From Fick's Law to the Mean Free Path

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1 Problem

In 1855, A. Fick (professor of anatomy) presented the first quantitative theory of diffusion [1] of a mass density ρ of one species in a solvent liquid,

$$\frac{\partial \rho}{\partial t} = D\,\nabla^2 \rho, \tag{1}$$

where the constant D is now called the diffusion constant.[1] Fick modeled his theory on Fourier's analysis of heat flow (so successfully that now heat flow is typically considered as an example of diffusion). He did not offer a molecular interpretation of diffusion, although already in 1850 Clausius [3] had written on a molecular interpretation of heat. Furthermore, in 1859, Clausius [4] introduced the concept of the mean free path of gas molecules as an explanation as to why diffusion of smoke is slow, but little further connection was made between diffusion and the mean free path until 1900,[2] when Bachelier[3] developed a theory of financial speculation based on random steps [8], which he called "diffusion of probability".[4]

Fick considered steady-state solutions to eq. (1), *i.e.*, to $\nabla^2 \rho = 0$, and noted that these include linear variation of density (concentration) ρ accompanied by a steady mass flow. He gave no equation representing such solutions, but they obey,[5]

$$\mathbf{J}_m = -D\,\boldsymbol{\nabla}\rho, \tag{2}$$

where the (steady) mass flux $\mathbf{J}_m$ obeys $\boldsymbol{\nabla} \cdot \mathbf{J}_m = -\partial\rho/\partial t = 0$ in view of eq. (1).

Consider a molecular view in which the diffusing molecules have a characteristic microscopic velocity v that is large compared to the speed of the diffusion. Consider also the possibility of a linear density gradient with zero density at some location. Show that this hypothesis is not actually consistent with Fick's laws, but the contradiction manifests itself only on a very short length scale (now identified as the mean free path).

[1] Equation (1) has come to be called Fick's second law of diffusion. For a historical review, see [2].

[2] In 1860, Maxwell [5] discussed aspects of diffusion invoking the then-new concept of the mean free path, relating this not to Fickian diffusion, but rather to what is now called Maxwell-Stefan diffusion. He considered Fickian diffusion in 1868, pp. 199-204 of [6], without relating this to the mean free path.

[3] Bachelier [7] was a student of Poincaré.

[4] The term "random walk" was coined by Pearson in 1905 [9]. Rayleigh immediately noted [10] that a random walk obeys mathematics he had previously considered in 1880 [11] and 1889 [12] (without making any connection to diffusion).

[5] Although Fick did not write eq. (2) in his original paper, it has come to be known as Fick's first law of diffusion.

2 Solution

If the diffusion is due to microscopic motion of particles with a characteristic speed v, then the maximum possible mass flux is,

$$J_{m,\max} = \rho v, \tag{3}$$

in the unlikely event that all particles move in the same direction. If we also assume that it is possible to maintain zero density/concentration of the diffusing particles at some point, say, $x = 0$, with a constant, negative density gradient, $d\rho/dx = -K$ for, say, $-x_0 < x < 0$, then, the mass density has the form

$$\rho(x) = -Kx \qquad (-x_0 < x < 0), \tag{4}$$

and Fick's first law (2) takes the form,

$$J_m = -D\frac{d\rho}{dx} = KD \qquad (-x_0 < x < 0). \tag{5}$$

We expect that the steady mass flow (5) is less than the maximum (3) possible in our microscopic model,

$$J_m < J_{m,\max}, \qquad \Rightarrow \qquad KD < \rho v, \qquad \rho > \frac{KD}{v}\,. \tag{6}$$

In view of the density profile (4), this inequality is only satisfied for,

$$x < -\frac{D}{v}\,, \tag{7}$$

independent of the density gradient K.

Thus, Fick's law of diffusion, which is based on the notion of a continuous mass density, leads to an inconsistency at distances smaller than D/v.

This (short) length scale was belatedly recognized as the mean free path of the diffusing particles some 50 years after Fick stated his law.[6] The concept of a steady, macroscopic mass flow is only reasonable when averages are taken over distances larger than the microscopic mean free path.

References

[1] A. Fick, *On Liquid Diffusion*, Phil. Mag. **10**, 30 (1855),
http://kirkmcd.princeton.edu/examples/fluids/fick_pm_10_30_55.pdf

[2] J. Philibert, *One and a Half Century of Diffusion: Fick, Einstein, before and beyond*, Diff. Fund. **2**, 1 (2005), http://kirkmcd.princeton.edu/examples/fluids/philibert_df_2_1_05.pdf

[6]Strictly, the mean free path is $2D/v$, as could be inferred from the formalism in [8, 11, 12]. The earliest explicit statement of this may be on p. 778 of [13].

[3] R. Clausius, *On the Moving Force of Heat, and the Laws regarding the Nature of Heat itself which are deducible therefrom*, Phil. Mag. **2**, 1 (1851),
http://kirkmcd.princeton.edu/examples/statmech/clausius_pm_2_1_51.pdf

[4] R. Clausius, *On the Mean Length of the Paths described by the separate Molecules of Gaseous Bodies on the occurrence of Molecular Motion: together with some other Remarks upon the Mechanical Theory of Heat*, Phil. Mag. **17**, 81 (1859),
http://kirkmcd.princeton.edu/examples/statmech/clausius_pm_17_81_59.pdf

[5] J.C. Maxwell, *Illustrations of the Dynamical Theory of Gases.–Part I. On the Motions and Collisions of Perfectly Elastic Spheres*, Phil. Mag. **19**, 19 (1860),
http://kirkmcd.princeton.edu/examples/statmech/maxwell_pm_19_19_60.pdf
Phil. Mag. **20**, 21 (1860), http://kirkmcd.princeton.edu/examples/statmech/maxwell_pm_20_21_60.pdf

[6] J.C. Maxwell, *On the Dynamical Theory of Gases*, Phil. Mag. **35**, 129 (1868),
http://kirkmcd.princeton.edu/examples/statmech/maxwell_pm_35_129_68.pdf

[7] J. Bernstein, *Bachelier*, Am. J. Phys. **73**, 395 (2005),
http://kirkmcd.princeton.edu/examples/statmech/bernstein_ajp_73_395_05.pdf

[8] L. Bachelier, *Théorie de la spéculation*, Ann. Sci. Ecole Normal Sup. **17**, 21 (1900),
http://kirkmcd.princeton.edu/examples/statistics/bachelier_asens_17_21_00.pdf
http://kirkmcd.princeton.edu/examples/statistics/bachelier_asens_17_21_00_english.pdf

[9] K. Pearson, *The Problem of Random Walk*, Nature **72**, 294 (1905),
http://kirkmcd.princeton.edu/examples/statistics/pearson_nature_72_294_05.pdf

[10] Rayleigh, *The Problem of Random Walk*, Nature **72**, 318 (1905),
http://kirkmcd.princeton.edu/examples/statistics/rayleigh_nature_72_318_05.pdf

[11] Lord Rayleigh, *On the Resultant of a large Number of Vibrations of the same Pitch and of arbitrary Phase*, Phil. Mag. **10**, 73 (1880),
http://kirkmcd.princeton.edu/examples/statistics/rayleigh_pm_10_73_80.pdf

[12] Lord Rayleigh, *On James Bernouilli's Theorem in Probabilities*, Phil. Mag. **47**, 246 (1899), http://kirkmcd.princeton.edu/examples/statistics/rayleigh_pm_47_246_99.pdf

[13] M. von Smoluchowski, *Zur kinetischen Theorie der Brownschen Molekularbewegung und der Suspensionen*, Ann. Phys. **21**, 756 (1906),
http://kirkmcd.princeton.edu/examples/statmech/smoluchowski_ap_21_756_06.pdf