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How to reach the Fick's second law of diffusion from a general theory

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TVBM-7170

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How to Reach the Fick's Second Law of Diffusion from a General Theory

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Abstract

1 Balance of mass for several components, the mixture theory

1.1 Balance of mass for individual components including for the possibilities of chemical reactions

The balance of mass for a mixture consists of two parts: The first is the balance of mass for each constituent, and the second the balance of mass for the mixture as a whole.

Associated with each constituent is a quantity called its *mass supply*, denoted \hat{c}_a . The fact that mass can be exchanged among the constituents, for example due to chemical reactions must be considered to guarantee mass balance for the individual constituents.

The mass density ρ for the whole mixture is defined to be the sum of the individual mass densities ρ_a for the constituents, i.e.

$$\rho = \rho(\mathbf{x}, t) = \sum_{a=1}^{\mathfrak{R}} \rho_a \quad (1)$$

The mass concentration c_a is defined as

$$c_a = c_a(\mathbf{x}, t) = \rho_a / \rho \quad (2)$$

From (1) and (2) it follows that

$$\sum_{a=1}^{\mathfrak{R}} c_a = 1 \quad (3)$$

must hold.

A mean velocity $\dot{\mathbf{x}}$ is introduced as

$$\dot{\mathbf{x}} = \dot{\mathbf{x}}(\mathbf{x}, t) = \frac{1}{\rho} \sum_{a=1}^{\mathfrak{R}} \rho_a \mathbf{x}'_a \quad (4)$$

where \mathbf{x}'_a is the velocity of the a th constituent following the motion of the same constituent.

Further a so-called diffusion velocity \mathbf{u}_a is introduced as

$$\mathbf{u}_a = \mathbf{x}'_a - \dot{\mathbf{x}} \quad (5)$$

which is the velocity of the a th constituent in relation to the velocity of the mixture $\dot{\mathbf{x}}$.

If \mathfrak{R} is a fixed spatial volume and $\partial\mathfrak{R}$ is the boundary area of the volume \mathfrak{R} , the axiom of balance for the a th constituent is

$$\frac{\partial}{\partial t} \int_{\mathfrak{R}} \rho_a dv = - \oint_{\partial\mathfrak{R}} \rho_a \mathbf{x}'_a \cdot ds + \int_{\mathfrak{R}} \hat{c}_a dv \quad (6)$$

where dv is the element of volume and ds the outward-drawn normal vector element of area. The rate of change of the mass density in a fixed volume must be balanced by the mass density flow through the boundary of the considered volume plus the production of mass due to supply from the other constituents present in the volume \mathfrak{R} .

The axiom of balance of mass for the mixture is

$$\frac{\partial}{\partial t} \int_{\mathfrak{R}} \rho dv = - \oint_{\partial\mathfrak{R}} \rho \dot{\mathbf{x}} \cdot ds \quad (7)$$

If the divergence theorem is used on the first term on the right-hand side of (6), that is

$$\oint_{\partial\mathfrak{R}} \rho_a \mathbf{x}'_a \cdot ds = \int_{\mathfrak{R}} \text{div}(\rho_a \mathbf{x}'_a) dv \quad (8)$$

the alternative form of (6) becomes

$$\int_{\mathfrak{R}} \left[\frac{\partial \rho_a}{\partial t} + \text{div}(\rho_a \mathbf{x}'_a) - \hat{c}_a \right] dv = 0 \quad (9)$$

Assuming that (9) is valid for all parts of the volume \mathfrak{R} , the local form of balance of mass for the a th constituent is

$$\frac{\partial \rho_a}{\partial t} + \operatorname{div}(\rho_a \mathbf{x}'_a) = \hat{c}_a \quad (10)$$

The same argument is applied to the surface integral in (7), i.e. the divergence theorem gives

$$\oint_{\partial \mathfrak{R}} \rho \dot{\mathbf{x}} \cdot d\mathbf{s} = \int_{\mathfrak{R}} \operatorname{div}(\rho \dot{\mathbf{x}}) dv \quad (11)$$

Hence, the balance of mass for the mixture (7) can be written as

$$\int_{\mathfrak{R}} \left[\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \dot{\mathbf{x}}) \right] dv = 0 \quad (12)$$

That is, the local form is

$$\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \dot{\mathbf{x}}) = 0 \quad (13)$$

It is supposed that a summation of the individual constituent equation describing balance of mass should result in the balance of mass for the whole mixture. To see under which conditions this is true consider the summation of all constituent equations (10), i.e.

$$\frac{\partial}{\partial t} \sum_{a=1}^{\mathfrak{R}} \rho_a + \operatorname{div} \sum_{a=1}^{\mathfrak{R}} (\rho_a \mathbf{x}'_a) - \sum_{a=1}^{\mathfrak{R}} \hat{c}_a = 0 \quad (14)$$

Using (1), i.e. $\rho = \sum_{a=1}^{\mathfrak{R}} \rho_a$, and (4), i.e. $\rho \dot{\mathbf{x}} = \sum_{a=1}^{\mathfrak{R}} \rho_a \mathbf{x}'_a$ the expression (14) takes the form

$$\frac{\partial \rho}{\partial t} + \operatorname{div} \rho \dot{\mathbf{x}} - \sum_{a=1}^{\mathfrak{R}} \hat{c}_a = 0 \quad (15)$$

In order to assure that (13) and (15) to be identical one must have that

$$\sum_{a=1}^{\mathfrak{R}} \hat{c}_a = 0 \quad (16)$$

Thus, balance of mass for the mixture is equal to the requirement that there be no net production of mass in \mathfrak{R} .

In the following it will be explained how the mass balance equations can be rewritten in terms of mass concentrations c_a instead of mass density ρ_a .

By using $\mathbf{u}_a = \mathbf{x}'_a - \dot{\mathbf{x}}$, i.e. (5), the mass balance for the a th constituent (10) can be rewritten as

$$\frac{\partial \rho_a}{\partial t} + \operatorname{div}(\rho_a \dot{\mathbf{x}}) = -\operatorname{div}(\rho_a \mathbf{u}_a) + \hat{c}_a \quad (17)$$

That is, $\operatorname{div}(\rho_a \mathbf{x}'_a) = \operatorname{div}(\rho_a \dot{\mathbf{x}}) + \operatorname{div}(\rho_a \mathbf{u}_a)$ is used. In accordance with (2), i.e. $\rho_a = \rho c_a$, the first term on the left-hand side of (17) is

$$\frac{\partial \rho_a}{\partial t} = \frac{\partial (c_a \rho)}{\partial t} = c_a \frac{\partial \rho}{\partial t} + \rho \frac{\partial c_a}{\partial t} \quad (18)$$

where the rule of differentiating a product is used. The second term on the left-hand side of (17) is rewritten by use of (2) as

$$\operatorname{div}(\rho_a \dot{\mathbf{x}}) = \operatorname{div}(c_a \rho \dot{\mathbf{x}}) = c_a \operatorname{div}(\rho \dot{\mathbf{x}}) + \rho \dot{\mathbf{x}} \cdot \operatorname{grad} c_a \quad (19)$$

If (18) and (19) are inserted into (17), that is, the expressions for $\operatorname{div}(\rho_a \dot{\mathbf{x}})$ and $\partial \rho_a / \partial t$ in (18) and (19) are inserted into (17) to yield

$$c_a \left[\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \dot{\mathbf{x}}) \right] + \rho \frac{\partial c_a}{\partial t} + \rho \dot{\mathbf{x}} \cdot \operatorname{grad} c_a = -\operatorname{div}(\rho_a \mathbf{u}_a) + \hat{c}_a \quad (20)$$

The terms in brackets in (20) cancels due to the axiom of mass balance for the mixture (13). This means that (20) can be written as

$$\rho \dot{c}_a = -\operatorname{div}(\rho_a \mathbf{u}_a) + \hat{c}_a \quad (21)$$

where \dot{c}_a is the mass concentration following the motion defined by $\dot{\mathbf{x}}$, i.e.

$$\dot{c}_a = \frac{\partial c_a}{\partial t} + \dot{\mathbf{x}} \cdot \operatorname{grad} c_a \quad (22)$$

The equation (21) holds for all constituents. Equation (21) is an alternative version of (10) where the mass densities ρ_a is used instead of the mass concentrations c_a .

By using the identity

$$\operatorname{div}(\rho_a \mathbf{x}'_a) = \rho_a \operatorname{div} \mathbf{x}'_a + \mathbf{x}'_a \cdot \operatorname{grad} \rho_a \quad (23)$$

together with the definition

$$\Gamma' = \frac{\partial \Gamma}{\partial t}(\mathbf{x}, t) + [\operatorname{grad} \Gamma(\mathbf{x}, t)] \mathbf{x}'_a(\mathbf{x}, t) \quad (24)$$

with $\Gamma'_a = \rho'_a$, i.e.

$$\rho'_a = \frac{\partial \rho_a}{\partial t} + \text{grad}(\rho_a) \cdot \mathbf{x}'_a \quad (25)$$

yet another version of (10) is obtained as

$$\rho'_a + \rho_a \text{div} \mathbf{x}'_a = \hat{c}_a \quad (26)$$

Where the material time derivative is used together with the mass density description.

1.2 Summary of the balance of mass for individual constituents

The general mass balance equation for chemically reacting constituents was derived in the previous section. This equation is often referred to as the diffusion-convection equation with mass exchange.. The following was obtained

$$\rho \frac{\partial c_a}{\partial t} + \rho \dot{\mathbf{x}} \cdot \text{grad} c_a = -\text{div}(\rho_a \mathbf{u}_a) + \hat{c}_a \quad (27)$$

$$\sum_{a=1}^{\mathfrak{R}} \hat{c}_a = 0 \quad (28)$$

1.3 Fick's first and second law of diffusion

The Fick's first law, is not actually a physical 'law' by rather an equation of state or equally a constitutive equation for the mass density flow $\rho_a \mathbf{u}_a$, as

$$\rho_a \mathbf{u}_a = -D_a \text{grad} c_a; \quad \text{Fick's first 'law'} \quad (29)$$

where D_a is a material property referred to as the diffusion coefficient.

The Fick's second law is an approximation to the general mass balance equation (27) together with the material assumption (29). In order to obtain the Fick's second 'law' the mean velocity $\dot{\mathbf{x}}$ must vanish, i.e. $\dot{\mathbf{x}} \approx 0$ and no chemical reactions or equally no mass exchange is considered between the different constituent, i.e. $\hat{c}_{a=1, \dots, \mathfrak{R}} = 0$. The approximative mass balance equation is then

$$\rho \frac{\partial c_a}{\partial t} + \text{div}(\rho_a \mathbf{u}_a) = 0 \quad (30)$$

And the Fick's second 'law' is then obtained by combining the material assumption (29) and the approximative mass balance equation (30) to yield

$$\rho \frac{\partial c_a}{\partial t} = \text{div}(D_a \text{grad} c_a); \text{ Fick's second 'law'} \quad (31)$$

This is a field equation determining the mass concentration field $c_a(\mathbf{x}, t)$ for arbitrary geometries where boundary conditions in terms of inflow of mass or description of the mass concentration is introduced. The field equation (31) is useful in situations where the mean velocity is small $\dot{\mathbf{x}} \approx 0$ and when no chemical reactions or equally no mass exchange takes place between constituents. Typical applications is the calculation of concentration fields for dissolved diffusing inert substances with very low concentration.