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Interpretation of diffusion measurements in cholesterics

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An interpretation of the pitch and time dependence of diffusion in the cholesteric liquid crystalline phase is proposed. Experimental results on nematics twisted by chiral dopands are discussed. The model predicts a decay of the translational diffusion coefficient D_P in the helix direction with the observation time and a decrease of D_P with shorter pitch length p_0, in accord with experiment. From comparison with experimental data it is concluded that rotational diffusion in these samples is a collective phenomenon.

1. Introduction

The diffusion coefficient of nematic liquid crystals is a second rank tensor with two independent components, $D_\parallel$ parallel to the direction $\mathbf{n}$ and $D_\perp$ perpendicular to $\mathbf{n}$, in its principle axes system. Cholesteric phases, induced by the addition of a chiral compound to a nematic, can be considered as a stack of quasi-nematic layers with a continuous rotation of $\mathbf{n}$ along the direction of the layer normals, the helix axis, x. This rotation of $\mathbf{n}$ in an undeformed cholesteric is given by

$$\mathbf{n} = \mathbf{e}_y \cos 2\pi x/p_0 + \mathbf{e}_z \sin 2\pi x/p_0, \qquad (1)$$

where $\mathbf{e}_y$, $\mathbf{e}_z$ are unit vectors in the y and z directions. Within the quasi-nematic layers, we may expect similar behaviour to that of nematics, with a macroscopic averaging of the diffusion coefficient perpendicular to the helical axis,

$$D_S = (D_\parallel + D_\perp)/2.$$

Diffusion parallel to the pitch axis is strongly influenced by the chirality of the sample, and we expect the diffusion coefficient in the helix direction, D_P, to be different to $D_\perp$ of the corresponding nematic. NMR measurements of this diffusion coefficient in cholesterics show that, indeed, D_P does depend strongly upon the pitch p_0. The measured values of D_P for short p_0 are smaller than the diffusion coefficients of nematics by nearly one order of magnitude [1–5, 17]. Several authors have proposed a square dependence of D_P on the pitch [1, 2]. A lower than quadratic dependence of D_P on p_0 was measured by Oehler [5] using ^{13}C NMR. Moreover, it was found from proton NMR experiments that the diffusion coefficient decays with the observation time [3, 4]. A satisfactory theoretical understanding of these effects is required. In this paper, we discuss the calculations of Yaniv *et al.* [1], leading to the prediction of a quadratic dependence of D_P on the pitch. We propose a model of coupling between rotational and translational diffusion in cholesterics which is able to predict the measured time and pitch dependencies qualitatively. In order to test the theory quantitatively, more experiments and accurate data are necessary.

Our model is valid for diffusion parallel to the helix axis. The diffusion coefficient perpendicular to the helix [3, 6–8] has to be discussed separately. The present experimental data are inconsistent with the model of diffusion in quasi-nematic layers.

2. Discussion of the existing theory

Yaniv and co-workers were the first to measure the decay of the diffusion coefficient with shorter pitch length, and the first to attempt a theoretical description of this effect. At the beginning we reconsider the idea proposed by Yaniv *et al.* [1] for an interpretation of the quadratic pitch dependence of D_P, subsequently we shall include some refinements. In their original model, the energy dissipation per unit volume caused by molecular rotational motion along the helix axis is assumed to be $\gamma_1\,(2\pi v/p_0)^2$ [16], where v is the velocity of the diffusing molecule and γ_1 is the rotational viscosity. The energy dissipation per molecule can be characterized by an expression fv^2, where the friction constant f is introduced. Calculating the number of molecules per volume from the Avogadro constant N_A, the mass density ρ and the molar mass M of the sample, we find, by comparison of both expressions,

$$\gamma_1(2\pi v/p_0)^2 = v^2 f(N_A\rho/M). \tag{2}$$

Therefore, the friction coefficient f can be related to the rotational viscosity γ_1 and the pitch p_0 by

$$f = M/(\rho N_A)\gamma_1 4\pi^2/p_0^2. \tag{3}$$

Now, we can make use of the well-known Einstein relation [9], that is applied [1] in the form

$$D = D_0\exp(-\Delta E/(RT)), \quad D_0 = kT/f. \tag{4}$$

Here D is equivalent to the diffusion coefficient D_P. Inserting the constant f into equation (4), we obtain

$$D = N_A\rho kTp_0^2/(4\pi^2\gamma_1 M)\exp(-\Delta E/(RT)). \tag{5}$$

With typical values assumed for the quantities $\rho \approx 1\,\mathrm{g\,cm^{-3}}$, $M \approx 273\,\mathrm{g/mol}$, $\gamma_1 \approx 1\,\mathrm{g\,cm^{-1}\,s^{-1}}$, and with the experimentally determined activation energy $\Delta E \approx 32{\cdot}3\,\mathrm{kJ/mol}$ (see figure 1) Yaniv *et al.* [1] computed a value for D/p_0^2 of $6{\cdot}2\,\mathrm{s^{-1}}$ in approximate agreement with the experimental value $1{\cdot}8\,\mathrm{s^{-1}}$, at room temperature, for 4-methoxybenzylidene-4′-*n*-butylaniline (MBBA).

However, equation (4) is not correct in the form given here. At any temperature T, the Einstein relation should be

$$D(T) = kT/f(T), \tag{6}$$

and hence equation (5) becomes

$$D = N_A\rho kTp_0^2/(4\pi^2\gamma_1 M). \tag{7}$$

Obviously the Arrhenius-like behaviour of the quantity D is already contained in the temperature dependence of the rotational viscosity γ_1. We can express this idea in a different way. If the relation (4) is used, then the constant f represents the friction at infinite temperature, i.e. we have to insert into equation (5) the corresponding rotational viscosity γ_{10}, with

$$\gamma_1 = \gamma_{10}\exp(\Delta E'/(RT).$$

Comparing the temperature dependence of the expression Dp_0c measured in [1] (c is a constant and p_0 is nearly independent of temperature) with the curve $1/\gamma_1$, which is calculated from the Leslie coefficients of MBBA given by Kneppe [10], we can check the good correspondence of both activation energies within the cholesteric temperature range; this becomes evident from figure 1.

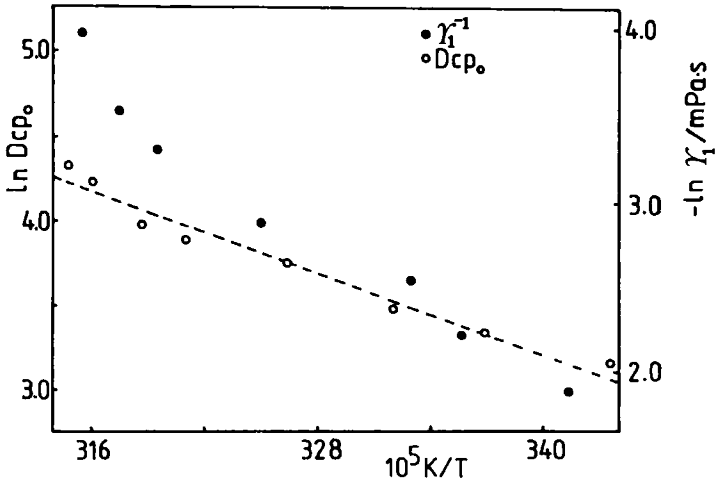


Figure 1. The temperature dependence of the diffusion coefficient parallel to the helix direction, measured by Yaniv *et al.* [1] (open circles, dashed line) and the reciprocal of the rotational viscosity γ_1 calculated from the Leslie coefficients given by Kneppe [10] (full circles).

The problem arising after the correction of equation (4) to equation (7) is that after the elimination of the exponential in this equation we have, instead of the mismatch with experiment by a factor of about 3, a discrepancy of the order of 10^{-6}, which is roughly the value of the factor $\exp(-\Delta E/(RT))$ at room temperature. We now try to provide a simple explanation of this phenomenon. Generally, the constant f which enters the Einstein formula is the friction coefficient of a diffusing particle. We think that it is not justified to relate this diffusing particle in the experiment to a single molecule. For rotational motion, the diffusion processes are of a more complex nature. The single molecule is free only to undergo 180° jumps about the short axes, relative to its neighbours, but not to perform a real dissipative rotational diffusion. The main contribution to the latter originates from cluster rotations, this means collective motion of a large number of molecules n_c (about 10^6). The friction constant f has to be multiplied by this factor, as the number of diffusing particles is not equal to the number of molecules per unit volume but rather to the amount of clusters. Equation (7) has to be divided by n_c and can be matched to the correct order of magnitude.

$$D = N_A/n_c\rho kTp_0^2/(4\pi^2\gamma_1 M). \qquad (7a)$$

If these cluster rotations are not included in the calculations, any friction by dissipative rotational motion is much too weak to account for the hindering of translational diffusion in cholesterics which is found experimentally.

Our simple model discusseed in this section considers only the influence of energy dissipation by rotations coupled to translational diffusion. It neglects the influence of the diffusion mechanisms present in nematics. Therefore, the model is valid only in the range of very short pitch. At the transition to the nematic phase, $p_0 \rightarrow \infty$, the diffusion coefficient according to equations (7) and (7 *a*) is divergent. Furthermore, the time dependence of the diffusion coefficient cannot be derived from this simplified model. The range of its applicability will be discussed later.

In the next section, we propose a more detailed model which takes into account rotational as well as translational mobility. Both are coupled by the chiral phase structure. The model is able to predict the expected time dependence and provides a generalized pitch dependence of D_P. Under certain conditions, in the limits of short pitch and strong translational mobility, the equations of the previous approximations are regained.

3. Coupling model for rotational and translational motions

For a more accurate description of the phenomena involved in self-diffusion of cholesteric liquid crystals we propose an approach slightly different to that discussed in the previous section. At first we derive expressions connecting infinitesimal translational and rotational diffusion steps to parameters known from the nematic phase. At an infinitesimal local scale, where the chiral structure is not experienced by the diffusing particle, we expect the cholesteric to behave like a nematic. The translational diffusion in regions small compared to the pitch length is assumed to be similar to that of the corresponding nematic. As the average orientation of the molecular long axes is perpendicular to the helix direction, the component D_T in the x direction is equal to the corresponding nematic diffusion coefficient, $D_\perp$.

For the calculation of the rotational mobility about an axis perpendicular to the director, characterized by the angle θ, we use the procedure developed by Einstein [9] in his work on brownian motion. We are interested in the temporal evolution of the quantity $\langle \theta^2 \rangle$. The equation for the rotational motion is

$$I\ddot{\theta} = -f\dot{\theta} + \Gamma, \tag{8}$$

where I the momentum of inertia per unit volume, Γ is the angular momentum of this volume, and $f(\equiv \gamma_1)$ is the rotational viscosity. We multiply this equation by 2θ and average over the sample

$$2I\langle \ddot{\theta}\theta \rangle = -2\gamma_1 \langle \dot{\theta}\theta \rangle + 2\langle \theta\Gamma \rangle. \tag{9}$$

At small angles θ, where the molecular field potential can still be considered constant, the term $\langle \theta\Gamma \rangle$ vanishes as Γ is not correlated to θ. The effects of a hindering potential will be included later. The first term of equation (8) can be substituted by introduction of the quantity

$$g = \langle \dot{(\theta^2)} \rangle = \langle 2\dot{\theta}\theta \rangle, \quad \dot{g} = \langle 2\ddot{\theta}\theta \rangle + \langle 2\dot{\theta}^2 \rangle; \tag{10}$$

we obtain

$$I\dot{g} - 2I\langle \dot{\theta}^2 \rangle + \gamma_1 g = 0. \tag{11}$$

The term $\langle \dot{\theta}^2 \rangle$ has to be substituted in this equation. We use the equipartition theorem of thermal energy. Equation (11) is multiplied by a volume V which corresponds to an assumed structure (cluster) with motional freedom of rotation about the angle θ. We let

$$IV\langle \dot{\theta}^2 \rangle = kT$$

and equation [11] becomes

$$I V \dot{g} - 2kT + V\gamma_1 g = 0.$$

From this differential equation the quantity g is derived

$$g = 2kT/(V\gamma_1)(1 - \exp(-\gamma_1 t/I)),$$

and so

$$\begin{aligned}\langle\theta^2\rangle &= \int_0^t g(\tau)\,d\tau, \\ &= 2kT/(V\gamma_1)\{t - I/\gamma_1[1 - \exp(-\gamma_1 t/I)]\}. \qquad (12)\end{aligned}$$

The exponential term is a rapidly decaying function, with a time constant $\tau = I/\gamma_1 \approx 10^{-13}$ s. At longer time scales, the quantity $\langle\theta^2\rangle$ is proportional to the time t. We introduce the proportionality factor $2D_R$,

$$2D_R t = \langle\theta^2\rangle = 2kT/(V\gamma_1)t$$

and so

$$D_P = kT/(V\gamma_1). \qquad (13)$$

This equation links the rotational viscosity γ_1 to the evolution of the quantity $\langle\theta^2\rangle$ for the substance. In the cholesteric the connection

$$\theta(x) = 2\pi x/p_0 \qquad (14)$$

between the rotation angle θ about the helix axis and the translation x along this axis holds. We can calculate the diffusion coefficient in the direction of the helix axis,

$$\left.\begin{aligned} D_P &= \langle x^2\rangle/2t \\ &= \langle\theta^2\rangle/2tp_0^2/(4\pi^2)\end{aligned}\right\}. \qquad (15)$$

and regain an equation equivalent to (7 a).

We have already given a physical interpretation of the volume V, appearing in (13). If we connect it with the volume corresponding to one molecule, then D_R would be much too large to effect a hindering of the translational diffusion in cholesterics. Hence V may be considered as the volume of a molecular cluster, i.e. the volume occupied by a number of molecules which perform collective rotational motions. The coefficient D_R in equation (13) describes the evolution of $\langle\theta^2\rangle$ in time, as long as the rotational mobility is not hindered by a potential, e.g. of elastic, electromagnetic or intermolecular dispersive forces. We shall not discuss here the nature of this potential, since it depends upon the choice of size of the diffusing particle. It is clear that in the nematic phase free rotational diffusion is impossible, hindering forces result, e.g. from the Maier–Saupe potential for single molecules, and from the elastic deformation energy for whole clusters of molecules. The effect of such a potential on diffusion is now discussed.

We introduce a potential W which is a minimum at the orientation $\theta_0 = 0$. A diffusing particle rotating into another orientation will experience a restoring force towards $\theta_0 = 0$. The phase symmetry requires that

$$W(\theta) = W(-\theta) = W(\pi - \theta);$$

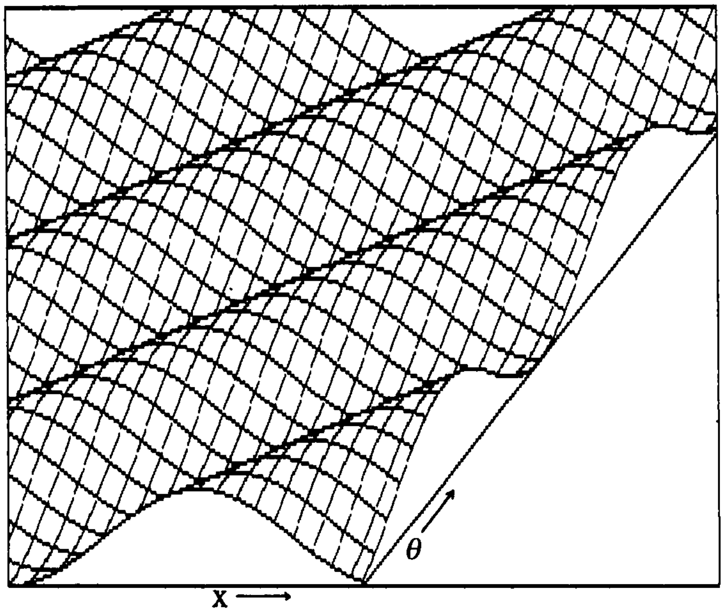


Figure 2. Schematic picture of the potential W in the (x, θ) plane.

we assume a cosine potential as a useful approximation. In cholesterics, the simplest expression for W is that of a cosine potential with the minimum valley twisted along the helix, following the local director orientation

$$W = -\phi_0 kT \cos(4\pi x/p_0 - 2\theta). \tag{16}$$

Because of this potential rotational and translational motions are coupled to each other. Any motion in the two dimensional (x, θ) space will be influenced by $W(x, \theta)$. With ϕ_0 sufficiently large ($\gg 1$), the equilibrium distribution in this potential is responsible for the helical arrangement of the molelcular orientations. For a very steep potential ($\phi_0 > kT$), all motions occur only along the bottom of the potential W, at $2\pi x/p_0 - \theta = 0$. Then we arrive again at the condition (14) leading to equations (7 *a*) and (15).

At very short measurement times, D_T and D_R represent the limits for the observed translational and rotational diffusion coefficients, respectively. If the mobility in the direction of one coordinate is much greater than that along the other coordinate, the faster of them will be slowed down by condition (14) with increasing observation time. The slower of both motions will not be influenced by coupling to the much faster motion. If both mobilities are of the same order of magnitude ($D_R \approx D_\perp p_0^2/(4\pi^2)$), rotational as well as translational diffusion will be reduced with increasing observation time.

The quantitative calculation of diffusion in a cosine potential was performed numerically. We have used a statistical method. The results for the long time diffusion coefficient coincide with the relations found by Dianoux and Volino [11] in their calculations of a similar problem, namely diffusion in smectic A phase; the mathematical approach is contained in Appendix A. The problem of coupling two dimensional motion by the two dimensional (twisted) cosine potential in equation (16) is discussed in Appendix B. If the quantities D_R, D_T are substituted into the equations given there, we arrive at the expressions

$$\left.\begin{aligned}\langle x^2(t)\rangle &= 2D_T\Delta u\, t/K_R + 2D_T t/K_T,\\ \langle \theta^2(t)\rangle &= 2D_R\Delta u\, t/K_T + 2D_R t/K_R,\end{aligned}\right\} \tag{17}$$

where

$$\begin{aligned}K_T &= 1 + 4\pi^2 D_T/(p_0^2 D_R),\\ K_R &= 1 + D_R p_0^2/(4\pi^2 D_T).\end{aligned}$$

where $\Delta u(t)$ represents a function strongly dependent upon the potential barrier height ϕ_0. $\Delta u(t)$ is a decaying function of time with limits

and

$$\left.\begin{aligned}\Delta u(t=0) &= 1\\ \Delta u(t\rightarrow\infty) &= I_0^{-2}(\phi_0),\end{aligned}\right\} \tag{18}$$

where I_0 is the modified first Bessel function of order zero. The computed shape of $\Delta u(t)$ for different potentials ϕ_0 is shown in figure 3; a statistical ensemble of 10 000 particles was used in the computations. It is obvious from equation (17) that in this model the hindering of diffusion by the chiral structure is intrinsically connected to the time dependence of the diffusion coefficient. This means that the proportionality factor between $\langle x^2\rangle$ and the time t determined by the experiment (e.g. in field gradient NMR where a gaussian distribution of $x - x_0(t)$ is assumed) decreases with the observation time. The corresponding decay time scale is given approximately by the time a particule needs, on average, to cross the potential minimum.

At short diffusion times ($\Delta u(t) \approx 1$) we observe undisturbed rotational and translational diffusion

$$\left.\begin{aligned}\lim_{t\rightarrow 0}\langle x^2(t)\rangle &= 2D_T t,\\ \lim_{t\rightarrow 0}\langle \theta^2(t)\rangle &= 2D_R t\end{aligned}\right\} \tag{19}$$

and the long-time behaviour for $\phi_0 \gg 1$ ($I_0^{-2}(\phi_0) \approx 0$) is

$$\left.\begin{aligned}\lim_{t\rightarrow\infty}\langle x^2(t)\rangle &= 2D_T t/K_T\\ \lim_{t\rightarrow\infty}\langle \theta^2(t)\rangle &= 2D_R t/K_R.\end{aligned}\right\} \tag{20}$$

Figure 4 shows the evolution of $D_P = \langle x^2\rangle/2t$ in the long-time limit (see equation (20)) scaled by D_T.

For very slow rotational mobility $D_T \gg D_R p_0^2$ we have

$$K_T = 4\pi^2 D_T/(p_0^2 D_R), \quad K_R = 1.$$

Again we find the quadratic pitch dependence of $\langle x^2\rangle/t$, proposed by Yaniv *et al.*, as the long-time limit of equation (17)

$$\lim_{t\rightarrow\infty}\langle x^2(t)\rangle/t = 2D_R p_0^2/(4\pi^2). \tag{21}$$

A less than quadratic dependence of D_P upon t is expected:

(1) If the long-time limit of equation (17) is not yet reached, which means if the experimental observation time is shorter than the decay time of $\Delta u(t)$;

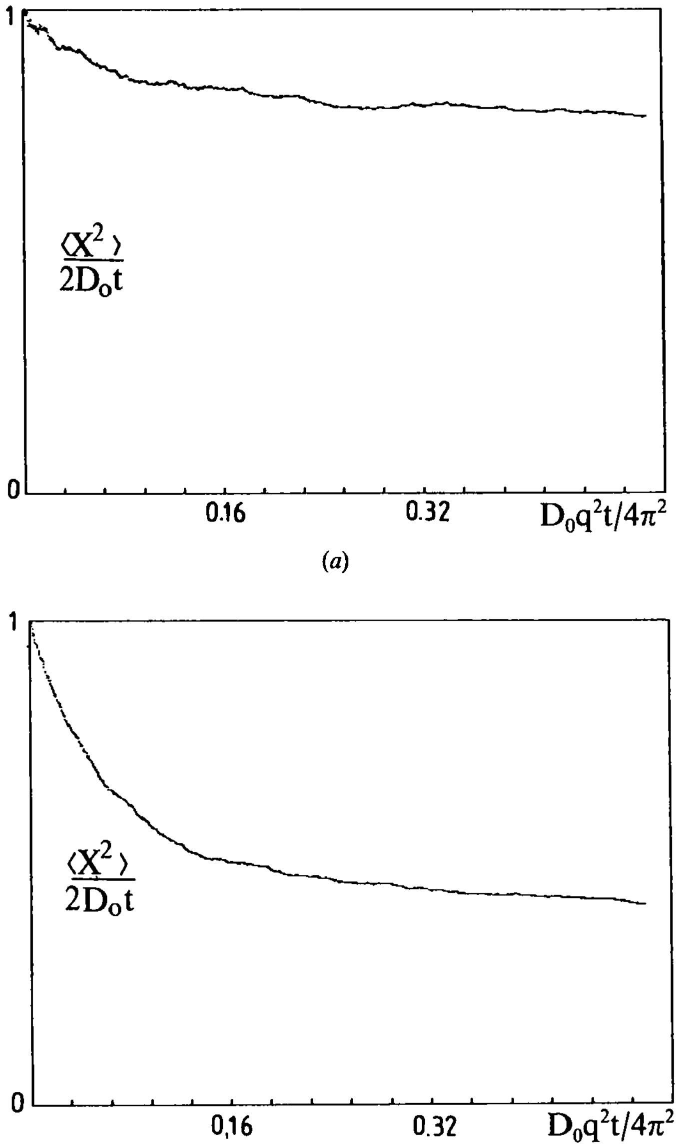
or

(2) if the constant D_R responsible for the reorientational behaviour is not small compared to $4\pi^2 D_\perp/p_0^2$. This is true in particular for very large pitch lengths p_0.

In equations (17), a divergence of the diffusion coefficient in the limit of large p_0 is avoided. In this limit the diffusion coefficient D_P according to our model reaches the value $D_\perp$ of the nematic.

The diffusion coefficient D_R calculated from γ_1 for single molecule rotational diffusion yields a value too large by about 6 to 7 orders of magnitude. Under these conditions would expect $D_R \gg 4\pi^2 D_T/p_0^2$ with the resulting relations

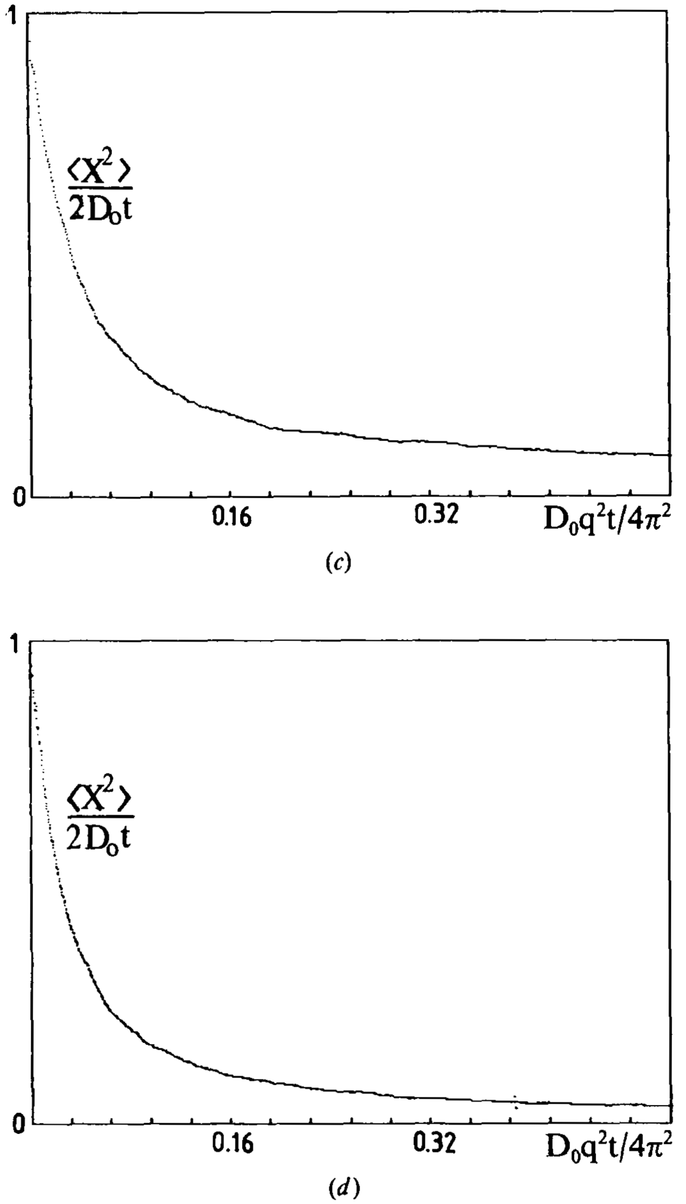
$$K_T = 1, \quad K_R = D_R p_0^2/(4\pi^2 D_T)$$



(*a*)

(*b*)

Figure 3.



(*c*)

(*d*)

Figure 3. The time dependence of the quantity $\Delta u(t) = \langle x^2 \rangle/(2D_0 t)$ for diffusion in a cosine potential for different potential heights, (*a*) $\phi_0 = 0{\cdot}75$, (*b*) $\phi_0 = 1{\cdot}5$, (*c*) $\phi_0 = 3{\cdot}0$ and (*d*) $\phi_0 = 4{\cdot}0$.

and

$$\lim_{t\to\infty} \langle x^2(t) \rangle = 2D_{\mathrm{T}} t, \tag{22a}$$

$$\lim_{t\to\infty} \langle \theta^2(t) \rangle = 8\pi^2/p_0^2 D_{\mathrm{T}} t, \tag{22b}$$

in contradiction with experiment.

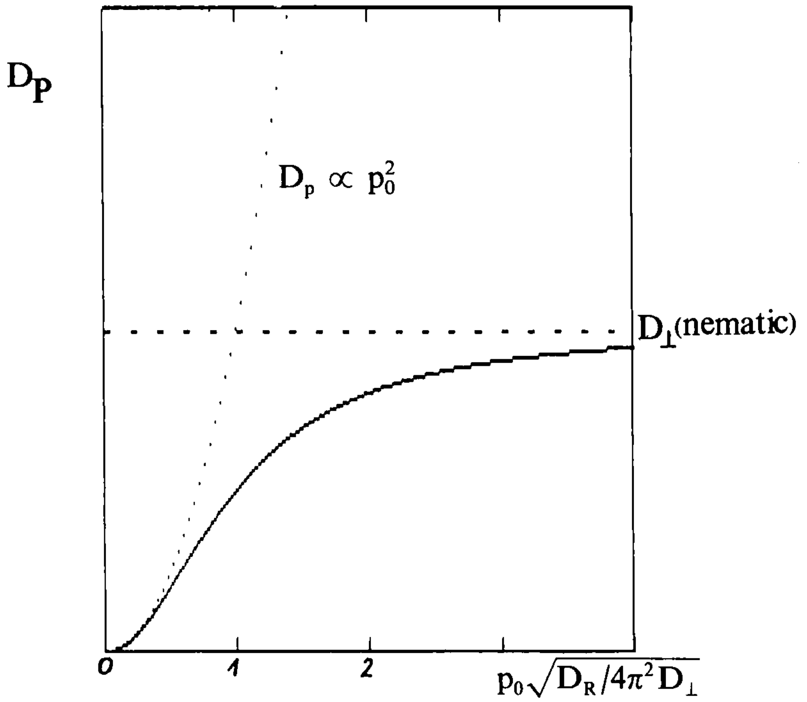


Figure 4. The dependence of the long-time behaviour of the diffusion coefficient D_p for $\phi_0 \gg 1$ on the pitch length p_0; the dotted line gives the quadratic relation $D \approx p_0^2$.

4. Results

Experimental data on self diffusion of pure cholesteric liquid crystals are rare. Most measurements have been performed on cholesterics formed from nematics by adding a small amount of cholesteric substance. The typical pitch lengths in these experiments range from about 0·5 to 10 μm. The available data show a time dependence of the diffusion coefficient D_P in accord with our model [3, 4]. Different results have been published on the pitch length dependence. All of the experimental D_P are smaller than the values expected for the corresponding nematic at the same temperature. The ^{2}D NMR measurements of Vaz *et al.* [12] with cholesterics distorted by a magnetic field give clear evidence that the translational diffusion coefficient depends strongly upon the local twisting of the structure. In distorted cholesterics with a partial unwinding of the helix this results in a spatial modulation of the diffusion coefficient D_P. The ^{2}D NMR measurements of Yaniv *et al.* [1] were performed on very short pitch cholesterics ($p_0 < 1{\cdot}3\,\mu$m). In such strongly twisted samples, the condition $D_R p_0^2/(4\pi^2) \ll D_T$ can be fulfilled. As the decay time of the quantity $\Delta u(t)$ is also proportional to the square of the pitch, we expect that the long-time limit is nearly reached. Then the observed quadratic pitch dependence measured by these authors is in accord with equation (21). ^{13}C NMR measurements of Oehler *et al.* [5, 17] were performed on cholesteric samples with pitch lengths between about 2 and 8 μm. As these pitch lengths are considerably larger, conditions 1 and 2 given previously become effective. They prevent the observation of a quadratic pitch length dependence of D_P. The diffusion coefficient is still a function decreasing with larger twist (shorter p_0), but with a much less than quadratic dependence. These experimental results can also be interpreted within the proposed model. The results published by Luzar *et al.* [2] have already been discussed in [13], where we have shown that the ^{13}C NMR line shape simulations procedure applied in [2] should be modified.

5. Conclusions

This paper presents an interpretation for diffusion in cholesteric liquid-crystalline mesophases. We have shown that our model of coupling between rotational and translational motions by a simple cosine potential in cholesterics is able to predict the effects observed in experiment. In order to determine the parameters ϕ_0, D_R and D_T quantitatively, the amount and accuracy of available experimental data is insufficient. In particular it would be desirable to have data on γ_1, $D_\parallel$ and $D_\perp$ of the nematic and the diffusion coefficients D_P and D_S measured in the cholesteric phase of the same substance for different pitch lengths. This includes the large scale investigation of the $D_P(p_0, t)$ dependence. It could provide an exact quantitative test of the theory proposed here and sketches a programme for future diffusion investigations.

From the comparison of available experimental data with the predictions of equations (7), (15) and (17) we conclude that the mechanisms of the rotational reorientations that are coupled to the translational diffusion are collective phenomena involving some 10^6 molecules, clusters. The existence of such motions was stated already in Franklin [14].

Finally it should be stressed that this theory treats only diffusion processes in the helical direction, because it is this component of the diffusion tensor which is affected by conditions different to those of the nematic phase. Several optical mass transport measurements [6–8] and a ^{1}H NMR investigation [3] have been used to determine the diffusion coefficient perpendicular to the helix. The observed pitch and time dependencies of these data are clearly in contradiction with a model of diffusion within quasi-nematic layers perpendicular to the twist axis. Further measurements and a thorough theoretical investigation are needed to provide a comprehensive understanding of this process. ^{1}H NMR field gradient methods are already at their limits in cholesteric liquid crystals, because of the short relaxation time T_2 and the slow diffusion compared to liquids, where field gradient methods are applied very successfully. Moreover, the orientation of the sample in the magnetic field of the spectrometer is problematic. Most of the investigated thermotropic liquid crystals have a positive diamagnetic susceptibility anisotropy $\Delta\chi$ which causes the helix axes to distribute over all directions perpendicular to the magnetic field. In samples containing cyclohexane derivates, $\Delta\chi$ is negative but very weak and orientation is poor. If we are interested in the measurement of D_s, we need additional electric fields to orient the helix axes uniformly.

Mass transport investigations are sensitive only to D_s due to the geometrical arrangement of the helices in the diffusion cells. It has been shown in detail [7, 15] that the experimental conditions of mass transport methods have to be improved substantially in order to yield reliable data. In particular, we should use the method of diffusion with a source of constant initial concentration of cholesteric [7]. Even then, the concentration profiles are very insensitive to the exact D_s versus concentration (or $D_s(p_0)$) dependence. We can measure, with good reliability, the average diffusion coefficient over the pitch range in the diffusion cell. It would be preferable to perform different experiments where in each experiment the difference between the source concentration and the initial concentration of cholesteric substance in the diffusion cell is very small. With a set of experiments covering a sufficiently large concentration (pitch) range, the dependence of diffusion on the pitch length of the sample could be gained. Preliminary experiments done in this laboratory gave no clear decision on the pitch dependence of D_s. These experiments will be continued and published elsewhere.

The author acknowledges interesting and helpful discussions with Professors H. Schmiedel and St. Oehler.

Appendix A

Diffusion in a cosine potential

The solution of the diffusion equation

$$\dot{c}(x,t) = \partial/\partial x D_0(\partial/\partial x c(x,t) + 1/kT \partial W/\partial x c(x,t)) \qquad \text{(A 1)}$$

for arbitrary shapes of the function $W(x)$ cannot be found analytically. We have used a statistical approach to compute the quantity

$$\langle x^2(t)\rangle = \int dx c(x,t) x^2 \Big/ \int dx c(x,t).$$

An ensemble of particles initially Boltzmann distributed along the coordinate x is allowed to perform discrete diffusion steps along x. The coordinate x is divided into discrete positions x_i with distances Δx. Discrete time steps Δt and the dimensionless diffusion coefficient

$$d_0 = D_0 \Delta t/\Delta x^2$$

are introduced. The potential has the shape

$$\phi = W/kT = -\phi_0 \cos(qx),$$

in discrete form

$$\phi_i = -\phi_0 \cos(2\pi x_i/N).$$

The number of particles in the interval $(x_i - \Delta x/2, x_i + \Delta x/2)$ is n_i. Equation (A 1) transforms to

$$\begin{aligned} \Delta n_i = d_0\{&[n_{i+1} + n_{i-1} - 2n_i] \\ &+[\phi_{i+1} - \phi_i][n_{i+1} + n_i]/2 \\ &-[\phi_i - \phi_{i-1}][n_i + n_{i-1}]/2\}. \end{aligned}$$

We did not solve equation (A 2) by successive calculation of the n_i at times t_j but applied a jump model with transition probabilities for each particle between adjacent positions

$$\left.\begin{aligned} p(i)_- &= p(i \rightarrow i-1) = d_0(1 + \tfrac{1}{2}\Delta\phi_i), \\ p(i)_+ &= p(i \rightarrow i+1) = d_0(1 - \tfrac{1}{2}\Delta\phi_i). \end{aligned}\right\} \qquad \text{(A 3)}$$

$\Delta\phi_i$ represents the derivative of ϕ at the location x_i.

$$\Delta n_i = p(i+1)_- n_{i+1} + p(i-1)_+ n_{i-1} - [p(i)_- + p(i)_+]n_i. \qquad \text{(A 4)}$$

The initial distribution of the ensemble is $n_i = \exp(-\phi_i)$. Because of the symmetry of the function ϕ it is sufficient to limit this distribution to the interval $(-N/2, N/2)$.

At each diffusion step every particle will jump from its position x_i with a probability p_- and p_+, respectively, to the new position x_{i-1} or x_{i+1}. The average taken over the ensemble gives

$$d = \langle (x(n) - x(0))^2 \rangle / 2n, \tag{A 5}$$

where $x(i)$ designates the position of a particle at the ith time step, gives the diffusion coefficient in units of $\Delta x^2/\Delta t$.

We see that for ϕ = constant. Equations (A 3) reduce to $p_- = p_+ = d_0$.

Then equations (A 5) may be transformed to

$$\begin{aligned} d = {} & \tfrac{1}{2}n(\langle (x_n - x_{n-1})^2 \rangle + \langle (x_{n-1} - x_0)^2 \rangle \\ & + 2\langle (x_n - x_{n-1})(x_{n-1} - x_0) \rangle). \end{aligned} \tag{A 6}$$

The last term vanishes as the direction of the last diffusion step $(x_n - x_{n-1})$ is independent of $(x_{n-1} - x_0)$ and after recursive application of equation (A 6) we find

$$d = n\langle (x_1 - x_0)^2 \rangle / 2n = d_0, \tag{A 7}$$

As expected, the diffusion coefficient in a constant potential is time independent.

In figure 3 we show the calculated time dependence of the observed diffusion constant $D = d\Delta x^2/\Delta t$ for different potential heights ϕ_0. They were calculated according from equation (A 5) from an ensemble of $\geqslant 10^4$ particles. The statistical fluctuations observed in these figures are due to the relatively small size of the number of particles that was chosen to minimize the calculation time. At short diffusion times the observed D curve starts at the value D_0, being determined by the free diffusion of the particles. With increasing time intervals D decays monotonously. The long-time diffusion coefficient approaches a limiting value which is determined by the number of particles which are able to pass the potential wall into the adjacent minimum of the cosine potential. This value $D_\infty = D(t \to \infty)$ depends strongly on ϕ_0. According to Volino and Dianoux [11] this limiting value is

$$D_\infty(\phi_0) = D_0/I_0^2(\phi_0), \tag{A 8}$$

with the modified Bessel function of order zero,

$$I_0(x) = J_0(ix).$$

At potential heights $\phi_0 \gg 1$, equation (A 8) becomes approximately $D_\infty(\phi_0) = D_0 \exp(-2\phi_0)$.

Figure 5 shows the dependence of D_∞ on ϕ_0 according to the statistical calculations (crosses) and equation (A 8) (solid line). The values calculated by the statistical method are in good agreement with the results of [11] which have also been determined empirically.

All $D(t)$ curves have the initial value $D(0) = D_0$. The characteristic slope is determined by the potential ϕ. At $t = 0$ it can be approximated by the tangent

$$\begin{aligned} D(t) &\approx D_0(1 - \delta_t) \\ &= D_0(1 - D_0 q^2 \phi_0 t / 2\langle \cos qx \rangle), \end{aligned}$$

where

$$\langle \cos(qx) \rangle = \int \exp(\phi_0 \cos(qx)) \cos(qx)\, dx \Big/ \int \exp(\phi_0 \cos(qx))\, dx$$

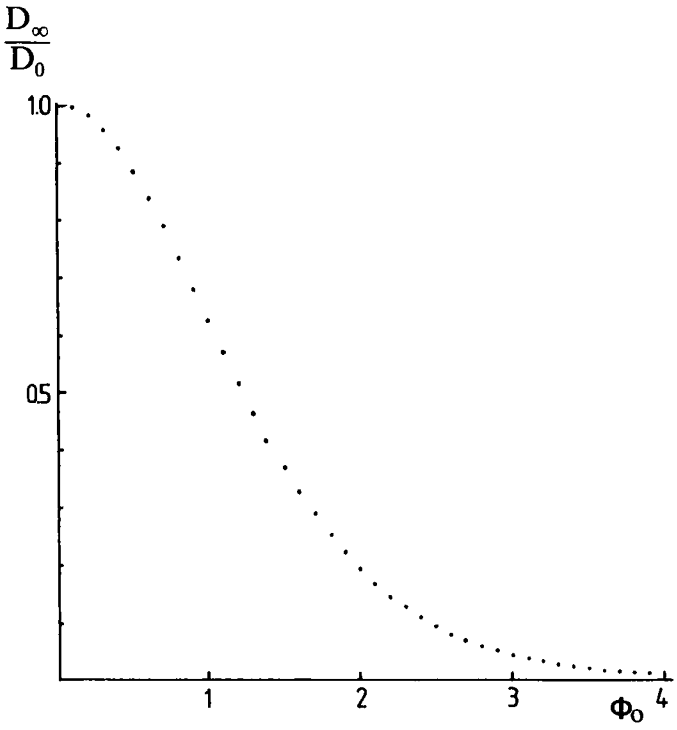


Figure 5. The dependence of the long-time behaviour D_∞ in units of the free diffusion coefficient D_0 on the potential height ϕ_0.

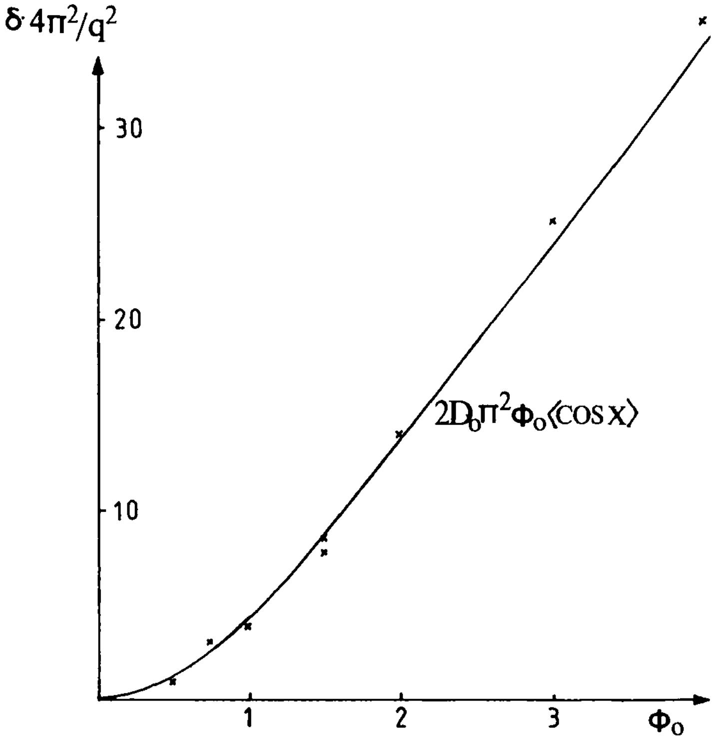


Figure 6. The initial slope δ of the functions $D(t)$ for different ϕ_0.

represents the average of $\cos(qx)$ over the distribution n_i. The initial decay constant δ is shown in figure 6 as a function of ϕ_0. At large $\phi_0 (\gg 1)$ the average $\langle\cos(qx)\rangle$ yields 1 (all particles are distributed in the vicinity of $x = 0$), and

$$D(t) = D_0(1 - D_0 t\phi_0 q^2/2).$$

At low potentials $\phi_0 \lesssim 1$ we can use the series expansion

$$\begin{aligned} D(t) &= D_0(1 - \delta t), \\ -\delta &= D_0\phi_0^2 q^2(-1 + \phi_0^2/4 - \phi_0^4/48 \ldots). \end{aligned}$$

The time for the establishment of the long-time limiting value is of the order of $\pi^2/(2D_0q^2)$.

Appendix B

Connection between diffusive processes in two dimensions by a twisted cosine potential

In Appendix A we calculated the evolution of a statistical ensemble of particles in the one-dimensional cosine potential. Now we discuss the two dimensional case. Diffusion is described, in an x, y coordinate space. (With respect to the particular problem of cholesterics, x represents the spatial coordinate parallel to the helix and y is the rotation angle around the helix axis.) x and y are principle axes of a diffusion tensor $\mathbf{D}$; the corresponding compositions of $\mathbf{D}$ are D_{xx} and D_{yy}, and the diffusion equation reads

$$\left.\begin{aligned} \partial c(x,y,t)/\partial t &= \partial/\partial x D_{xx}(\partial c/\partial x + c\partial\phi/\partial x) \\ &\quad + \partial/\partial y D_{yy}(\partial c/\partial y + c\partial\phi/\partial y). \end{aligned}\right\},$$

The potential ϕ has the form (see figure 2)

$$\phi = V/kT = -\phi_0\cos(4\pi x/p_0 - 2y) \tag{A 11}$$

such that it is invariant to a translation x' along the helix axis of the cholesteric structure and simultaneous rotation by an angle $y' = 2\pi x'/p_0$.

At first we perform a transformation

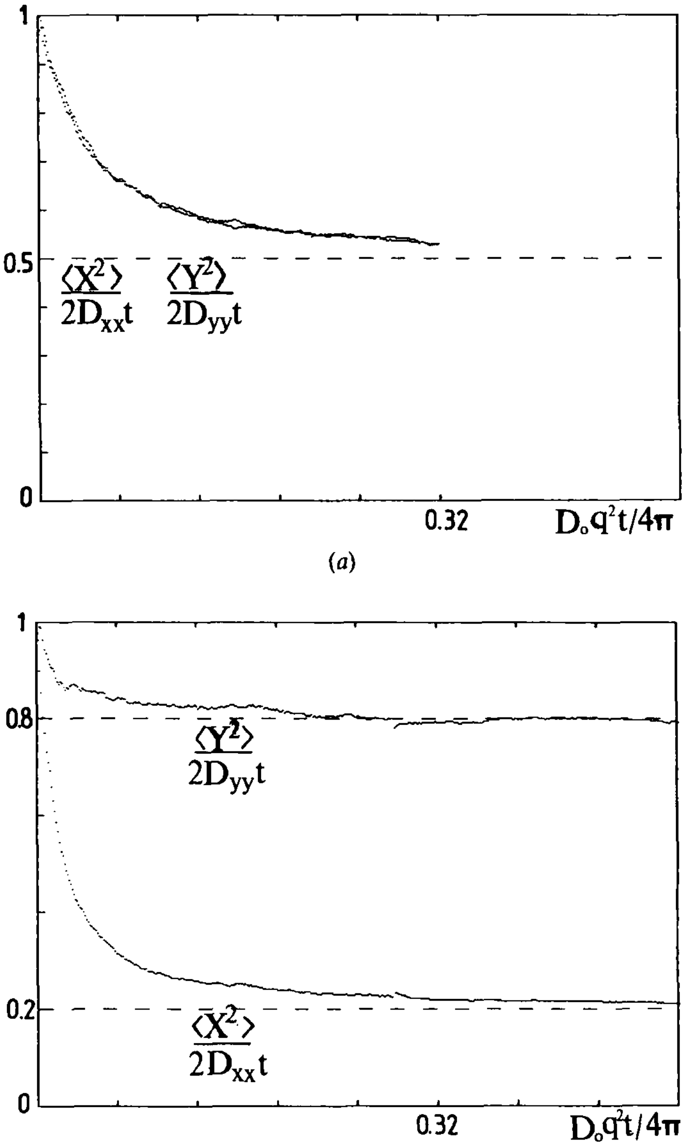
$$\begin{aligned} X &= xD_{xx}^{-1/2}, \\ Y &= yD_{yy}^{-1/2}, \\ \phi &= -\phi_0\cos(4\pi X D_{xx}^{1/2}/p_0 - 2YD_{yy}^{1/2}), \\ \partial c(X,Y,t)/\partial t &= \partial/\partial X(\partial c/\partial X + c\partial\phi/\partial X) \\ &\quad + \partial/\partial Y(\partial c/\partial Y + c\partial\phi/\partial Y). \end{aligned} \tag{A 12}$$

After the substitutions

$$\begin{aligned} u &= X\cos\alpha - Y\sin\alpha, \\ v &= X\sin\alpha + Y\cos\alpha, \\ \phi &= -\phi_0\cos(qu), \end{aligned} \tag{A 13}$$

with

$$\begin{aligned} q &= (16\pi^2 D_{xx}/p_0^2 + 4D_{yy})^{1/2}, \\ \cos\alpha &= 4\pi D_{xx}^{1/2}/q, \\ \sin\alpha &= 2D_{yy}^{1/2}/q, \end{aligned}$$



(*a*)

(*b*)

Figure 7. The decay of $\langle x^2(t)\rangle$ and $\langle y^2(t)\rangle$ for (*a*) $D_{xx} = D_{yy} = D_0$, $\Phi_0 = 5{\cdot}0$, and (*b*) $D_{xx} = 4D_{yy} = 4D_0$, $\Phi_0 = 5{\cdot}0$.

we have collected the spatial inhomogeneity of the potential into the direction of one coordinate, u. We factorize the concentration $c(u, v, t)$ into

$$c(u, v, t) = c_u(u, t)c_v(v, t),$$

and two decoupled equations

$$\partial c_u(u, t)/\partial t = \partial/\partial u(\partial c_u/\partial u + c_u \partial\phi/\partial u), \qquad \text{(A 14}a)$$

$$\partial c_v(v, t)/\partial t = \partial^2 c_v/\partial v^2 \qquad \text{(A 14}b)$$

are obtained.

For the quantity c_v we find, with the boundary and initial conditions $c_v(v,0) = \delta(v)$, $c_v(\pm\infty, t) = 0$ the well-known gaussian solution

$$\begin{aligned} c_v(v,t) &= (4\pi t)^{-1/2}\exp(-v^2/(4t)), \\ \langle v^2\rangle &= 2t, \end{aligned}$$

while for $c_u(u,t)$ we can use the solutions obtained in Appendix A. The numerical values of figures 3–6 describe the diffusional behaviour of $c_u(u,t)$ with $D_0 = 1$ and

$$\langle u^2\rangle = 2\Delta u(t)t, \quad \Delta u(0) = 1, \quad \Delta u^\infty = I_0^{-2}(\phi_0).$$

If x and y are resubstituted again, we have

$$\left.\begin{aligned} x &= D_{xx}^{1/2}(u\cos\alpha + v\sin\alpha), \quad y = D_{yy}^{1/2}(-u\sin\alpha + v\cos\alpha), \\ \langle x^2\rangle &= D_{xx}\{\langle u^2\cos^2\alpha\rangle + \langle v^2\sin^2\alpha\rangle + 2\langle uv\sin\alpha\cos\alpha\rangle\} \\ &= D_{xx}\{\cos^2\alpha\langle u^2\rangle + \sin^2\alpha\langle v^2\rangle\}, \\ \langle y^2\rangle &= D_{yy}\{\langle u^2\sin^2\alpha\rangle + \langle v^2\cos^2\alpha\rangle - 2\langle uv\sin\alpha\cos\alpha\rangle\} \\ &= D_{yy}\{\sin^2\alpha\langle u^2\rangle + \cos^2\alpha\langle v^2\rangle\}. \end{aligned}\right\} \qquad (A\ 15)$$

We find the time dependences of $\langle x^2\rangle$ and $\langle y^2\rangle$

$$\left.\begin{aligned} \langle x^2(t)\rangle &= 2D_{xx}\Delta ut/K_y + 2D_{xx}t/K_x, \\ \langle y^2(t)\rangle &= 2D_{yy}\Delta ut/K_x + 2D_{yy}t/K_y, \end{aligned}\right\} \qquad (A\ 16)$$

where

$$\begin{aligned} K_x &= 1 + 4\pi^2 D_{xx}/(p_0^2 D_{yy}), \\ K_y &= 1 + D_{yy}p_0^2/(4\pi^2 D_{xx}), \end{aligned}$$

At short diffusion times the limiting values are (cf. Appendix A)

$$\lim_{t\to 0}\langle x^2(t)\rangle = 2D_{xx}t, \quad \lim_{t\to 0}\langle y^2(t)\rangle = 2D_{yy}t$$

and the long-time limits for $\phi_0 \gg 1$ ($I_0^{-2}(\phi_0) \approx 0$) are

$$\lim_{t\to\infty}\langle x^2(t)\rangle = 2D_{xx}t/K_x, \quad \lim_{t\to\infty}\langle y^2(t)\rangle = 2D_{yy}t/K_y.$$

Figure 7 shows the result of a statistical computation with the two-dimensional analogue of equations (A 2)–(A 6). The representation is the same as that of figure 3. We have chosen $D_{xx} = D_{yy} = D_0$, and $D_{xx} = 4D_{yy} = 4D_0$ as examples.

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