusion in a layered system with screw dislocations. When the transverse diffusion coefficient is small compared to the in-plane diffusion coefficient, tracer particles are transported in the direction normal to the layers by encircling screw dislocations. We study the evolution of a cloud of tracer particles and find that its height grows faster than its width.

To make quantitative predictions, we must estimate the conventional transverse tracer diffusion coefficient $D_\perp$. Tracer particles can be transported along dislocation cores or point defects such as pores, necks, and passages as suggested by Constantin and Oswald in [18]. They measured transverse diffusion in a thin sample of lamellar phase of a surfactant/water mix. Since their sample contained only a few dislocations across its thickness, our effect would not be operative. The effect of an isolated screw dislocation (see Ref. [15]) is negligible compared with conventional diffusion $D_\perp$.

When many screw dislocations are present, we need to estimate the time after which the superdiffusion due to dislocations will dominate conventional transverse diffusion. We consider the $f_+ = f_-$ situation, which is more relevant to experiments. The height of the cloud due to conventional diffusion is roughly equal to the height due to superdiffusion when $D_\perp T \sim d^2 fDT \log(DT/a^2)$, where d is the interlayer distance. Assuming that the dislocation core size is equal to the interlayer spacing, we find that if the crossover time,

$$T_c \sim \frac{d^2}{D} \exp\left(\frac{D_\perp/D}{d^2 f}\right), \tag{12}$$

is comparable to the experimentally available time, our phenomenon should be observable.

The preexponential factor in Eq. (12) in a lamellar phase of a lyotropic surfactant can be estimated by taking $D \sim 10^{-10}$ m^2/s and $d \sim 50$ Å from Ref. [18] to obtain fractions of a microsecond. In diblock copolymer systems, this prefactor is about 1000 times larger. The feasibility of the experiment therefore hinges on the value of the exponent in Eq. (12). Hamersky *et al.* [4] measured the anisotropy of the diffusion coefficient in clean samples of diblock copolymer to be $D_\perp/D \approx 10^{-2}$. Therefore, in order for our effect to manifest itself, the defect density must be 2 orders of magnitude larger than $d^2 f \approx 10^{-5}$ observed in the shear aligned diblock copolymer system of Ref. [4]. The diffusion of water mixed with egg phosphatidylcholine [5] is even more anisotropic $D_\perp/D \approx 10^{-3}$ so that our effect can be observed for smaller defect densities. A promising system is a mixture of lipid and surfactant which undergoes a lamellar to nematic transition via proliferation of screw dislocations [9,18].

Finally, we offer a rough estimate of the contribution of the "pipe" diffusion along dislocation cores to $D_\perp/D$. Assuming that dislocation cores are filled with a medium through which the tracer moves with diffusivity D, we obtain $D_\perp/D \sim d^2 f$, which is just the fraction of the area covered by the cores. The exponent in (12) is then of order unity. Thus, if the only source of $D_\perp$ were pipe diffusion, our effect should be easily observable.

In conclusion, we mention situations that require a modification of our predictions. First, if screw dislocations are mobile, they will tend to form bound dipole pairs of size comparable to the core size. Since the bound pairs do not contribute to the transverse transport of the tracer, only the density of free dislocations must be used in Eq. (11). Second, the dislocation motion [11,19] will lead to an additional mechanism for normal transport of the tracer. Third, the presence of edge dislocations impedes in-plane diffusion of the tracer. This fact may be successfully taken into account by renormalizing the in-plane diffusivity.

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