Derivation of the modified diffusion equations in a gas mixture

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The derivation of the modified diffusion equations is presented. These equations of a relaxational type generalize Fick's law and are applicable for large spatial and temporal gradients. The telegraph equation for the concentration is found in the simplest case. The derivation and the equations themselves are similar, except for the intrinsic velocity, to those for heat and momentum transfer in hydrodynamics of fast processes proposed earlier by one of the authors [Khonkin, Fluid Mech. Sov. Res. **9**, 93 (1980)]. The concentration distribution from the δ-shaped source is given as an illustration.

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I. INTRODUCTION

In the past decades there has been a great deal of work done on generalized forms of Fick's law of diffusion. The Boltzmann equation or its models [e.g., the Bhatnagar-Gross-Krook (BGK) model] are usually the basic kinetic equations giving rise to such forms. Though the first attempts were purely heuristic (see [1] and references therein), later attempts and achievements were based on the more or less solid grounds of the kinetic theory and irreversible thermodynamics.

Equations for mixtures were investigated in [2–7], non-Fickian diffusion in [8–12] (in [13–15] for the special case of uniform shear flow). In [16–19] the telegraph (hyperbolic) equation resulting as a special case was analyzed. Taylor dispersion has also been under research using these alternative diffusion equations [20]. General questions of the kinetic theory and the extended irreversible thermodynamics leading to relaxation and other nonclassical transport equations and the relations of the two approaches were treated in various articles [21–28] and monographs [29–31].

We should especially mention a kinetic approach by Eu, which for mixtures was begun in [8]. General aspects of this approach were then analyzed in [32–34] and finally summarized in a monograph [35] published on the subject and related topics (see also [36,37]).

Some years ago one of the authors (Khonkin [21]) derived from the Boltzmann equation the system of hydrodynamical equations for fast and large-gradient phenomena, when the linear laws of momentum and heat transport (Navier-Stokes and Fourier laws) are no longer valid. In this derivation Khonkin [21] assumed that the hydrodynamical parameters can vary on small spatiotemporal scales, i.e., the Knudsen number is of the order of unity. These equations were then applied to the description of shock-wave structure [38]. The results obtained were in good agreement with experiments and simulations.

In this paper we use the method of Ref. [21] for the gas mixture and to derive the diffusion equation that generalizes Fick's law. We would like to note the simplicity of the obtained constitutive relations [Eq. (5)] in comparison with other relations proposed in the literature. Section II is devoted to analysis and Sec. III is for conclusions.

II. ANALYSIS

Consider the system of the Boltzmann equations for the N-component gas mixture in the usual notation [39],

$$\frac{\partial f_i}{\partial t}+\mathbf{v}_i\cdot\nabla f_i=\sum_{j=1}^{N}\int\int\int(f_i'f_j'-f_if_j)g_{ij}b\,db\,d\epsilon\,d^3v_j\ ,\qquad i=1,\ldots,N\ , \tag{1}$$

and the conservation laws for the hydrodynamical parameters which result from Eq. (1) after its multiplication by m_i, $m_i\mathbf{v}_i$, and $m_iv_i^2$ and integration over $\mathbf{v}_i$:

$$\begin{aligned}&\frac{\partial\rho_i}{\partial t}+\nabla\cdot(\rho_i\mathbf{u}+\mathbf{J}_i)=0\ ,\\&\rho\frac{d\mathbf{u}}{dt}+\nabla\cdot\pi=0\ ,\\&\tfrac{3}{2}nk\frac{dT}{dt}+\pi:\nabla\mathbf{u}+\nabla\cdot\mathbf{q}=0\ .\end{aligned} \tag{2}$$

Here

$$\frac{d}{dt}=\frac{\partial}{\partial t}+\mathbf{u}\cdot\nabla,\quad \mathbf{J}_i=m_i\int\mathbf{c}_if_id^3v_i,\quad \mathbf{c}_i=\mathbf{v}_i-\mathbf{u}\ .$$

Let the distribution functions be as follows:

$$\begin{aligned}&f_i=f_i^0(1+\phi_i)\ ,\\&f_i^0=n_i(2\pi kT/m_i)^{-3/2}\exp[-m_i(\mathbf{v}_i-\mathbf{u})^2/(2kT)]\ .\end{aligned}$$

Then we can get from Eqs. (1) and (2)

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$$\frac{d(\phi_i f_i^0)}{dt}+\mathbf{c}_i\cdot\nabla(\phi_i f_i^0)$$
$$=A_i^1-A_i^2+\sum_{j=1}^{N}I_{ij}+\sum_{j=1}^{N}\int\int\int f_i^0 f_j^0(\phi_i'\phi_j'-\phi_i\phi_j)g_{ij}b\,db\,d\epsilon\,d^3v_j\ , \tag{3}$$

where

$$A_i^1=(f_i^0 m_i c_{i\beta})/(\rho kT)\nabla_\alpha P_{\alpha\beta}+(f_i^0/p)[m_i c_i^2/(3kT)-1](P_{\alpha\beta}\nabla_\beta u_\alpha+\nabla_\alpha q_\alpha)+(f_i^0/\rho_i)\nabla_\alpha J_{i\alpha}\ ,$$
$$A_i^2=f_i^0 m_i/(kT)(c_{i\alpha}c_{i\beta}-\tfrac{1}{3}c_i^2\delta_{\alpha\beta})\nabla_\alpha u_\beta+f_i^0 c_{i\alpha}[m_i c_i^2/(2kT)-\tfrac{5}{2}]\nabla_\alpha \ln T+f_i^0 c_{i\alpha}(n/n_i)d_{i\alpha}\ ,$$
$$I_{ij}=\int\int\int f_i^0 f_j^0(\phi_i'+\phi_j'-\phi_i-\phi_j)g_{ij}b\,db\,d\epsilon\,d^3v_j\ ,$$
$$P_{\alpha\beta}=\pi_{\alpha\beta}-p\delta_{\alpha\beta},\quad \mathbf{d}_i=\nabla(n_i/n)+(n_i/n-\rho_i/\rho)\nabla\ln p\ .$$

If $\phi_i \ll 1$ and $d/dt\simeq 1/\tau$, where τ is the mean free time (this case corresponds to moderate spatial and temporal gradients [21]), then we can neglect A_i^1, $\mathbf{c}_i\cdot\nabla(\phi_i f_i^0)$, and the last term on the right-hand side of Eq. (3) as these terms are of the first order in the small parameter. Therefore

$$\frac{d(\phi_i f_i^0)}{dt}+A_i^2-\sum_{j=1}^{N}I_{ij}=0\ .$$

We now multiply this relation by $m_i\mathbf{v}_l$ and integrate over $\mathbf{v}_i$. Using the symmetry properties of I_{ij} we obtain

$$\frac{d\mathbf{J}_i}{dt}+p\mathbf{d}_i+\sum_{j=1}^{N}\mathbf{B}_{ij}=\mathbf{0}\ ,$$

where

$$\mathbf{B}_{ij}=m_i\int f_i^0 f_j^0(\phi_i+\phi_j)(\mathbf{c}_i-\mathbf{c}_i')d\Gamma\ ,$$
$$d\Gamma=g_{ij}b\,db\,d\epsilon\,d^3v_i d^3v_j\ . \tag{4}$$

To calculate $\sum_{j=1}^{N}\mathbf{B}_{ij}$ we use the result of Ferziger and Kaper [39] obtained during the determination of the diffusion coefficient by the Chapman-Enskog method. We have

$$\sum_{j=1}^{N}\int f_i^0 f_j^0(\mathbf{D}_i^k+\mathbf{D}_j^k-\mathbf{D}_l^{k\prime}-\mathbf{D}_j^{k\prime})d\gamma\,d^3c_j$$
$$=-(n^2/n_i)f_i^0(\delta_{ik}-\rho_i/\rho)\mathbf{c}_i\ ,$$

where

$$d\gamma=g_{ijb}\,db\,d\epsilon,\quad \mathbf{D}_i^k=n/(kT)m_i D_{ik}\mathbf{c}_i\ ,$$

Hence after doing some algebra and accounting for the momentum conservation,

$$m_i\mathbf{c}_i+m_j\mathbf{c}_j=m_i\mathbf{c}_i'+m_j\mathbf{c}_j'\ ,$$

we obtain

$$m_i\sum_{j=1}^{N}(D_{ik}-D_{jk})\int f_j^0(\mathbf{c}_i-\mathbf{c}_i')d\gamma\,d^3c_j$$
$$=(p/n_i)(\delta_{ik}-\rho_i/\rho)\mathbf{c}_i\ ,$$

taking into account $\sum_{j=1}^{N}\rho_j D_{ij}=0$.

Substitution of these formulas into Eq. (4) leads to the following expression for $\sum_{j=1}^{N}\mathbf{B}_{ij}$:

$$\sum_{j=1}^{N}\mathbf{B}_{ij}=-(kT/n)\sum_{j=1}^{N}(m_i m_j D_{ij})^{-1}(\rho_i J_j-\rho_j\mathbf{J}_i)\ .$$

Consequently

$$\frac{d\mathbf{J}_i}{dt}+p\left[\mathbf{d}_i-(kT/n)\sum_{j=1}^{N}(m_i m_j D_{ij})^{-1}\times(\rho_i\mathbf{J}_j-\rho_j\mathbf{J}_i)\right]=\mathbf{0}\ . \tag{5}$$

Thus we can see that Fick's law follows from these relations if we neglect $d\mathbf{J}_i/dt$. Combining Eqs. (2) and (5) for the simplest case of the binary mixture $N=2$, $m_1=m_2=m$, $\mathbf{u}=\mathbf{0}$, $\rho=$const we have for the isothermal diffusion the telegraph equation

$$(m/kT)\frac{\partial^2 y}{\partial t^2}=\Delta y-(1/D)\frac{\partial y}{\partial t}\ . \tag{6}$$

Here Δ is the Laplace operator and $y=\rho_1/\rho$ is the mass concentration of the first component. Equation (6) differs from the usual diffusion equation

$$\frac{\partial y}{\partial t}=D\Delta y \tag{7}$$

by its left-hand side. Due to that term, Eq. (6) is hyperbolic (the so-called telegraph equation).

The solution of the initial-value problem for Eq. (6) is determined by both the initial value $y(\mathbf{r},0)$ and the time derivative $\partial y(\mathbf{r},t)/\partial t|_{t=0}$. Therefore to compare the solutions of Eqs. (6) and (7) we are to find the Green's function of Eq. (6), i.e., the solution of the equation

$$(1/c_T^2)\frac{\partial^2 y}{\partial t^2}-\Delta y+(1/D)\frac{\partial y}{\partial t}=\delta(\mathbf{r},t)\ .$$

According to Morse and Feshbach [40], we have in the one-dimensional case ($n=1$, $x=x_1$)

$$y(x,t)=\frac{c_T}{2}\exp\left[-\frac{c_T^2 t}{2D}\right]\times I_0\left[\frac{c_T}{2D}\sqrt{c_T^2t^2-x^2}\right]h(c_Tt-x)\ ,$$

in the two-dimensional case ($n=2$, $\rho=\sqrt{x_1^2+x_2^2}$)

$$y(\rho,t)=\frac{c_T}{2\pi}\exp\left[-\frac{c_T^2t}{2D}\right](c_T^2t^2-\rho^2)^{-1/2}\times\cosh\left[\frac{c_T}{2D}\sqrt{c_T^2t^2-\rho^2}\right]h(c_Tt-\rho)\ ,$$

and in the three-dimensional case ($n=3$, $r=\sqrt{x_1^2+x_2^2+x_3^2}$)

$$y(\mathbf{r},t)=\frac{c_T}{4\pi r}\exp\left[-\frac{c_T^2t}{2D}\right]\times\left[\delta(c_Tt-r)+\frac{c_Tr}{2D}(c_T^2t^2-r^2)^{-1/2}\times I_1\left[\frac{c_T}{2D}\sqrt{c_T^2t^2-r^2}\right]\times h(c_Tt-r)\right],$$

where $h(x)$ is the Heaviside step function [$h(x)=0$ when $x<0$, $h(x)=1$ when $x\geq 0$]. The Green's function for Eq. (7) is

$$y(\mathbf{r},t)=D(2\sqrt{\pi Dt})^{-n}\exp(-r^2/4Dt)h(t)\ .$$

In contrast to this function the Green's functions for the modified diffusion equation (6) are zero for $r>c_Tt$, i.e., concentration disturbances propagate with a finite speed. Unlike the case of the adiabatic sound speed $c_S=(\gamma kT/m)^{1/2}$ intrinsic for the propagation of acoustical waves [21] (here γ is the ratio of specific-heat capacities), concentration disturbances in a uniform medium propagate with isothermal sound speed $c_T=(kT/m)^{1/2}$.

The main difference between these Green's functions is for $r\geq c_Tt$. For $r\ll c_Tt$ the modified Green's functions turn into classical ones. This can be proven with the use of the asymptotic expansions of the Bessel functions and the hyperbolical cosine for large arguments. Figure 1 illustrates this difference between the classical and the modified diffusion equations in a qualitative way.

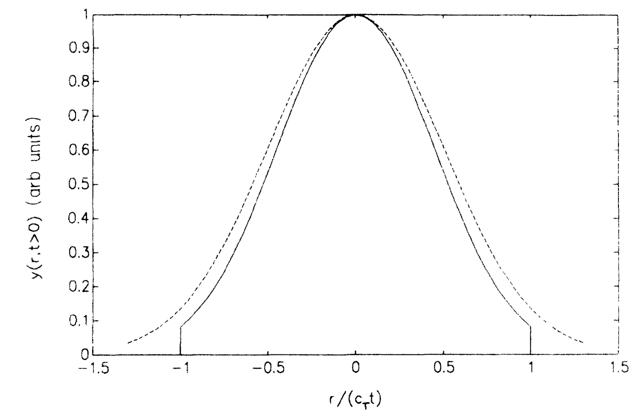

FIG. 1. Green's functions for the classical and the modified diffusion equations.

So the solutions of the modified diffusion equation are different from the solutions of the classical equation in the vicinity of the disturbance front, but when we move away from the front to the trail region these differences are smoothed out due to the small value of the relaxation time $\rho D/p$.

III. CONCLUSIONS

Using the method proposed in Ref. [21] we have derived in this paper the diffusion equation which is the generalization of Fick's law. The presented equation can be used to describe the phenomena of the mass transport for large concentration gradients and/or time derivatives. Furthermore, in the simplest case the equation for the concentration is hyperbolic rather than parabolic thus predicting the finite velocity of the propagation of disturbances. Therefore the presented results can be another way to solve the old paradox of the infiniteness of this velocity.

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