



# FINITE SPEED OF DIFFUSION PROPAGATION IN A TWO-COMPONENT CONTINUOUS MEDIUM<sup>†</sup>

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It is shown that the problem of the finite propagation speed of disturbances of the impurity concentration in a multicomponent fluid may be related to the corresponding separation of energy into the internal and macroscopic. If the total kinetic energy of the mixture of components combined with the potential energy of external forces is taken as the macroscopic energy, then, within the framework of the linear local equilibrium thermodynamics of irreversible processes, the diffusion is described by equations of the hyperbolic type. Because of the relative shortness of the local relaxation time for fairly large-scale disturbances, the equations are simplified to the usual diffusion equations of the parabolic type. © 2001 Elsevier Science Ltd. All rights reserved.

The physical concepts concerning the finiteness of the propagation speed of signals often make it necessary to revise the usual theories of diffusion and heat conduction, the conclusions of which contradict the finiteness expected [1, 2]. It seems that a hyperbolic diffusion equation (the telegraph equation) free from the paradox of an infinite speed was first obtained in an analysis of random walks by Fock as far back as 1926 [3]. The necessary thermodynamic revision occurred much later and involved a generalization of the thermodynamics of irreversible processes that had been formulated by that time. However, it was often formal [4] or based on the axiomatic introduction of a memory into the relations between the thermodynamic fluxes and forces [5], upon the introduction of dissipative thermodynamic fluxes into a number of the parameters determining the thermodynamic state [6] and, finally, upon the formal axiomatics of “rational thermodynamics” [7]. Below it will be shown that a significant generalization of the thermodynamics of irreversible processes is not necessary in this case – it is sufficient, when using the traditional local equilibrium thermodynamics of irreversible processes in the theory of continuous media, to apply a non-standard and, it seems, a more acceptable splitting of the total energy density of the mixture into kinetic and internal. The question as to a similar improvement in traditional construction with the kinetic energy of diffusion separated from the total energy, rather than the kinetic energy of the centre of mass of the mixture, was correctly raised in [8] (see Chapter III, §4); however, the corollaries of such a splitting were not analysed, in particular the hyperbolic nature of the corresponding diffusion equation.

For each point mass of a multi component continuous medium, the individual components are characterised by mass densities  $\rho_{(n)}$ , velocities  $\mathbf{v}_{(n)}$ , and so on (to avoid confusion between the numbers of the components of the medium and the vector and tensor indices, we will enclose the former in parenthesis). We will confine ourselves to an examination of fluid mixtures with two components without chemical reactions. Then the total density and momentum are obtained by summation, in which  $n$  takes values of 1 and 2, and the equations of conservation of mass of the individual components and of the mixture are written in the form (below, the summation sign represents summation with respect to the components)

$$\frac{\partial \rho_{(n)}}{\partial t} + \operatorname{div}(\rho_{(n)} \mathbf{v}_{(n)}) = 0, \quad \frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \mathbf{v}) = 0$$

$$\rho = \sum \rho_{(n)}, \quad \rho \mathbf{v} = \sum \rho_{(n)} \mathbf{v}_{(n)}$$

When the mass concentrations of the components and the relative velocities (with respect to the motion of the centre of mass) and “diffusion fluxes”

$$c_{(n)} \equiv \rho_{(n)} / \rho, \quad \mathbf{w}_{(n)} \equiv \mathbf{v}_{(n)} - \mathbf{v}, \quad \mathbf{J}_{(n)}^c \equiv \rho_{(n)} \mathbf{w}_{(n)} \quad (1)$$

are used, they can be rewritten as follows:

$$\rho \frac{dc_{(n)}}{dt} + \operatorname{div} \mathbf{J}_{(n)}^c = \frac{\partial(\rho c_{(n)})}{\partial t} + \operatorname{div}(\rho c_{(n)} \mathbf{v} + \mathbf{J}_{(n)}^c) = 0, \quad \sum c_{(n)} = 1, \quad \sum \mathbf{J}_{(n)}^c = 0 \quad (2)$$

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The main balance relations, reflecting the other laws of conservation when there are no sources, can be written in a similar differential form. Thus, the balance momentum for the individual components and for the mixture as a whole is represented by the equations (below, external force sources will be neglected for simplification)

$$\begin{aligned} \frac{\partial(\rho_{(n)}v_{(n)i})}{\partial t} + \frac{\partial}{\partial x_\alpha}(\rho_{(n)}v_{(n)i}v_{(n)\alpha} - \tau_{(n)i\alpha}) &= 0 \\ \rho \frac{dv_i}{dt} - \frac{\partial \tau_{\alpha i}}{\partial x_\alpha} &= \frac{\partial(\rho v_i)}{\partial t} + \frac{\partial}{\partial x_\alpha}(\rho v_i v_\alpha - \tau_{\alpha i}) = 0 \\ \tau_{ij} &\equiv \Sigma(\tau_{(n)ij} - w_{(n)i}w_{(n)j}) = -p\delta_{ij} + \sigma_{ij} \end{aligned} \quad (3)$$

Although the problem of writing the balance of the total energy density can be solved just as simply, if  $e$  and  $\mathbf{J}^e$  are understood as the total specific energy and its flux, and  $e_{(n)}$ ,  $\mathbf{J}_{(n)}^e$  and  $P_{(n)}^e$  are understood as the specific energy, the flux and production of the component  $n$

$$\begin{aligned} \frac{\partial \rho_{(n)}e_{(n)}}{\partial t} + \text{div}\{\mathbf{J}_{(n)}^e + \rho_{(n)}e_{(n)}\mathbf{v}_{(n)}\} &= P_{(n)}^e, \quad \rho \frac{de}{dt} + \text{div}\mathbf{J}^e = 0 \\ p_e &= \Sigma \rho_{(n)}e_{(n)}, \quad \mathbf{J}^e = \Sigma\{\mathbf{J}_{(n)}^e + \rho_{(n)}e_{(n)}\mathbf{w}_{(n)}\}, \quad \Sigma P_{(n)}^e = 0 \end{aligned}$$

in a consideration of the balance of internal energy on the basis of the given relations, alternative versions arise when the kinetic energy is separated from the total energy of the mixture. If, as usual, the kinetic energy of the mixture is understood to be the kinetic energy of the centre of mass  $\rho v^2/2$ , then subsequent thermodynamic analysis leads to the well-known Fick's law [8–10]. The diffusion process is then described by partial differential equations of the parabolic type, and here the paradox of unlimited velocities of small large-scale disturbances arises. However, attention must be drawn to the possibility of a different choice, and here the total kinetic energy of the mixture is separated from the energy density.

$$\frac{1}{2}\Sigma \rho_{(n)}v_{(n)}^2 = \frac{1}{2}\rho v^2 + \frac{1}{2}\Sigma \rho_{(n)}w_{(n)}^2$$

as characterizing the macroscopic motion (see the brief discussion of this in [8]). Then, for the internal energy reflecting the energy of thermal motions and short-range interatomic interactions, the following balance relation will be satisfied.

$$\begin{aligned} \rho \frac{d\varepsilon}{dt} + \text{div}\mathbf{J}^q &= \tau_{\alpha\beta}e_{\alpha\beta} - \Sigma \mathbf{J}_{(n)}^e \cdot \left( \frac{d\mathbf{w}_{(n)}}{dt} + \nabla \frac{w_{(n)}^2}{2} \right) \\ \varepsilon &= e - \Sigma \frac{c_{(n)}}{2} v_{(n)}^2, \quad J_i^q = J_i^e + v_\alpha \tau_{i\alpha} - \Sigma \frac{\rho_{(n)}}{2} w_{(n)}^2 w_{(n)i}, \quad e_{ij} = \frac{1}{2} \left( \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) \end{aligned}$$

It is obtained by subtracting from the equation of the total energy the equation of the kinetic energy, and the latter is a simple corollary of equations of motion (3) when there are no external forces.

These corollaries of the conservation laws must be supplemented with relations of a thermodynamic nature. Within the framework of the normal hypothesis of local thermodynamic equilibrium of a flowing medium, these are primarily relations for the functions of state, for example, for the internal energy

$$\varepsilon = \varepsilon(s, \rho, c_1, c_2), \quad d\varepsilon = Tds + p\rho^{-2}d\rho + \Sigma \mu_{(n)}dc_{(n)}$$

The multicomponent nature of the medium is reflected, apart from the dependence of the state on the concentrations of the components, in the appearance of conjugate chemical potentials  $\mu_{(n)}$  in the differential Gibbs relation. The single-temperature approximation used here to describe the two-component mixture does not contradict singling out the kinetic energy of diffusion from the total energy employes above. From the viewpoint of kinetic theory, this temperature predetermines the average velocities of the thermal motions of the molecules of each of the components, while the internal energy stems from the statistical spread of their velocities about these average values. Thus, it is natural when determining the internal energy to separate out from the total energy the sum of the kinetic energies of the components of the mixture, rather than the energy of their centre of mass.

Since there are relations between the concentrations and fluxes of the components, reflected in formulae (2), it is convenient to exclude one of the components from explicit consideration, taking the other to be the "impurity

in solution" of concentration  $c \equiv c_{(1)}$ , and also to introduce the following altered notations

$$\mathbf{J} \equiv \mathbf{J}_{(1)}^c, \quad \mu \equiv \mu_{(1)} - \mu_{(2)}, \quad \mathbf{w} \equiv \mathbf{w}_{(1)} - \mathbf{w}_{(2)} = \mathbf{v}_{(1)} - \mathbf{v}_{(2)} \quad (4)$$

Then the above equation of internal energy balance, together with the slightly simplified Gibb's relation

$$d\varepsilon = Tds + p\rho^{-2}d\rho + \mu dc$$

and the mass balance equations, enables us to write the equation of entropy balance

$$\rho \frac{ds}{dt} + \operatorname{div} \mathbf{J}^s = P^s \geq 0, \quad T\mathbf{J}^s = \mathbf{J}^q - \mu\mathbf{J}$$

$$TP^s = \sigma'_{\alpha\beta} e'_{\alpha\beta} - \mathbf{J}^s \cdot \nabla T - \mathbf{J} \cdot \left( \nabla \mu + \frac{d\mathbf{w}}{dt} + \nabla \frac{w_{(1)}^2 - w_{(2)}^2}{2} \right) + \frac{1}{3} \sigma_{\gamma\gamma} e_{\alpha\alpha}$$

where  $\mathbf{J}^s$  and  $P^s$  are the flux and production of entropy.

The non-negative entropy production here is the sum of bilinear products of the scalar, vector and tensor thermodynamic fluxes  $\sigma_{\eta/3}$ ,  $\mathbf{J}_s$ ,  $\mathbf{J}$  and  $\sigma'_{ij}$  and the thermodynamic forces of the corresponding tensor dimensionality  $e_{\alpha\alpha}$ ,  $\nabla T$ ,  $\nabla \mu + d\mathbf{w}/dt$  and  $e'_{ij}$ . As usual, spherical parts are isolated from the second-rank tensors here, and the remaining deviator parts are denoted by the same letters with primes. Assuming the deviation of the system from thermodynamic equilibrium to be small, a linear relations should exist between them. To this accuracy, in the penultimate expression for the thermodynamic force we will omit the non-linear expression with a gradient of the kinetic energy of diffusion  $\nabla(w_{(1)}^2 - w_{(2)}^2)/2$ . Since, in an isotropic medium, cross-relations between the characteristics of different tensor dimensionality in a linear approximation are impossible, then (taking into account the Onsager symmetry relations for vector effects), we obtain the relations

$$\sigma_{\alpha\alpha} = 3\zeta e_{\beta\beta}, \quad \sigma'_{ij} = 2\eta e'_{ij}$$

$$\mathbf{J} = -\alpha \left( \nabla \mu + \frac{d\mathbf{w}}{dt} \right) - \beta \nabla T, \quad \mathbf{J}^s = -\beta \left( \nabla \mu + \frac{d\mathbf{w}}{dt} \right) - \frac{\gamma}{T} \nabla T \quad (5)$$

$$TP^s = \zeta e_{\alpha\alpha}^2 + 2\eta (e'_{\alpha\beta})^2 + \frac{\kappa}{T} (\nabla T)^2 + \frac{1}{\alpha} \mathbf{J} \cdot \mathbf{J} \geq 0, \quad \kappa = \gamma - \frac{\beta^2}{\alpha} T$$

from which it can be seen that, in the case of an isotropic fluid, the multicomponent nature in the absence of chemical reactions has no effect on viscous phenomena, and the flow of the fluid will be described by the same Navier–Stokes equations as for a single-component medium. Viscous processes also have no direct inverse effect on vector (diffusion and heat conduction) and scalar thermodynamic processes.

The requirement that the quadratic form of entropy production must be non-negative means that the two coefficients of viscosity, the thermal conductivity and a further additional coefficient must be non-negative, i.e.

$$\zeta \geq 0, \quad \eta \geq 0, \quad \kappa \geq 0, \quad \alpha \geq 0 \quad (6)$$

It is convenient to rewrite the vector thermodynamic relations obtained, bearing in mind the nature of the dependence of chemical potential on the pressure, temperature and impurity concentration [10], in the slightly transformed form

$$\mathbf{J} + \frac{d}{dt}(\theta\mathbf{J}) = -\rho D \left( \nabla c + \frac{k_T}{T} \nabla T + \frac{k_p}{p} \nabla p \right), \quad D \equiv \frac{\alpha}{\rho} \left( \frac{\partial \mu}{\partial c} \right)_{p,T}, \quad \theta \equiv \frac{\alpha}{\rho c(1-c)} \quad (7)$$

$$\mathbf{J}^s = \frac{\beta}{\alpha} \mathbf{J} - \frac{\kappa}{T} \nabla T, \quad \mathbf{J} = \rho c(1-c)\mathbf{w}$$

The latter linear relation between the impurity flux and the difference in the velocities of the components follows from relations (1), (2) and (4). By virtue of the fact that the coefficient  $\alpha$  indicated above is non-negative, taking into account the corollary of thermodynamic stability  $(\partial \mu / \partial c)_{p,T} > 0$  [10], the diffusion coefficient and the local relaxation time of the impurity flux should be non-negative:

$$D \geq 0, \quad \theta \geq 0$$

The thermal diffusion and pressure diffusion coefficients  $k_T$  and  $k_p$  have no constrains of this kind.

If the simplest case of a homogeneous fluid at rest with small changes in the impurity concentration and slight

changes in pressure and temperature is considered, the kinetic coefficients can be assumed to be constant. Then, using relations (2) and (7), for the impurity concentration we obtain the telegraph equation

$$\theta \frac{\partial^2 c}{\partial t^2} + \frac{\partial c}{\partial t} = D \Delta c$$

i.e. an equation of the hyperbolic type with a finite speed propagation of disturbances. From dimensional considerations, in this case the characteristic scales of time  $\theta$ , length  $\sqrt{\theta D}$  and velocity  $\sqrt{D/\theta}$  are singled out. Disturbances with smaller space scales propagate at such a velocity, decay everywhere with the same characteristic time. For larger-scale disturbances ( $L^2/D \gg \theta$ ), local relaxation ends, and we have the normal spatial diffusional spreading. The telegraph equation in this case is converted into the well-known diffusion equation of the parabolic type. The diffusion relaxation time is normally very short in the case of a mixture at the molecular level, since it reflects the finiteness of the short free path time (a derivation of the generalized diffusion equation by an asymptotic analysis of the system of Boltzmann kinetic equations for a mixture of gases taking into account changes in the distribution functions in such times was given earlier [11, 12]). Its magnitude proves to be much greater in cases of a large-scale inhomogeneous supermolecular structure of the components of the mixture.

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