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Anomalous diffusion producing normal relaxation and transport

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Abstract

From the Arrhenius law a probability distribution of timescales is derived by treating both the prefactor and the activation energy as random variables. In the defect-diffusion model this probability distribution is used to calculate the properties of the anomalous diffusion of defects. The timescales represent the pausing time distribution between movements of a defect. The conditions are determined for these mobile defects to produce stretched exponential relaxation. The diffusion of a single defect is anomalous, but the collective effect of all defects produces a characteristic relaxation timescale. The temperature and pressure dependence of this timescale is used to determine conductivity, dielectric relaxation, and viscosity.

1. Introduction

Einstein skillfully applied a random walk analysis to the problem of Brownian motion. His goal was to determine the size of a molecule and his method exploited a fluctuation phenomenon. His work was so successful that mathematical Brownian motion with its Gaussian probability became a paradigm for physical fluctuations. However, the theoretical Brownian particle velocity was infinite and not well defined. To address the velocity question, Langevin introduced a stochastic differential equation for the velocity with additive white noise, but then the acceleration became infinite and not well defined. Employing coloured noise produced finite velocities and accelerations, but greatly increased the complexity of analysing the Langevin equation.

Montroll [1] approached the random walk with a simpler model. He developed an easy to use, but powerful, Green's function approach for studying discrete-time random walks on regular lattices. This approach allowed the calculation of many random walk questions. For example, his method provided, for the first time, the exact analytical answer to the probability

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of a random walker to return to its origin. There was no explicit velocity in the original Montroll random walk model, but velocity was there implicitly because the walker could at most travel n lattice spacing in n jumps. Montroll and Weiss [2] generalized this discrete-time approach to a continuous-time random walk approach. A waiting time distribution $\psi(t)$ was added, as a memory term, to allow the walker to pause for a random time between jumps. Initially, this generalization to continuous-time random walks did not seem to add much to the analysis, except to replace the step number, n, by $t/\langle t\rangle$, where $\langle t\rangle$ is the mean waiting time between jumps. As an example, the mean square displacement after time t on a cubic lattice was proportional to $t/\langle t\rangle$, instead of to n. All of this changed when Scher and Montroll [3] investigated the jumping of charges in a amorphous semiconductor thin film. To explain the data, they discovered the need for a waiting time distribution with an infinite mean (actually, physically, a mean time longer than the time of the experiment was sufficient). It is demonstrated, in the next section, that it is easy to derive such types of waiting time distributions. The set of jump times looks like a randomized Cantor set with its sparse fractal set of points. This has been called a fractal-time random walk [4]. This type of random walk is employed to describe the motion of defects in glass-forming liquids. The effect of these fractal-time defects on relaxation and transport phenomena is examined.

2. The waiting time distribution: random energies

Usually, one considers the Arrhenius law to define a timescale τ, where

$$\tau = \tau_0 \exp(\Delta/kT), \tag{1}$$

where Δ is the activation barrier energy, T is the temperature, and the prefactor τ_0 is a constant. A probability density $h(\Delta)$ of activation energies Δ induces a probability density $\psi(\tau)$ of waiting times τ. Note that $h(\Delta)$ has units of inverse energy and $\psi(\tau)$ has units of inverse time. These probability densities are connected by

$$\psi(\tau)\,\mathrm{d}\tau = h(\Delta)\,\mathrm{d}\Delta. \tag{2}$$

Choosing $h(\Delta) = (1/\Delta_0)\exp(-\Delta/\Delta_0)$ with Δ_0 being the mean barrier height, and employing equation (1) to write Δ as a function of τ, gives the equality

$$\exp(-\Delta/\Delta_0) = (\tau/\tau_0)^{-kT/\Delta_0}$$

which together with $\mathrm{d}\tau/\mathrm{d}\Delta = \tau/kT$ yields

$$\psi(\tau) = \beta\frac{\tau_0^{\beta}}{\tau^{1+\beta}}, \qquad \text{for } \tau > \tau_0, \tag{3}$$

where $\beta = kT/\Delta_0$. When $\beta < 1$, we get anomalous diffusion because the first moment, the mean waiting time $\langle t\rangle = \int_0^{\infty} t\psi(t)\,\mathrm{d}t$, is infinite.

3. The waiting time distribution: random energies and random prefactors

The case when both the activation energy Δ and the τ_0 prefactor are random variables is now presented. Consider first the question of how to determine the probability distribution function for the product of two random variables. Let X, Y and Z be random variables with probability distributions $f(x)$, $g(y)$ and $p(z)$.

Let $Z = XY$.

Then

$$p(z) = \int_{-\infty}^{\infty} f\left(\frac{z}{y}\right)g(y)\frac{\mathrm{d}y}{y}. \tag{4}$$

The $1/y$ term comes from the Jacobian $J = \partial(x, y)/\partial(z, y)$ of the transformation from (x, y) to (z, y). The probabilities are related by

$$P(z, y)\mathrm{d}z\,\mathrm{d}y = F(x, y)\,\mathrm{d}x\,\mathrm{d}y,$$

where

$$F(x, y) = f\left(\frac{x}{y}\right)g(y) \qquad \text{and} \qquad p(z) = \int_{-\infty}^{\infty} P(z, y)\,\mathrm{d}y$$

Thus,

$$P(z, y) = F(x, y)J$$

with

$$J = \begin{vmatrix} \partial x/\partial z & \partial x/\partial y \\ \partial y/\partial z & \partial y/\partial y \end{vmatrix} = \begin{vmatrix} 1/y & -z/y^2 \\ 0 & 1 \end{vmatrix} = 1/y.$$

Integrating $P(z, y)$ over y gives equation (4).

In our case, the random variables τ, τ_0, and Δ are related by $\tau = \tau_0 \exp(\Delta/kT)$.

Set $X = \tau_0$ and $Y = \exp(\Delta/kT)$. Note when Δ is zero that $Y = 1$, so equation (4) becomes

$$p(z) = \int_1^{\infty} f(z/y)g(y)\frac{\mathrm{d}y}{y}. \tag{5}$$

Choosing $f(t) = (2/\sqrt{\pi})\exp(-t^2)$, so there is more weight towards smaller attempt times t, and keeping equation (3) for the Y distribution yields

$$p(\tau) = \frac{2\beta}{\sqrt{\pi}}\int_1^{\infty} \exp(-\tau^2/y^2)\frac{\mathrm{d}y}{y^{2+\beta}}. \tag{6}$$

Let $u = 1/y^2$ and $\mathrm{d}u = -2/y^3\,\mathrm{d}y$, then

$$\begin{aligned} p(\tau) &= \frac{\beta}{\sqrt{\pi}}\int_0^1 \exp(-u\tau^2)y^3\frac{\mathrm{d}u}{y^{2+\beta}} \\ &= \frac{\beta}{\sqrt{\pi}}\int_0^1 \exp(-u\tau^2)\frac{\mathrm{d}u}{u^{(1-\beta)/2}}. \end{aligned} \tag{7}$$

Writing $q = u\tau^2$ yields

$$p(\tau) = \frac{1}{\sqrt{\pi}}\frac{\beta}{\tau^{1+\beta}}\int_0^{\tau^2} \exp(-q)q^{(\beta-1)/2}\,\mathrm{d}q \tag{8}$$

with the integral going to a constant as $\tau \to \infty$. Thus, $p(\tau)$, at long times, behaves as $1/\tau^{1+\beta}$, the same as if the prefactor was fixed and not random.

While equations (3) and (8) have the same long-time asymptotic behaviour, their short-time behaviour is quite different. From equation (8) $p(\tau) \approx (\beta/\sqrt{\pi})\exp(-\tau^2)$ for small times, while equation (3) has a minimum time τ_0.

As another example, choose

$$f(t) = t^{\nu-1}\exp(-t)/\Gamma(\nu), \qquad \nu > 1;$$

then

$$p(\tau) = \frac{\beta}{\Gamma(\nu)}\int_1^{\infty} (\tau/z)^{\nu-1}\exp(-\tau/z)\frac{\mathrm{d}z}{z^{1+\beta}}, \tag{9}$$

which can be written as

$$p(\tau) = \frac{\beta}{\tau^{1+\beta}\Gamma(\nu)}\int_0^{\tau} \exp(-x)x^{\nu+\beta-1}\,\mathrm{d}x$$

with the familiar $1/\tau^{1+\beta}$ behaviour at long times and $\beta\tau^{\nu-1}\exp(-\tau)/\Gamma(\nu)$ behaviour at short times.

4. The target problem

The target problem [4] refers to a target site in a sea of mobile random walkers. The problem is to determine the probability distribution for the first time that the target is reached by any of the walkers. Dielectric relaxation can be discussed in terms of the target problem when a frozen-in dipole is the target and it is relaxed when it is first reached by any mobile defect that encapsulates enough free volume to allow the dipole to rotate.

Experimentally, it has been found, for many glass-forming materials, that relaxation phenomena, including dielectric relaxation, volumetric relaxation, stress relaxation, and magnetization relaxation, all follow a stretched exponential relaxation over many timescales (except at short times),

$$\Phi(t) = \exp(-(t/\tau)^{\beta}), \qquad \beta < 1. \tag{10}$$

The stretched exponential was used by Frederick Kohlrausch in 1863 in the study of creep in silk and glass fibres. This law was rediscovered by Williams and Watts in the study of dielectric relaxation in glass-forming materials in 1970 [5].

We assume that the glass-forming material contains a concentration c of defects and that each defect performs a random walk. Due to the random nature of the supercooled liquid there is a distribution of timescales for the waiting time between jumps of a defect. We denote the waiting time probability density (between jumps of a given defect) to be $\psi(t)$. If the mean time to make a jump is finite, then for times much longer than the mean time many jumps will occur and a standard type of random walk will be produced. The mean number of jumps in a time t will be proportional to t. If the waiting time distribution has an infinite mean waiting time then the mean number of jumps will grow more slowly than linearly with time. The algebraic long-time asymptotic form derived in section 3, $\psi(t) \approx t^{-1-\beta}$, with $\beta < 1$, has the number of jumps only growing as t^{β}.

Consider the problem of dielectric relaxation in a glassy material involving a frozen-in dipole that can be relaxed only when it is hit by a mobile defect. This problem involves the first passage time of random walkers (defects) to reach the frozen-in dipole. The mathematical analysis of the problem is in the form of letting there be V lattice sites and letting N walkers be initially randomly distributed among these sites, not including the origin where the dipole is placed. The probability $\Phi(t)$ that none of the walkers has reached the origin by time t is given by

$$\Phi(t) = \left[1 - \frac{1}{V}\sum_{\mathbf{r}\neq 0}\int_0^t F(\mathbf{r},\tau)\,\mathrm{d}\tau\right]^N, \tag{11}$$

where $F(\mathbf{r},\tau)$ is the probability density that a walker starting at site $\mathbf{r}$ will reach the origin for the first time at time τ. The integral allows for a first passage of a walker to the origin in the interval $(0,t)$. The $1/V$ enters as the probability of a walker starting at a particular site, and a sum over all possible starting points for a walker is performed. The bracket calculates the probability that a particular walker has not reached the origin and it is raised to the Nth power for the probability that none of the N walkers has yet reached the origin. The problem is easier in the limit $N \to \infty$, $V \to \infty$, but with the ratio remaining constant $N/V = c$. In this limit, with $S(t)$ being the number of distinct sites a walker visits in time t,

$$\Phi(t) = \exp\left\{-\left(c\sum_{\mathbf{r}}\int_0^t F(\mathbf{r},\tau)\,\mathrm{d}\tau\right)\right\} = \exp(-cS(t)). \tag{12}$$

The simplification involving $S(t)$ was accomplished by noting that any of the sites from which a walker can reach the origin in a time t are exactly the same sites a walker starting at the origin

can reach in a time t. In three dimensions, $S(t)$ has the following form for the random walk jumps governed by $\langle t \rangle$ finite ($\beta = 1$) and infinite ($\beta < 1$):

$$cS(t) \approx ct^{\beta}. \tag{13}$$

The stretched exponential (the $\beta < 1$ case) is found to be a probability limit distribution. This distribution has a well-defined timescale $\tau = c^{-1/\beta}$ even though a single individual jump of a single defect does not. In the next section, the behaviour of this timescale is explored as a function of temperature and pressure. It will be seen that even though τ is well defined it will have an essential singularity at a finite critical temperature.

5. A Vogel-like law for a diverging timescale

A second property of many glass-forming materials is that quantities such as the relaxation time τ and the viscosity diverge as the glass transition temperature T_g is approached from above. In terms of a timescale, the law is given by

$$\tau = \tau_0 \exp\left(\frac{B}{T - T_0}\right), \tag{14}$$

where B is a constant and T_0 is a temperature below the glass transition temperature. This empirical law was first proposed by Vogel [6] in 1921, on studying the effect of temperature on the viscosity of lubricants, and later by Fulcher [7] and Tammann and Hesse [8]. This is to be compared to the well-known Arrhenius law, $\tau = \nu_0^{-1} \exp(\Delta/kT)$, introduced in 1889 to incorporate the concept of an activation energy. The Arrhenius law was derived by Kramers, in 1940, in terms of the trajectory of a particle successfully crossing an energy barrier of height Δ, with an attempt frequency of ν_0. The interpretation of the parameters B and T_0 in the Vogel law is not so straightforward.

There have been several attempts to derive the Vogel law or alternative laws. In the defect diffusion model the timescale in the stretched exponential law depends on the mobile defect concentration. In this model, as the temperature is lowered, defects cluster to lower the entropy. It is further assumed that the clustered defects are immobile. Thus, as the temperature is lowered the number of mobile defects decreases and the material becomes more viscous (rigidity begins to set in). At T_g, rigidity percolates and the glassy state is formed. Relaxation, however, is still occurring. A phase transition in the number of mobile defects as the temperature is lowered creates the behaviour characterized by equation (14), as is shown below. The single defects have concentration c_1. We replace c in equation (13) by c_1 because only mobile defects will cause relaxation to occur. To have a single (isolated) defect at a site, one must first have a defect there with probability c and also have all of the z neighbouring sites within its correlation volume unoccupied, i.e.,

$$c_1 = c(1 - c)^z \tag{15}$$

with $z = \xi_x \xi_y \xi_z / d^3$, where ξ_i is the defect–defect correlation length in the ith direction, and d is the nearest-neighbour average spacing. In a mean field lattice gas model, the correlation length ξ between the defects grows near and above a critical temperature T_c as $\xi_i(T) \approx L_i(\frac{T_c}{T - T_c})^{1/2}$, where L_i is a constant with units of length and T_c is the temperature at which single defects disappear. With increasing pressure, the nearest-neighbour mean spacing d is assumed to decrease isotropically as $d^3 = d_0^3(1 - \delta(T, P))$, where $1 - \delta(T, P) = V(T, P)/V(T, 0)$ is the fractional volume change of the material as pressure increases and d_0 is the mean nearest-neighbour spacing at zero pressure. The timescale in the stretched exponential can now be

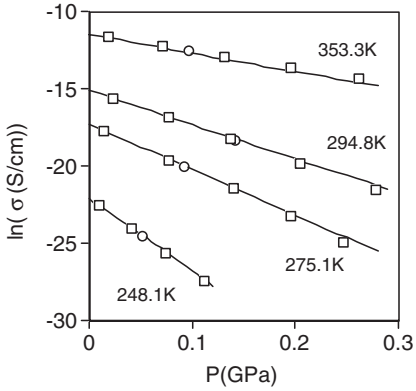

Figure 1. Electrical conductivity versus pressure for PPG:$NaCF_3SO_3$. The solid lines are the best fit to equation (16) with the 3/2 exponent. The results are discussed in detail in [10].

expressed as [9]

$$\tau \approx c_1^{-1/\beta}\tau_0 = c^{-1/\beta}\tau_0 \exp\left(\frac{BT_c^{3/2}}{(T-T_c)^{3/2}(1-\delta(T,P))}\right), \tag{16}$$

where $B = -(L_1L_2L_3/d_0)^3 \ln(1-c)/\beta$. This is a new relaxation law that is Vogel-like with a 3/2 temperature exponent. The 3 comes from the three dimensions and the 1/2 comes from the mean field behaviour of the correlation length. As c decreases, note that B decreases and that the prefactor increases. Materials such as poly(propylene glycol) appear to exhibit this type of behaviour. If it is assumed that T_c is a function of P, both the pressure and temperature effects can be accounted for in materials such as poly(propylene glycol). When the correlation volume grows in two dimensions, and not fully in three dimensions, then the 3/2 power is replaced by a 2/2 power and the standard Vogel equation is obtained. Glycerol appears to exhibit standard Vogel behaviour [10].

As an application of the defect diffusion theory consider the conductivity of an ion-doped glass-forming material. We assume that ion can only jump when reached by a mobile defect. As the temperature is lowered, defects aggregate to lower the entropy of the system. It is assumed that when two defects combine to form a cluster the free volume associated with the cluster is smaller than the total volume associated with two single defects. As the defects cluster, one does not find large bubbles of free volume, but the immobilization of pairs with diminished free volume. A lower temperature then implies a lower conductivity due to a smaller mobile defect population. This is seen experimentally in figure 1.

6. Conclusions

The manner in which randomness in activation energies and prefactors in an Arrhenius law can produce distributions with long-time tails has been explored. Although these distributions do not have a well-defined timescale they can, in a parallel reaction scheme, produce a stretched exponential distribution. The stretched exponential does possess a well-defined timescale in terms of the concentration of mobile defects. An expression for this timescale was derived that is similar to the empirical Vogel–Fulcher law with its essential singularity at a critical temperature. We also include the pressure dependence in our expression. Once the timescale τ is defined, we can employ the Einstein relations to determine a dielectric loss

peak $\omega = 1/\tau$, a diffusion constant $D = L^2/6\tau$, conductivity $\sigma = q^2 nD/kT$, and viscosity $1/\eta = 6\pi Dr/kT$. One can also determine the dependence of free volume on temperature and pressure within this theory [11].

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