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Irreversible Thermodynamics of Polydisperse Fluids[1]

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The entropy production, conservation laws, and linear constituative equations that describe the irreversible behavior of polydisperse fluids near equilibrium are presented. The problems of computing transport coefficients and solving the hydrodynamic equations are discussed.

KEY WORDS: entropy; hydrodynamics; nonequilibrium thermodynamics; polydisperse fluids; transport properties.

1. INTRODUCTION

In this paper we present a brief, formal description of polydisperse fluids that are not far removed from equilibrium. Our derivation of this description closely parallels the methods described by de Groot and Mazur [1] in their treatment of the irreversible thermodynamics of multicomponent mixtures, and we assume that the reader is familiar with that work. Our objective is to create a general framework within which a hydrodynamic description of mixtures (polydisperse and multicomponent) may be cast. We think that this will ultimately prove to be as useful as the polydisperse formulation of the equilibrium properties of fluids. That is, we expect that the formulation of the irreversible thermodynamics of polydisperse fluids will stimulate the development of new techniques for solving the hydrodynamic equations for fluids in the same way that the polydisperse description of equilibrium properties has stimulated the development of new methods for determining the equilibrium properties of fluids [2–5].

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In Section 2 we derive an expression for the entropy production and formulate the conservation laws and linear constituative equations. In Section 3 we discuss how several solution techniques, developed for equilibrium polydisperse fluids, may be applied to hydrodynamic problems.

2. IRREVERSIBLE THERMODYNAMICS

The composition of a mixture may be described by a mole-fraction distribution function, D. We assume, for simplicity, that the identity of the molecular species present in the system can be represented by the scalar variable I that assumes values in the interval $(0, \infty)$. $D(I)$ is defined to be the fraction of molecular species with identities less than I. Thus if there are N molecules in the system, $ND(I)$ of those molecules have an identity label that is less than I. Clearly $D(I)$ is a nondecreasing function of I that may assume values in the interval $[0, 1]$. If the system is a mixture of several species $D(I)$ will consist of a sum of step functions, and one often refers to such systems as being discrete or multicomponent. If D is a continuous function of I, implying that there exists a continuum of species, the system is called polydisperse. When $D(I)$ is continuous and increasing in intervals separated by one or more discontinuities, the system may be thought of as a mixture of discrete and polydisperse species; there is no generally recognized name for such systems.

Although the distinction between discrete mixtures and polydisperse mixtures is often made, there is no compelling mathematical reason for it [2, 3]. In fact, there is good reason for dropping such distinctions because the macroscopic properties of the system may be expressed in a form that applies equally well to either case. Since $D(I)$ has the same properties as a probability distribution function, the mathematical framework used to treat both discrete and continuous distributions may be used here. Some of the advantages of using this general description for equilibrium properties are discussed in Ref. 3. The purpose of this paper is to provide the same general description for the hydrodynamic properties.

The mole fraction of species with identities in the interval (I_1, I_2) is given by $D(I_2) - D(I_1)$, and it is convenient to introduce a mole-fraction distribution density function, $F(I)$, defined by

$$F(I) = dD(I)/dI \tag{1}$$

so that

$$D(I) = \int_0^I dI' F(I') \tag{2}$$

and

$$1 = \int_0^\infty dI' F(I') \tag{3}$$

For a system with N particles and a total mass M, $N(I) = NF(I)$ is then the number distribution density, $M(I) = m(I)\,N(I)$ is the mass distribution density, and $c(I) = M(I)/M$ is the mass-fraction distribution density, where $m(I)$ is the mass of a molecule of species I.

The internal energy, U, of an equilibrium system is an extensive (homogeneous of order 1) function of the state variables S and V and functional of $M(I)$—that is, U depends on integrals of the function $M(I)$. The combined first and second laws for the system, expressed in terms of specific quantities, $u = U/M$, $s = S/M$, $v = V/M$, and $c(I)$, is

$$Tds = du + pdv - \int dI\mu^*(I)\,\delta c(I) \tag{4}$$

where

$$T = (\partial U/\partial S)_{V,M(I)}, \quad p = -(\partial U/\partial V)_{S,M(I)}, \quad \text{and} \quad \mu^*(I) = [\delta U/\delta M(I)]_{S,V} \tag{5}$$

Here T is the temperature, p is the pressure, and $\mu^*(I)$ is the chemical potential distribution density. {We have included a superscript asterisk in our symbol for the chemical potential to emphasize its difference from $\mu(I) = [\delta U/\delta N(I)]_{S,V}$ that we use in kinetic theory calculations [6].}

The description of the irreversible properties of the system is obtained from Eq. (4) by assuming that there exists within small mass elements a state of local equilibrium such that Eq. (4) remains valid for those mass elements followed along their center of mass motion, i.e.,

$$T\frac{ds}{dt} = \frac{du}{dt} + p\frac{dv}{dt} - \int dI\mu^*(I)\frac{dc(I)}{dt} \tag{6}$$

where

$$d/dt = \partial/\partial r + \mathbf{u}\cdot\nabla \tag{7}$$

$$\mathbf{u} = \int dIc(I)\,\mathbf{v}(I) \tag{8}$$

and $\mathbf{v}(I)$ is the velocity of species I. Note that since we are describing states out of equilibrium, the local thermodynamic variables will change with time, t, and location, $\mathbf{r}$. To avoid notational clutter we have chosen not to indicate explicitly the dependence of the variables on t and $\mathbf{r}$.

We now express the right-hand side of Eq. (6) as the divergence of an entropy flux plus an entropy production term. We begin by defining the mass flux of species I in the local center of mass (barycentric) frame

$$\mathbf{J}(K) = \rho c(K)[\mathbf{v}(K) - \mathbf{u}] \tag{9}$$

where $\rho = M/V = 1/v$. The mass conservation (balance) equations are then

$$\rho dc(K)/dt = -\nabla \cdot \mathbf{J}(K) \tag{10}$$

and

$$\rho dv/dt = \nabla \cdot \mathbf{u} \tag{11}$$

These equations allow us to eliminate the derivatives $dc(K)/dt$ and dv/dt in Eq. (6). The equation of motion for the system (momentum balance) is

$$\rho d\mathbf{u}/dt = -\nabla \cdot \mathbb{P}^{(1)} - \nabla p + \rho \int dKc(K)\,\mathbf{F}^{\mathrm{m}}(\mathrm{K}) \tag{12}$$

where $\mathbf{F}^{\mathrm{m}}(K)$ is the external force per unit mass exerted on molecules of species K (we assume that $\mathbf{F}^{\mathrm{m}}(K)$ is independent of the time); $\mathbb{P}^{(1)}$ is defined by

$$\mathbb{P} = p\mathbf{I} + \mathbb{P}^{(1)} \tag{13}$$

where $\mathbf{I}$ is the unit tensor and $\mathbb{P}$ is the pressure tensor. The energy balance equation is used to define a heat flux $\mathbf{J}_q$:

$$\rho du/dt = -\nabla \cdot \mathbf{J}_q - p\nabla \cdot \mathbf{u} - \mathbb{P}^{(1)}\colon \nabla\mathbf{u} + \int dK\mathbf{J}(K) \cdot \mathbf{F}^{\mathrm{m}}(K) \tag{14}$$

Note that the u on the left-hand side of this equation is the specific internal energy and should not be confused with the local fluid velocity $\mathbf{u}$.

If we now substitute the expressions for du/dt, dv/dt, and $dc(K)/dt$ given by the balance equations into Eq. (6) and make use of Eq. (12) for $d\mathbf{u}/dt$ we obtain

$$\rho ds/dt = -\nabla \cdot \mathbf{J}_{\mathrm{s}} + \sigma \tag{15}$$

where the entropy flux, $\mathbf{J}_{\mathrm{s}}$, is defined by

$$\mathbf{J}_{\mathrm{s}} = \frac{1}{T}\left[\mathbf{J}_q - \int dK\mu^*(K)\,\mathbf{J}(K)\right] \tag{16}$$

and the entropy production, σ, is defined by

$$\sigma = -\frac{1}{T}\mathbf{J}_q \cdot \nabla \ln T - \frac{1}{T}\int dK\mathbf{J}(K) \cdot \{T\nabla[\mu^*(K)/T] - \mathbf{F}^{\mathrm{m}}(K)\} - \frac{1}{T}\mathbb{P}^{(1)}\colon \nabla\mathbf{u} \tag{17}$$

In order to separate variables according to their different tensorial characters, it is necessary to decompose the tensors $\mathbb{P}^{(1)}$ and $\nabla\mathbf{u}$ into sums of diagonal and traceless tensors:

$$\mathbb{P}^{(1)}=\pi\mathbf{I}+\mathring{\mathbf{\Pi}} \tag{18}$$

and

$$\nabla\mathbf{u}=\tfrac{1}{3}(\nabla\cdot\mathbf{u})\mathbf{I}+(\mathring{\nabla\mathbf{u}}) \tag{19}$$

then the term $(1/T)\mathbb{P}^{(1)}\colon\nabla\mathbf{u}$ that appears in Eq. (17) may be written as

$$-\frac{1}{T}\mathbb{P}^{(1)}\colon\nabla\mathbf{u}=-\frac{\pi}{T}\nabla\cdot\mathbf{u}-\frac{1}{T}\mathring{\mathbf{\Pi}}\colon(\mathring{\nabla\mathbf{u}}) \tag{20}$$

and the entropy production takes the form of a sum of scalar products

$$\begin{aligned}\sigma=&-\frac{\pi}{T}\nabla\cdot\mathbf{u}-\frac{1}{T}\mathbf{J}_q\cdot\nabla\ln T-\frac{1}{T}\int dK\mathbf{J}(K)\\&\cdot\{T\nabla[\mu^*(K)/T]-\mathbf{F}^{\mathrm{m}}(K)\}-\frac{1}{T}\mathring{\mathbf{\Pi}}\colon(\mathring{\nabla\mathbf{u}})\end{aligned} \tag{21}$$

That is, σ is a sum of scalar products of fluxes $[\pi, \mathbf{J}_q, \mathbf{J}(K)$, and $\mathring{\mathbf{\Pi}}]$ and forces $(-(1/T)\nabla\cdot\mathbf{u}$, $-(1/T)\nabla\ln T$, $-(1/T)\{T\nabla[\mu^*(K)/T]-\mathbf{F}^{\mathrm{m}}(K)\}$, and $-(1/T)(\mathring{\nabla\mathbf{u}}))$.

The description of the nonequilibrium state is completed by assuming that the fluxes are linearly related to the forces. Thus we set

$$\pi=-\frac{L_{uu}}{T}\nabla\cdot\mathbf{u} \tag{22}$$

$$\mathbf{J}_q=-\frac{L'_{qq}}{T}\nabla\ln T-\int dK\frac{L'_q(K)}{T}\{T\nabla[\mu^*(K)/T]-\mathbf{F}^{\mathrm{m}}(K)\} \tag{23}$$

$$\mathbf{J}(I)=-\frac{L''_q(I)}{T}\nabla\ln T-\int dK\frac{L''(I,K)}{T}\{T\nabla[\mu^*(K)/T]-\mathbf{F}^{\mathrm{m}}(K)\} \tag{24}$$

$$\mathring{\mathbf{\Pi}}=-\frac{L}{T}(\mathring{\nabla\mathbf{u}}) \tag{25}$$

The set of phenomological coefficients L_{uu}, L'_{qq}, $L'_q(K)$, $L''_q(K)$, $L''(I,K)$, and L must be such that $\sigma\geqslant 0$. And the generalization of the Onsager reciprocity theorem leads us to the reciprocal relations

$$L'_q(K)=L''_q(K) \tag{26}$$

$$L''(I,K)=L''(K,I) \tag{27}$$

The functions $L'_q(K)$ and $L''(I, K)$ are related to the polydisperse analogue of the thermal diffusion and mutual diffusion coefficients, respectively; L'_{qq} is related to the thermal conductivity; and L_{uu} and L are related to the bulk and shear viscosity, respectively.

3. DISCUSSION

In this section we discuss some of the difficulties involved in trying to extract useful information from the polydisperse generalization of irreversible thermodynamics and make some observations on how the use of the new techniques developed to solve equilibrium problems may be employed to solve polydisperse transport problems.

Section 2 is a rather straightforward generalization of the usual development of irreversible thermodynamics. Because it is a purely formal development, it does not really bring us to a description of nonequilibrium states that is, from a practical point of view, much superior to the discrete mixture formulation. In fact one could argue that this description is more complicated in the sense that we have replaced sums over discrete indices by integrals. However, the slightly more complicated and mathematically more sophisticated representation we have described can stimulate the development of new solution methods and/or more efficient solution methods.

3.1. The Transport Coefficients

Since there is relatively little experimental information about the transport coefficients of binary mixtures, it is unlikely that there will be many experimental data for the transport coefficients of mixtures with more than two components in the foreseeable future. At present the only analytical means for predicting how a transport coefficient depends on T, ρ, and $F(I)$ is through the use of kinetic theory. Xu and Stell [7] have addressed this problem recently. They have calculated (in the first Enskog approximation) the shear viscosity of a polydisperse system of hard spheres of equal mass and a distribution of diameters $\sigma(I)$ using both the Boltzmann and the Enskog kinetic equations. The only tractable method for obtaining an analytic expression for the transport coefficients, that we know of now, for more general types of mixtures (in particular, ones for which different species have different masses) is to use the type of perturbation expansion described in Ref. 2, namely an expansion about a one-component fluid: $m(I) = m_0 + m_1(I)$ and $\phi(r, I, J) = \phi_0(r) + \phi_1(r, I, J)$, treating $m_1(I)$ and $\phi_1(r, I, J)$ as small quantities. [Here m_0 and $\phi_0(r)$ are the mass and intermolecular potential of some species I_0.] A special case of this method—and somewhat easier to implement—is realized when $F(I)$ has some parameter, e, which in the limit $e \rightarrow 0$, $F(I) \rightarrow \delta(I-I_0)$. Then one expands in powers of e. (See Refs. 2, 3, and 8.) This is the nearly monodisperse fluid. An alternative numerical procedure based on the quadrature method of Cotterman and Prausnitz [4] is also possible. The quadrature method essentially chooses a small, optimum set of pseudocomponents with which to represent the complete mixture. The pseudocomponents are chosen such that integrals over $F(I)$ are well represented by summations over the pseudocomponents.

At the end of Section 2 we mentioned that the phenomological coefficients were related to the transport coefficients. We did not give specific relationships because there is a rather wide variation of the definitions of diffusion, thermal diffusion, and thermal conductivity coefficients. However, the definition of the shear viscosity, η, and the bulk viscosity, κ, by

$$\mathbb{P} = p\mathbf{I} - 2\eta(\overset{\circ}{\nabla\mathbf{u}}) - \kappa(\nabla \cdot \mathbf{u})\mathbf{I} \tag{28}$$

is widely accepted, and thus

$$\eta = L/(2T) \qquad \text{and} \qquad \kappa = L_{uu}/T \tag{29}$$

In light of Xu and Stell's work [7], it would be useful to recast Eqs. (21)–(26) into a form that is more directly related to the variables used in kinetic theory, that is, transform Eqs. (23) and (24) into a form more directly related to that which arises naturally when one solves the Boltzmann or Enskog kinetic equations. To this end, we introduce a new heat flux,

$$\mathbf{J}'_q = \mathbf{J}_q - \int dK H(K)\, \mathbf{J}(K) \tag{30}$$

where

$$H(K) = \mu^*(K) - T\frac{\partial \mu^*(K)}{\partial T} \tag{31}$$

the "thermal force,"

$$\mathbf{X}_q = -\frac{1}{T}\nabla \ln T \tag{32}$$

and a new "mass force,"

$$\mathbf{X}(K) = -\frac{1}{T}[\nabla_T \mu^*(K) - \mathbf{F}^m(K)] \tag{33}$$

Here ∇_T is the gradient operator at a constant temperature. Since

$$-\frac{1}{T}\{T\nabla[\mu^*(K)/T]-\mathbf{F}^{\mathrm{m}}(K)\}=\mathbf{X}(K)-H(K)\mathbf{X}_q \tag{34}$$

the entropy production is given by

$$\sigma=-\frac{\pi}{T}\nabla\cdot\mathbf{u}+\mathbf{J}'_q\cdot\mathbf{X}_q+\int dK\,\mathbf{J}(K)\cdot\mathbf{X}(K)-\frac{1}{T}\mathring{\mathbf{\Pi}}:(\overset{\circ}{\nabla\mathbf{u}}) \tag{35}$$

In terms of these new variables the linear relations, Eqs. (23) and (24), become

$$\mathbf{J}'_q=\tilde{L}'_{qq}\mathbf{X}_q+\int dK\,\tilde{L}'_q(K)\,\mathbf{X}(K) \tag{36}$$

and

$$\mathbf{J}(I)=\tilde{L}''_q\mathbf{X}_q+\int dK\,L''(I,K)\,\mathbf{X}(K) \tag{37}$$

with $\tilde{L}'_q(K)=\tilde{L}''_q(K)$ and $L''(I,K)=L''(K,I)$.

With this description, the phenomological transport coefficients defined in Ref. 6 (after taking the polydisperse limit [7]) may be directly related to $\tilde{L}'_q(K)$, $\tilde{L}''_q(K)$, and $L''(I,K)$. In this manner the transport coefficients may be obtained at either the Boltzmann or the Enskog level.

3.2. Solving the Hydrodynamic Equations

3.2.1. Simple Problems

In cases where mutual diffusion and thermal diffusion can be ignored, $F(I)$ is spatially uniform, and the fluid is incompressible, the standard techniques of fluid mechanics and heat transfer can be used to solve for the velocity field, $\mathbf{u}(\mathbf{r},t)$, and the temperature field, $T(\mathbf{r},t)$, given the initial and boundary conditions.

3.2.2. Difficult Problems

Still with the assumptions of incompressible flow and that mutual and thermal diffusion can be ignored, when $F(I)$ is not spatially uniform the phenomological coefficients L and L'_{qq} (i.e., the shear viscosity and thermal conductivity) will depend on $\mathbf{r}$ not only through the spatial dependence of T, which can often be ignored, but also through the spatial dependence of $F(I)$. If the system is composed of molecules having a broad range of masses, we expect that L and L'_{qq} may vary significantly with position. Although there is a variety of numerical techniques for solving the hydrodynamic equations when the transport coefficients are not constant, a useful technique may be to expand $F(I)$ about a reference point. For example, consider the problem of finding the radial variation of $\mathbf{u}$ in steady isothermal, laminar flow in a pipe with stick boundary conditions and symmetry about the center of the pipe ($z=0$). Let us assume that the flow is in the x direction and that $\overset{\circ}{\mathbf{\Pi}}_{xz}$ is a linear function of z. If $F(I, \mathbf{r})$ is uniform throughout the fluid, the shear viscosity, η, will not depend on $\mathbf{r}$ and one obtains a parabolic velocity profile: $u_z = -\frac{1}{2}\Delta(z^2 - R^2)$, where R is the radius of the pipe and Δ is proportional to $1/\eta$. If the spatial variation of $F(I, \mathbf{r})$ is symmetric about the center of the pipe ($z=0$) and a weak function of z, we may approximate $F(I, \mathbf{r})$ by $F_0(I) + F_1(I)z + \cdots$ and η will have the form $\eta = \eta_0 + \eta_1 z + \cdots$. In this case one finds

$$u_z = -\frac{1}{2}\Delta_0(z^2 - R^2) + \frac{\Delta_0\eta_1}{3\eta_0}(z^3 - R^3) + \cdots \tag{38}$$

3.2.3. *Very Difficult Problems*

When the composition of the system is not uniform and when that nonuniformity depends on the boundary conditions, the hydrodynamic equations are very difficult to solve. Many technologically important problems fall into this category: condensation on a cold wall, flame propagation, and two-phase flow. An especially intriguing problem is to determine which properties of a mixture have a qualitative effect on the hydrodynamic stability of a system. For instance, Kolodner et al. [9] have recently suggested that thermal diffusion may have a marked effect on the Rayleight–Benard instability. We cannot suggest, at this time, any new analytical approaches for solving such problems. However, based on our experience with equilibrium polydisperse fluids, we are optimistic that by considering such problems within the general context of the polydisperse formulaition of the hydrodynamic equations, it will be possible to find new solution methods.

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