

February 28, 2013

COMMENTS ON DIFFUSION, DIFFUSIVITY AND DERIVATION OF HYPERBOLIC EQUATIONS DESCRIBING THE DIFFUSION PHENOMENA

Mental Experiment regarding 1D random walk

Consider a container of gas in thermal equilibrium and introduce a very small amount of the labeled gas (“special” gas) at a single spot in the container. The molecules are moving only by random motion as per the kinetic theory of gases. The ‘special’ or labeled gas molecules are identical in properties to the rest of the gas. To further simplify the treatment without loss in generality let us focus on a phenomenon occurring in one dimension along the x-axis. We assume that in the other directions perpendicular to x-axis there are no concentration gradients of the special gas.

Consider now an imaginary plane of unit area A

(Insert a diagram as sketched in class)

perpendicular to the x- direction and compute the net flow of the molecules of the special gas across that plane during time Δt . In order to count the number of special molecules that cross the plane in a time interval Δt , we first count the number of molecules in a volume $v\Delta t$ adjacent to the plane. Here v is the average actual molecular velocity in the x- direction.

The number of special molecules that passes from left to right is $n_-v\Delta t$ and from right to left $n_+v\Delta t$. Here, n_- , n_+ are the number density (number per unit volume) of special molecules to the left and to the right of our dividing plane at X.

The molecular flux, also called net molecular current (molecule/cm²s) from left to right, i.e. in the direction of the x-axis then is

$$j_x = \frac{n_-v\Delta t - n_+v\Delta t}{\Delta t} = (n_- - n_+)v \quad (1)$$

The question arises where do we count our molecular densities, n_- , n_+ ? We must count at positions where molecules started their flight, i.e at a distance equal to the mean free path ℓ away from the plane at X.

Now we would like to use a continuous function, c , to represent the concentration of the special molecules. Then

$$n_+ - n_- = \frac{dc}{dx} \Delta x = 2\ell \frac{dc}{dx} \quad (2)$$

Ignore the factor 2 and substitute eq. (2) into eq. (1).

$$j_x = -\ell v \frac{dc}{dx} = -D \frac{dc}{dx} \quad (3)$$

Hence, molecular diffusivity D is proportional to the mean free path and mean molecular velocity as indicated by eq. (4)

$$D \propto \ell v \quad (4)$$

The above development uses many approximations, v instead of v_x , n_+ and n_- measured at distance ℓ , while for molecules that do not travel perpendicularly to our plane it is a slant distance that counts. A more careful analysis reveals

$$j_x = \frac{1}{3} v \ell \frac{dc}{dx} \quad (3a)$$

so that

$$D = \frac{1}{3} \ell v \quad (4a)$$

The mean free path ℓ expresses how far the molecules travel between collisions (on the average).

We can also talk about the average time between collisions, τ . It is known that

$$\ell = \tau v \quad (5)$$

By collision cross section we mean the area within which the center of our particle (molecule) must be located if it is to collide with a particular other molecule.

$\sigma_c^2 = \pi(r_1^2 + r_2^2)$. Then

$$\sigma_c^2 n_o \ell = 1 \quad (6)$$

There is one collision on the average when the particle goes a distance ℓ in which the gathering molecules could just cover the total area.

Some additional comments:

If we have special molecules (S) and background molecules, then there is a specific force F acting on S imparting an average velocity on S.

$$v_{drift} = \frac{F\tau}{m} \quad (7)$$

Drift velocity is proportional to this force! (no general name for constant of proportionality). In electrical problems where $\vec{F} = q\vec{E}$ (charge x field)

$v_{drift} = \mu q\vec{E}$ where μ is mobility).

Let us adopt that name

$$v_{drift} = \mu F \quad (7a)$$

$$\text{Then } \mu = \frac{\tau}{m} \quad (8).$$

Ionic conductivity

$$v_{drift} = \mu q E = \mu q \frac{V}{b}$$

($v_{drift} \times t$) ions arrive at a plate. There are c_i ions per unit volume. The number reaching the plate is ($c_i A v_{drift} t$). Each ion carries charge q. The charge collected =

$$q c_i A v_{drift} t. \text{ Current } I = \frac{\text{charge collected}}{\text{unit time}} = q c_i A v_{drift}$$

$$I = \mu q^2 c_i \frac{V}{b} = \frac{V}{R}$$

$$R = \frac{b}{\mu q^2 c_i}$$

Relationship between resistances and molecular properties

$$\mu = \frac{\tau}{m}$$

So referring to the diffusion flux of (3a) we can represent it as:

$$j_x = \mu_i kT \frac{dc}{dx} \quad (3b)$$

$$D = \mu_i kT \quad (4b)$$

The diffusion coefficient is kT times the mobility coefficient.

This is called Ficks first law and the expression for the flux is repeated below.

$$j_x = -D \frac{dc}{dx}$$

Ficks 2nd law then states:

$$(Acc) = (in) - (out)$$

$$\Delta x \frac{\partial c}{\partial t} = j_x|_x - j_x|_{x+\Delta x}$$

Upon dividing with Δx and taking the limit one gets:

$$\frac{\partial c}{\partial t} = \frac{\partial j_x}{\partial x} = D \frac{\partial^2 c}{\partial x^2}$$

This is a 1D representation of the Ficks 2nd law of diffusion.

As a consequence of the nature of the above, the response to an impulse at $x = 0$ at $t = 0$ is felt instantaneously at all x (although exponentially small).

The infinite speed of signal propagation by diffusion equation is a paradox due to the theoretical nature of the diffusion equation. However, the molecules do not cover the free path λ instantaneously. So the time when concentrations are counted at the left and right side of the plane at X differs from the time when the molecular current is measured by approximately the mean time between collisions or $\tau = \ell / v$. Mathematically, the flux is evaluated at $t + \tau$ based on concentration difference that existed at t .

$$j_x(t + \tau) = -D \frac{\partial c(t)}{\partial x} \quad (9)$$

This yields (by expansion in Taylor series)

$$j_x(t + \tau) = j_x(t) + \frac{\partial j_x}{\partial t} \tau = -D \frac{\partial c}{\partial x} \quad (10)$$

This formulation avoids the infinite speed of propagation.

It has been derived by

Maxwell (1867)

Fick (1926)

Davidov (1935)

Goldstein (1951)

Davies (1954)

Cattineo (1948)

Vermotte (1958)

Alternative derivation of Ficks law

Derivation of Ficks law is only valid if c varies slowly so that one term Taylor expansion is permissible in equation (10). When that is not the case and concentration changes noticeably during τ or on the length scale ℓ , a more general approach is needed.

- Consider 1D general case when c can change considerably during a time period of τ or on the length of mean path λ .
- No convective flow

Consider particles in random walk along x axis, v_+ , v_- are velocities in each direction. Particle interacts instantaneously with surroundings and as a consequence changes directions. Each particle has the probability p_+ that it will move with v_+ and probability $p_- = 1 - p_+$ that it will move with v_- . Time spent moving in a certain direction is a random variable characterized by probability depending on this period.

We count again particles crossing from left to right and those from right to left, at a plane at x . The particles reaching x from the left at time t had their last collision at the time $t - \eta$, and at the point $x - \eta v_+$ ($\eta > 0$) and obtained the velocity v_+ in the direction of the plane at x , moved during time η without collisions and did not disappear during time of travel due to reaction.

The total number of collisions at point $x - \eta v_+$ and at time $t - \eta$, in terms of continuous function $c(x,t)$ describing the distribution of particles along the x -axis, is equal to $c(x - \eta v_+, t - \eta) / \tau$ where τ is the mean period of time between collisions.

The flux of particles at x and at t from left to right is

$$j_+(x, t) = \frac{p_+ v_+}{\tau} \int_0^{\infty} G(\eta) H(\eta) c(x - \eta v_+, t - \eta) d\eta \quad (11)$$

where

$G(\eta)$ = probability that a particle survives a time η without collisions

$H(\eta)$ = probability that a particle survives a time η without reacting.

Similarly

$$j_-(x,t) = \frac{p_- v_-}{\tau} \int_0^{\infty} G(\eta) H(\eta) c(x + \eta v_-; t - \eta) d\eta \quad (12)$$

If the probability that a particle moves without collision during time longer than a certain value does not depend on the history of particle movement, then for arbitrary t_1 and t_2 .

$$G(t_1)G(t_2) = G(t_1 + t_2) \quad (13)$$

so that

$$G(t) = e^{-t/\tau}$$

If we consider a first order reaction, then

$$H(t) = e^{-kt} \quad (14)$$

Now

Mass balance requires

$$p_+ v_+ = p_- v_- \quad (15a)$$

The concentration is defined by

$$c = \frac{j_+}{v_+} + \frac{j_-}{v_-} \quad (15b)$$

The net flux in the positive x-direction is:

$$j = j_+ - j_- \quad (15c)$$

Probabilities of all permissible events sum to one:

$$p_+ + p_- = 1 \quad (15d)$$

Consider now j_+ and for ease of writing drop the subscript + for now. Then, upon substituting equations (13) and (14) into equation (12) we get:

$$j = \frac{p v}{\tau} \int_0^{\infty} e^{-a\eta} c(x - \eta v, t - \eta) d\eta \quad (16)$$

with

$$a = \left(k + \frac{1}{\tau}\right) \quad (17)$$

Integration by parts of eq. (16) can be performed as indicated below:

$$dv = e^{-a\eta} d\eta \quad v = -\frac{1}{a}e^{-a\eta}$$

$$u = c(x - \eta v, t - \eta) \quad du = (-v \frac{\partial c}{\partial x} - \frac{\partial c}{\partial t})d\eta$$

and yields:

$$j = \frac{pv}{\tau} \left[-\frac{1}{a} e^{-a\eta} c(x - \eta v, t - \eta) \int_0^{\infty} -\frac{1}{a} \int_0^{\infty} e^{-a\eta} (v \frac{\partial c}{\partial x} + \frac{\partial c}{\partial t}) d\eta \right] \quad (18)$$

Upon substituting the integration limit in the first term above and splitting the second term into two, on multiplication by our constant 'a' one gets:

$$aj = \frac{pv}{\tau} c(x, t) - \frac{pv}{\tau} v \int_0^{\infty} e^{-a\eta} \frac{\partial c}{\partial x} (x - \eta v, t - \eta) d\eta - \frac{pv}{\tau} \int_0^{\infty} e^{a\eta} \frac{\partial c}{\partial t} d\eta \quad (19)$$

Differentiation of eq. (16) with respect to position and time yields:

$$\frac{\partial j}{\partial x} = \frac{pv}{\tau} \int_0^{\infty} e^{-a\eta} \frac{\partial c}{\partial x} d\eta \quad (20)$$

$$\frac{\partial j}{\partial t} = \frac{pv}{\tau} \int_0^{\infty} e^{-a\eta} \frac{\partial c}{\partial t} d\eta \quad (21)$$

Substitution of eqs. (20) and (21) into eq. (19) yields:

$$aj = \frac{pv}{\tau} c - v \frac{\partial j}{\partial x} - \frac{\partial j}{\partial t} \quad (22)$$

Now this has been derived and is valid for j_+ . A similar expression, only with the sign for

$\frac{\partial j}{\partial x}$ changed, because now one deals with $c(x + \eta v_-; t - \eta)$, can be derived for j_- . The

resulting equations are shown below:

$$(k + \frac{1}{\tau})j_+ = \frac{p_+ v_+}{\tau} c - \frac{\partial j_+}{\partial t} - v_+ \frac{\partial j_+}{\partial x} \quad (23)$$

$$(k + \frac{1}{\tau})j_- = \frac{p_- v_-}{\tau} c - \frac{\partial j_-}{\partial t} + v_- \frac{\partial j_-}{\partial x} \quad (24)$$

Divide eq.(23) with v_+ and (24) with v_- and add them up.

$$\left(k + \frac{1}{\tau}\right) \left(\frac{j_+}{v_+} + \frac{j_-}{v_-} \right) = \left(\frac{p_+}{\tau} + \frac{p_-}{\tau} \right) c - \left(\frac{1}{v_+} \frac{\tilde{q}_+}{\tilde{a}} + \frac{1}{v_-} \frac{\tilde{q}_-}{\tilde{a}} \right) - \left(\frac{\tilde{q}_+}{\tilde{a}} - \frac{\tilde{q}_-}{\tilde{a}} \right) \quad (25)$$

Recall eqs. (15b), (15c) and (15d) and use them in eq. (25) to obtain:

$$\left(k + \frac{1}{\tau}\right) c = \frac{1}{\tau} c - \frac{\tilde{a}}{\tilde{a}} - \frac{\tilde{q}}{\tilde{a}} \quad (26)$$

Upon cancellation of a common term this becomes:

$$\frac{\tilde{a}}{\tilde{a}} + \frac{\tilde{q}}{\tilde{a}} + kc = 0 \quad (27)$$

Subtract now eq. (24) from eq. (23) to get:

$$\left(k + \frac{1}{\tau}\right) (j_+ - j_-) = \left(\frac{p_+ v_+}{\tau} - \frac{p_- v_-}{\tau} \right) c - \frac{\partial}{\tilde{a}} (j_+ - j_-) - v_+ \frac{\tilde{q}_+}{\tilde{a}} - v_- \frac{\tilde{q}_-}{\tilde{a}} \quad (28)$$

Upon substitution of eqs. (15a) (15c) we get:

$$\left(k + \frac{1}{\tau}\right) j = -\frac{\tilde{q}}{\tilde{a}} - v_+ \frac{\tilde{q}_+}{\tilde{a}} - v_- \frac{\tilde{q}_-}{\tilde{a}} \quad (29)$$

Now we can add and subtract the following terms, given by expression (30), hence effectively adding zero) to eq. (29).

$$+v_+ \frac{\tilde{q}_-}{\tilde{a}} - v_+ \frac{\tilde{q}_-}{\tilde{a}} + v_- \frac{\tilde{q}_+}{\tilde{a}} - v_- \frac{\tilde{q}_+}{\tilde{a}} \quad (30)$$

Upon, use of (15c) and regrouping we get equation (31):

$$\left(k + \frac{1}{\tau}\right) j = -\frac{\tilde{q}}{\tilde{a}} - v_+ \frac{\tilde{q}}{\tilde{a}} + v_- \frac{\tilde{q}}{\tilde{a}} - v_- \frac{\tilde{q}_+}{\tilde{a}} - v_+ \frac{\tilde{q}_-}{\tilde{a}} \quad (31)$$

However from eq. (15b) it follows that

$$v_+ v_- \frac{\tilde{a}}{\tilde{a}} = v_- \frac{\tilde{q}_+}{\tilde{a}} + v_+ \frac{\tilde{q}_-}{\tilde{a}} \quad (32)$$

Substitution into eq. (31) yields:

$$\left(k + \frac{1}{\tau}\right) j = -\frac{\tilde{q}}{\tilde{a}} - (v_+ - v_-) \frac{\tilde{q}}{\tilde{a}} - v_+ v_- \frac{\tilde{a}}{\tilde{a}} \quad (33)$$

Upon multiplication by τ we get:

$$(k\tau + 1)j + \tau \frac{\partial j}{\partial t} + (v_+ - v_-)\tau \frac{\partial j}{\partial x} + v_+v_-\tau \frac{\partial c}{\partial x} = 0 \quad (34)$$

In summary, hyperbolic equations with finite speed of propagation describe the “diffusion” process more accurately. These equations are:

$$\frac{\partial c}{\partial t} + \frac{\partial j}{\partial x} + kc = 0 \quad (35)$$

$$(1 + k\tau)j + \tau \frac{\partial j}{\partial t} + \tau(v_+ - v_-)\frac{\partial j}{\partial x} + v_+v_-\tau \frac{\partial c}{\partial x} = 0 \quad (36)$$

Thus, equations (35) and (36) need to be solved simultaneously for concentration, $c(x,t)$, and for the flux, $j(x,t)$. this forms a system of hyperbolic equations and the speed of transmission of information is acknowledged as finite!

Read treatment by Richard Feynman in “ The Feynman Lectures on Physics” by Feynman, Leighton and Sands.

Read applications by Westerterp and colleagues to packed bed and other chemical engineering equipment.

. Wave model for longitudinal dispersion: analysis and applications

[Westerterp, K.R.](#) (Twente Univ of Technology); [Dil'man, V.V.](#); [Kronberg, A.E.](#);

[Benneker, A.H.](#) Source: *AIChE Journal*, v 41, n 9, Sep, 1995, p 2029-2039

ISSN: 0001-1541 CODEN: AICEAC

Publisher: AIChE

Abstract: An analysis and applications of the wave model for longitudinal dispersion are presented. Asymptotic forms of the wave model are considered and analytical solutions of typical linear stationary and nonstationary problems of chemical reactor engineering interest are obtained and compared to those for the Fickian dispersion model. The wave model leads to efficient analytical solutions for linear problems, which in principle differ from the solutions of the Fickian dispersion model; only for slowly varying concentration fields do the solutions of both models approach each other. Spatial and time moments of the concentration distribution are obtained for pulse-dispersion problems; the first three spatial moments of the mean, variance, and skewness have exact, large-time asymptotic forms in the case of Taylor dispersion. Old experiments that could not be explained with the standard dispersion model are reconsidered and explained: the change with time of the variance of a concentration

pulse when the flow direction is reversed and the difference in values of the apparent axial dispersion coefficient and the back-mixing coefficient in a rotating disk contactor. The experimental determination of model parameters is discussed. (29 refs.)

Wave model for longitudinal dispersion: Application to the laminar-flow tubular reactor

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Source: *AIChE Journal*, v 42, n 11, Nov, 1996, p 3133-3145

ISSN: 0001-1541 **CODEN:** AICEAC

Publisher: AIChE

Abstract: The wave model for longitudinal dispersion, published elsewhere as an alternative to the commonly used dispersed plug-flow model, is applied to the classic case of the laminar-flow tubular reactor. The results are compared in a wide range of situations to predictions by the dispersed plug-flow model as well as to exact numerical calculations with the 2-D model of the reactor and to other available methods. In many practical cases, the solutions of the wave model agree closely with the exact data. The wave model has a much wider region of validity than the dispersed plug-flow model, has a distinct physical background, and is easier to use for reactor calculations. This provides additional support to the theory developed elsewhere. The properties and the applicability of the wave model to situations with rapidly changing concentration fields are discussed. Constraints to be satisfied are established to use the new theory with confidence for arbitrary initial and boundary conditions.