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Fick's Law, Green-Kubo Formula, and Heisenberg's Equation of Motion

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Fick's law is important in transport theory and nonequilibrium statistical mechanics. The Heisenberg equation of motion for density is examined to see how it could be reduced to the diffusion equation, which is exactly equivalent to Fick's law. Conditions that are required have been noted and their implications explored.

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Introduction.—Fick's law of diffusion is widely used in transport theory [1]. It is also generally important in nonequilibrium statistical mechanics [2,3]. The law is a phenomenological statement of a *macroscopic* nature about the relationship between the mass current $J(r,t)$ and the particle density $n(r,t)$ of a fluid, with r the position and t the time. More precisely put, $J(r,t) = -D\,\text{grad}n(r,t)$, introducing the diffusion constant D, henceforth Fick's diffusion constant. Let us consider a homogeneous neutral fluid. If Fick's law is combined with the continuity equation $\dot{n}(r,t) + \nabla \cdot J(r,t) = 0$, there results the diffusion equation $\dot{n}(r,t) - D\nabla^2 n(r,t) = 0$, where $\int n(r,t)\,d^3r = N$, the total number of particles.

Since the continuity equation is an exact equation, Fick's law and the diffusion equation are exactly equivalent. Putting aside a generic understanding [3], we might ask how valid really is the diffusion equation or Fick's law? If the diffusion equation could be derived from a microscopic theory, we might be able to establish the validity of Fick's law precisely.

There is another diffusion constant, say D_s, attributed to self-diffusion, given in terms of the mean square displacement at large times. Although originated in a random walk model of Brownian motion, it may simply be regarded a definition since there is no equation of motion involved [3]. It would thus seem that D_s need not always be the same as Fick's constant D. Yet it has been often so assumed, based on some heuristic arguments [2]. To our knowledge there are no general proofs of $D_s = D$. If the diffusion equation could be derived from first principles, we might be able to address this question also.

Scalar diffusion equation.—The density function $n(r,t)$ of Fick's law is a *macroscopic* variable. We may regard it as a nonequilibrium average of the local density operator $\hat{n}(r,t)$ at large r and t: $n(r,t) = \langle \hat{n}(r,t) \rangle_{r,t\to\infty}$. If a fluid is perturbed by a small external field, linear response theory may be applied to obtain the density function. For r and t both very large, we obtain an asymptotic relationship [4]: $\langle \hat{n}(r,t) \rangle = C\chi(r,t)$, where C is a constant and χ is the density-density response function. Thus if by Fick's law the density function satisfies the diffusion equation, so then too must the density-density correlation function.

Let $\hat{n}_k \equiv \hat{n}_k(t=0)$ be the Fourier transform (FT) of $\hat{n}(r,t=0)$ and introduce the density-density correlation function $R_k(t) = \langle \hat{n}_k(t)\hat{n}_{-k} \rangle / \langle \hat{n}_k \hat{n}_{-k} \rangle$, where now the brackets mean an equilibrium ensemble average after linear response theory. Then the diffusion equation for the density function goes over to a scalar diffusion equation of the form

$$\dot{R}_k(t) + k^2 D R_k(t) = 0\,, \tag{1}$$

where $k \to 0$ and $t \to \infty$ are implied [5], which is solved by

$$R_k(t) = \exp(-k^2 D t)\,. \tag{2}$$

The form of the above solution would appear independent of any details of a system and in fact independent of a system itself provided that it is homogeneous.

The arguments behind Fick's law or the diffusion equation are evidently physically based and not implausible. But can they be justified from a more fundamental theory? Can Fick's law in fact be deduced from such a theory? It is established that if a system is Hermitian, (2) is not an admissible solution for an exact microscopic equation of motion [6]. Although not correct for small t, (2) could possibly be understood as an asymptotic form of an admissible solution, e.g., hyperbolic secant [7]. We are thus led to think that (1) must itself be an asymptotic form of an exact equation of motion. We shall therefore see under what conditions (1) could result from it.

Exact equation of motion.—Let $A \equiv A(t=0)$ be a dynamical variable (e.g., $\hat{n}_k$) of a system defined by a Hamiltonian H, assumed to be Hermitian. The equation of motion for $A(t)$ is

$$\dot{A}(t) = i[H, A(t)] \equiv i\{HA(t) - A(t)H\}\,. \tag{3}$$

To extract long time behavior from (3), we shall transform the Heisenberg equation by the recurrence relations method [8]. (Since we are interested in $A(t)$ for $t \geq 0$ only, it is convenient to let $A(t) = 0$ if $t < 0$.)

Let $A(t)$ be a vector in a *realized* Hilbert space S of d dimensions. The formal solution may be expressed as an orthogonal expansion in this space S as

$$A(t) = \sum_{m=0}^{d-1} a_m(t) f_m\,. \tag{4}$$

Here f_m form a complete set of basis vectors that span S, i.e., $(f_m, f_{m'}) = 0$ if $m \neq m'$, where $(\,,\,)$ means an inner product defined on S. The coefficients a_m denote the projection of $A(t)$ on to the basis vectors at time t, hence they are time dependent functions. [Also $a_m(t < 0) = 0$.] If we were to choose $f_0 = A$, then $a_m(t = 0) = 1$ or 0 if $m = 0$ or $1, 2, \ldots, d - 1$.

The recurrence relations method for solving (3) rests on the following premises: If the space S is realized by the Kubo scalar product and $A(t)$ evolves according to (3), there are unique recurrence relations for f_m and a_m, referred to as RR1 and RR2, respectively: For $0 \leq m \leq d - 1$,

$$f_{m+1} = \dot{f}_m + \Delta_m f_{m-1}, \tag{5}$$

$$\Delta_{m+1} a_{m+1}(t) = -\dot{a}_m(t) + a_{m-1}(t), \tag{6}$$

where $\Delta_m = (f_m, f_m)/(f_{m-1})/(f_{m-1}, f_{m-1})$, $\Delta_0 \equiv 1$, and $f_{-1} = a_{-1} \equiv 0$. It is sufficient to solve the recurrence relations, for their solutions are also the solutions for (3). There is now a large body of literature on the application of this method [9,10].

Consider b_m defined with respect to a_m as follows: For $m = 1, 2, \ldots, d - 1$,

$$a_m(t) = \int_0^t b_m(t') a_0(t - t')\, dt', \tag{7}$$

[where $b_m(t < 0) \equiv 0$ also]. If (4) is differentiated and substituted by (7) after itself being differentiated, we arrive at after some rearrangements

$$\dot{A}(t) = B(t) - \int_0^t \varphi(t') A(t - t')\, dt', \tag{8}$$

where $B(t) = \sum_{m=1}^{d-1} b_m(t) f_m$ and $\varphi(t) = \Delta_1 b_1(t)$. Observe that $(B(t), f_0) = 0$ for $t \geq 0$, so that $B(t)$ is a vector in a subspace of S. Equation (8) is an exact transformation of (3), convenient for long times [11]; see especially 11(c).

Diffusion equation from an exact equation.—By taking the inner product $(\dot{A}(t), A)/(A, A)$, with $\dot{A}(t)$ given by (8), we obtain

$$\dot{a}_0(t) + \int_0^t \varphi(t') a_0(t - t')\, dt' = 0, \tag{9}$$

still an exact expression. There are two classes of solutions for (9), depending on d, itself model dependent. If $d < \infty$, the spectra contain isolated singularities only. The solutions are periodic functions and do not have asymptotic forms. If $d \to \infty$, the spectra contain branches on Riemann surfaces. The solutions are nonperiodic functions and have asymptotic forms [12].

We consider systems for which $d \to \infty$ only (condition 1). Then, for $t \to \infty$, (9) may be written as

$$\dot{a}_0(t) + \not{D}(t) a_0 \approx 0, \tag{10}$$

where

$$\not{D}(t) = \int_0^t \varphi(t)\, dt. \tag{11}$$

Since $\not{D}(t)$ depends on t, (10) is still not in the form of the scalar diffusion equation (1). But if $\varphi(t)$ vanishes sufficiently rapidly for large t, $\not{D}(t) \approx \not{D}(t \to \infty) \equiv \not{D}$. We shall consider only those systems for which $\not{D}(t)$ may be replaced by a constant $\not{D}$ (condition 2).

The exact equation (9) is thus reduced to the scalar diffusion equation (1) by conditions 1,2 for $t \to \infty$. We can identify $\not{D} = kDk = k^2 D$, which through (11) can give microscopic interpretation to Fick's diffusion constant. Condition 2 completely erases model dependence in (10). Even more serious, it brings out a solution seemingly inadmissible. How can it be made compatible with (4)? (Henceforth the dynamical quantities obtained by conditions 1,2 will have primes attached.)

We can reconstruct the space S' by determining the basis vectors f'_m by (5). From (1) and (10), $f'_0 = A'(t = 0)$, where $A'(t) = \exp(-\not{D}t)\hat{n}_k$, we obtain $f'_m = (-)^m m!\, \not{D}^m \hat{n}_k$, $m = 1, 2, \ldots$. Thus, $(f'_m, f'_{m'}) = (-)^{m+m'} m!\, m'!\, \not{D}^{m+m'} \langle \hat{n}_k \hat{n}_{-k} \rangle$, $m' < m = 1, 2, \ldots$. The only way they can be mutually orthogonal is if and only if $\not{D} = k^2 D \to 0$, that is, if $k^2 \to 0$ (corollary 1).

The reconstructed space S' is deformed. As $k \to 0$, its subspace shrinks and to order k^2,

$$A'(t) = a'_0(t) f'_0 + 0(k^2), \tag{12}$$

where $a'_0(t) = \exp(-\not{D}t)$ and $f'_0 = \hat{n}_{k \to 0}$. If (12) is to be an admissible solution of (3), it must also satisfy the Bessel equality $(A(t), A(t)) = (A, A)$ [7,8]. From this we obtain $k^2 D t = 0(1)$, where $k \to 0$, $t \to \infty$ (corollary 2).

We have thus shown that the Heisenberg equation of motion at long times can be reduced to Fick's law for systems satisfying conditions 1,2. The general requirements of the equation of motion result in corollaries 1,2 for the solution of the reduced equation. If $k \to 0$ (corollary 1) is applied to the continuity equation, we can also deduce that $\omega \to 0$, with ω the frequency. We can thus define Fick's *domain* as $k \to 0$ and $t \to \infty$ but $k^2 t =$ finite, also $\omega \to 0$, all deduced strictly from the equation of motion.

Self-diffusion.—The self-diffusion constant D_s is also an integral of the velocity autocorrelation function (VAF), known as the Green-Kubo (GK) formula. For a homogeneous system in one dimension (for simplicity) [13],

$$D_s \equiv \lim_{t \to \infty} \langle \{x(t) - x(0)\}^2 \rangle / 2t = \int_0^\infty \langle v(t) v(0) \rangle\, dt, \tag{13}$$

where $v = dx/dt$. Whatever its origin, clearly (13) is simply a definition. There are no conditions attached (except stationarity in the VAF in the GK formula). It is possible that $D_s = D$ in Fick's domain. Outside the domain, D_s may still exist but transport is not by Fick's diffusion.

Consider (11) now, to which we apply the identity $\varphi(t) \equiv \Delta_1 b_1(t) = (B(t), B)/(A, A)$. Then replacing $B(t)$ using (8), and with Fick's conditions (conditions 1,2 and corollaries 1,2) implied, we obtain a general expression for Fick's constant,

$$\not{D} = \int_0^\infty (\dot{A}'(t), \dot{A}')/(A', A')\, dt\,, \tag{14}$$

where the double integral term may be shown to vanish owing to condition 2 [14]. Now in 1D, $A \equiv \hat{n}_k = \frac{1}{L}\sum_j \exp(ikx_j)$, where L is the length. Ignoring noncommutativity (for simplicity), $\dot{A} = \frac{ik}{L}\sum_j v_j \exp(ikx_j)$. Using these results in (14) under Fick's conditions, we proceed classically and obtain

$$D = \int_0^\infty \Psi_{k\to 0}(t)\, dt\,, \tag{15}$$

where

$$\Psi_k(t) = \frac{\sum_{jj'}\langle v_j(t)\exp\{ik(x_j(t) - x_{j'})\}v_{j'}\rangle}{\sum_{jj'}\langle\exp\{ik(x_j - x_{j'})\}\rangle}\,. \tag{16}$$

If $k \longrightarrow 0$ (corollary 1) in $\Psi_k(t)$, it is similar to applying the dipole approximation in, e.g., classical fields interacting with atoms, where a quasistatic state prevails [15]. Thus we obtain $\Psi_{k\to 0}(t) = \langle v(t)v\rangle$ for a *homogeneous* system. Hence,

$$D = \int_0^\infty \langle v(t)v\rangle\, dt = D_s\,. \tag{17}$$

The two diffusion constants are thus the same but if and only if Fick's conditions are satisfied in self-diffusion also. If otherwise (e.g., long time tails in the VAF), D_s may still exist but not D.

Discussion.—Most interesting, perhaps, is what is being implied by Fick's conditions, listed below: (1) Transport in a superfluid state, also in a superconducting state (see below), is not by Fick's diffusion (by condition 1). (2) What is sometimes called anomalous transport [16] (i.e., slow decay in the VAF) is not by Fick's diffusion (by condition 2). (3) The solution of the diffusion equation $n(r, t = 0) = N\delta(r)$ [17] is to be excluded since small t (including $t = 0$) is outside Fick's domain. It may, however, be interpreted in the sense of the dipole approximation (corollary 1) as a system being seen under very long wavelengths. (4) Ohm's law may be viewed as Fick's law for charged systems, in which Fick's constant becomes the inverse resistivity or the conductivity. Since the current results from motions of particles, Fick's diffusion constant and the conductivity or mobility must be linearly related (Einstein relation) [18]. (5) Fick's domain is established purely by the requirements of the equation of motion (corollaries 1,2), not by relying on any heuristic arguments. (6) Fick's constant is calculable by first principles methods. Equation (11) shows that the expression for Fick's constant is equivalent to Kubo's conductivity formula [19,20]. (7) Fick's constant is bounded (by condition 2). Hence if the resistivity vanishes, the transport process ceases to be by Fick's diffusion.

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[1] See, e.g., A. M. Weinberg and E. P. Wigner, *Physical Theory of Neutron Chain Reactions* (University of Chicago, Chicago, Illinois, 1958), p. 194; W. Jost, *Diffusion in Solids, Liquids and Gases* (Academic, New York, 1970); J. J. Duderstadt and W. R. Martin, *Transport Theory* (Wiley, New York, 1979); R. J. Borg and G. J. Dienes, *Solid State Diffusion* (Academic, New York, 1988); F. Despa and M. Apostol, Solid State Commun. **94**, 153 (1995); J. Phys. Chem. Solids **57**, 1231 (1996).

[2] (a) R. Kubo, Rep. Prog. Phys. **29**, 235 (1966); (b) in *Statistical Mechanics of Equilibrium and Nonequilibrium,* edited by J. Meixnen (North-Holland, Amsterdam, 1965), pp. 93–97.

[3] (a) P. Resibois and M. De Leener, *Classical Kinetic Theory of Fluids* (Wiley, New York, 1977); (b) W. Marshall and R. D. Lowde, Rep. Prog. Phys. **31**, 705 (1968).

[4] If a system is perturbed by a small external field $h(r, t)$, the density function is given by linear response theory [see, e.g., Ref. 3(b), Eq. (49)] as

$$\langle\hat{n}(r, t)\rangle = 1/V \int_{-\infty}^{t}\int h(r', t')\chi(r - r', t - t')\, d^3r'\, dt',$$

where χ is the density-density response function and d^3r' is over the volume V of the system. Ignored is the background density $n = N/V$, which does not affect Fick's law. If we take r and $t \longrightarrow \infty$,

$$\langle\hat{n}(r, t)\rangle = \chi(r, t)/V \int_{-\infty}^{t\to\infty}\int h(r, t)\, d^3r\, dt = C\chi(r, t)\,,$$

where C is some constant not depending on r and t. In linear response theory, if Fourier transformed, $\chi_k(t) = i\langle[\hat{n}_k(t), \hat{n}_{-k}]\rangle$, $t > 0$, for a homogeneous system, where the brackets denote an ensemble average when $h = 0$.

[5] Modern transport theory *assumes* that relevant autocorrelation functions exist and that they satisfy the diffusion equation (DE) if macroscopically. See, e.g., S. W. Lovesey, *Dynamic Correlations* (Benjamin, Reading, 1980), pp. 27–28. Physically it makes sense, since diffusion results from fluctuations in density at long wavelengths and long times. See Ref. 2(b). It is well known that the random walk model also yields DE for the density-density correlation function. Since the continuum limit of a discrete lattice model is supposed to give a fluid, this microscopic theory lends weight to the validity of DE for the autocorrelation functions in a fluid. See P. A. Egelstaff, *Introduction to the Liquid State* (Academic, New York, 1967), pp. 118–123; also Ref. 3(a), pp. 23–29. If not at short distances, lattice spins are also assumed to diffuse, that is, the spin-spin correlation functions to satisfy DE. There is experimental support for it. See Ref. 3(b), pp. 747–749, also W. Marshall and S. W. Lovesey, *Theory of Thermal Neutron Scattering* (Oxford University Press, New York, 1971), Ch. 11. Critical dynamics of spin models are premised on the spin autocorrelation functions satisfying DE. See H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford University Press, New York, 1971), Ch. 13. Given the scalar form of DE, we can deduce the vector form: $(d/dt + k^2 D)\hat{n}_k(t) = 0$, $k \longrightarrow 0$ and $t \longrightarrow \infty$.

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[11] (a) This is an elementary derivation of the generalized Langevin equation, originally due to H. Mori [Prog. Theor. Phys. **34**, 399 (1965)]. (b) Also see M. H. Lee, J. Math. Phys. **24**, 2512 (1983). (c) For more detail on the relationship between recurrence relations and GLE, see M. H. Lee, Phys. Rev. E **62**, 1769 (2000).

[12] M. H. Lee, I. M. Kim, and R. Dekeyser, Phys. Rev. Lett. **52**, 1579 (1984).

[13] In n dimensions, $D_s = \langle\{\boldsymbol{r}(t) - \boldsymbol{r}(0)\}^2\rangle/2nt$, $t \longrightarrow \infty$. See Ref. 2(a), p. 257; Ref. 3(a), p. 277.

[14] For the double integral term, after taking $t \longrightarrow \infty$ and then using $\Delta_1 a_1(t) = -\dot{a}_0(t)$, see Eq. (6), we obtain: $\int_0^\infty [\dot{a}_0(t)\, d\not{D}(t)/dt]\, dt$. We have assumed that $a_0(t \longrightarrow \infty) = 0$. See Ref. 11(b). Now if condition 2 is applied, this term vanishes. Note also that if the primes were removed from the right-hand side of (14), it would vanish since the integral is proportional to $a_1(t = \infty)$. See Ref. 2(a), Eq. (8.10); Ref. 11(b).

[15] See, e.g., K. Smith, *Calculation of Atomic Collision Processes* (Wiley, New York, 1971), p. 90; J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1962), p. 269.

[16] See, e.g., G. Müller, Phys. Rev. Lett. **60**, 2785 (1988); A. Greiner, L. Reggiani, T. Kuhn, and L. Varan, Phys. Rev. Lett. **78**, 1114 (1997); J. Bonca and S. A. Trugman, Phys. Rev. Lett. **79**, 4874 (1997); A. Widom, Phys. Rev. A **3**, 1394 (1971); J. M. Porra, K.-G. Wang, and J. Masoliver, Phys. Rev. E **53**, 5872 (1996); O. F. de Alcantara Bonfim and G. Reiter, Phys. Rev. Lett. **69**, 367 (1992).

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[18] The validity of Ohm's law is underscored by the same conditions and corollaries of Fick's law. Thus, Ohm's law cannot apply in, e.g., the persistent current in a superconductor.

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[20] Subject to conditions 1,2, the dynamic diffusivity $\tilde{D}(z)$ ($z = i\omega + 0$, ω frequency, k suppressed), may be defined from (11) as $\tilde{\not{D}}(z) = \int_0^\infty e^{-zt} \varphi(t)\, dt$, where $\varphi(t) = \Delta_1 b_1(t)$. It reduces to D in Fick's domain, i.e., $\tilde{D}(z = 0) = D$, $k \longrightarrow 0$ implied. Also see Ref. 2(b). One can calculate $\tilde{D}(z)$ for a microscopic model. See M. H. Lee and J. Hong, Phys. Rev. Lett. **48**, 634 (1982); Physica (Amsterdam) **298B**, 301 (1985).