An Examination of the Validity of the Onsager Reciprocal Relations Applied to Flow in the Presence of Thermal Stresses and Thermal Slip

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Abstract: It is experimentally known that a pressure difference is developed in a gas under continuum conditions contained in a closed capillary tube, the ends of which are maintained at different temperatures. However, in contradiction with this experimentally measurable thermomolecular pressure difference, the use of the methods of irreversible thermodynamics in conjunction with the Navier-Stokes equations subject to the no-slip boundary condition on velocity leads to the conclusion that there can be no thermomolecular pressure difference in a capillary of macroscopic radius. It has been proposed that in order to correctly describe slow, nonisothermal flows, certain Burnett stress terms, namely the thermal stresses, along with the thermal slip of velocity at the wall, reduce to the same order as the Navier-Stokes equations and must be accounted for at the Navier-Stokes level. In this work, the validity of the Onsager reciprocal relations applied to a gas undergoing nonisothermal flow is examined, and it is demonstrated that the Onsager relations are not obeyed when thermal stress and thermal slip effects are accounted for.

Introduction

It has long been known that there exists a class of problems wherein the Navier-Stokes equations used in conjunction with the no-slip condition on the velocity of the gas at the solid surface yield predictions inconsistent with experimental observations. An example of such a problem is the development of a pressure gradient in a capillary tube containing a gas, with one end of the tube maintained at a higher temperature than the other. This phenomenon was first observed in 1879 by Reynolds [1], who termed it thermal transpiration.

The first theoretical explanation for the development of a thermomolecular pressure gradient in the thermal transpiration tube was provided in 1879 by Maxwell [2]. Maxwell made use of the kinetic theory of gases to derive expressions for the thermal stresses arising in a gas of Maxwellian molecules (i.e., molecules that are point centers of repulsion, with the repulsive force between two molecules being inversely proportional to the fifth power of the distance between them), in the presence of temperature gradients, and an expression for the thermally-induced slip of the gas at its interface with the solid. However, Maxwell, arguing on the basis that the temperature must satisfy the Laplace equation, and hence that the thermal stresses derived by him can cause no motion of the gas, applied the thermal slip condition in conjunction with the incompressible Navier-Stokes equations to derive an expression for the thermomolecular pressure gradient. A rigorous derivation of the boundary conditions applicable at the surface bounding a gas through the asymptotic solution of the Boltzmann equation in the Knudsen layer adjoining the surface is provided in [3].

Further, it is argued by Kogan *et al.* [4, 5] that the prevalent asymptotic expansions of the Boltzmann equation in terms of the Knudsen number Kn by the methods of Chapman and Enskog [6] and Grad [7], which yield the Navier-Stokes equations at $O(\text{Kn})$, are inapplicable to slow, nonisothermal flows. The Knudsen number, which is the ratio of the mean free path of the gas molecules to the characteristic size of the macroscopic body in contact with the gas, may also be expressed as the ratio of the Mach number to the Reynolds number, i.e., $\text{Kn} = \text{M}/\text{Re}$. It is now evident that flows of small Knudsen numbers can occur in two situations, when the Mach number

is of $O(1)$ and the Reynolds number is large, or when the Mach number is small and the Reynolds number is of $O(1)$. In the latter case, a reexamination of the scaling that produces the Navier-Stokes equations at $O(\mathrm{Kn})$ is required.

Specifically, the Chapman-Enskog and Grad schemes are based on the non-dimensionalization of the gas velocity using the speed of sound as the characteristic velocity of the gas [3]. As such, the resulting equations apply to the flow of gases at large Reynolds number, whereas for slow flows, where the Reynolds number $\mathrm{Re} \leq 1$, the characteristic gas velocity is in fact the viscous velocity, given by $U = \nu/a$, where ν is the kinematic viscosity of the gas and a is the characteristic dimension of the solid in contact with the gas.

Upon rescaling the terms resulting from the Chapman-Enskog expansion at various orders, it is found that the thermal stresses, which were previously believed to be at the next level of approximation, reduce to the same order as the terms in the Navier-Stokes equations and hence appear alongside the Navier-Stokes viscous stress tensor. These terms correspond to the third and fifth of the terms derived by Burnett in the third approximation to the velocity distribution function of the Boltzmann equation [6].

The simultaneous flow of gas and heat, particularly with regard to flow in porous media, is typically modelled by assuming that the global fluxes of gas volume and heat, averaged over the cross-section of flow, are each linearly related to the gradients in pressure and temperature [8, 9, 10]. The coefficients appearing in these linear relations between the fluxes and the driving forces are assumed to follow the Onsager reciprocal relations, and hence the cross-coefficients are assumed to be equal. The Onsager reciprocal relations at the global scale, averaged over the cross-section of flow, have been derived using the Poiseuille flow profiles and the Onsager symmetry of the Navier-Stokes equations governing the flow pointwise in each individual pore [11]. Thus, the applicability of the Onsager reciprocal relations to the flow rates of gas and heat computed per unit area of cross-section (henceforth referred to as the global Onsager reciprocal relations in this context) presupposes that the gas velocity obeys the no-slip boundary condition, and that the governing hydrodynamic equations possess Onsager symmetry. However, in the present work, we demonstrate that in the presence of thermal stresses and with the imposition of the thermal slip condition on the gas velocity under nonisothermal flow conditions, neither of these assumptions holds.

The equations of nonisothermal gas flow

The Burnett thermal stresses found by Kogan *et al.* [4, 5] to reduce to the order of the Navier-Stokes viscous stress tensor are given by

$$\boldsymbol{\tau}_3 = -\omega_3 \frac{\mu^2}{\rho T} \boldsymbol{\nabla}\boldsymbol{\nabla}T \text{ and } \boldsymbol{\tau}_5 = -\omega_5 \frac{\mu^2}{\rho T^2} \boldsymbol{\nabla}T\boldsymbol{\nabla}T, \tag{1}$$

where the constants ω_3 and ω_5 depend on the potential of intermolecular interactions among the gas molecules. This modification results in the following set of equations:
the continuity equation

$$\frac{\partial \rho}{\partial t} + \boldsymbol{\nabla} \cdot (\rho \mathbf{v}) = 0, \tag{2}$$

the energy equation

$$\frac{\partial \epsilon}{\partial t} + \boldsymbol{\nabla} \cdot (\epsilon \mathbf{v}) = -\boldsymbol{\nabla} \cdot \mathbf{q} - P\boldsymbol{\nabla} \cdot \mathbf{v} + \boldsymbol{\tau} : \boldsymbol{\nabla}\mathbf{v}, \tag{3}$$

and the Navier-Stokes momentum equation modified to include the thermal stresses

$$\rho \frac{\partial \mathbf{v}}{\partial t} + \rho \mathbf{v} \cdot \boldsymbol{\nabla} \mathbf{v} = -\boldsymbol{\nabla} P + \mu \nabla^2 \mathbf{v} - \boldsymbol{\nabla} \cdot \left(\omega_3 \frac{\mu^2}{\rho T} \boldsymbol{\nabla} \boldsymbol{\nabla} T \right) - \boldsymbol{\nabla} \cdot \left(\omega_5 \frac{\mu^2}{\rho T^2} \boldsymbol{\nabla} T \boldsymbol{\nabla} T \right), \qquad (4)$$

where ϵ refers to the internal energy per unit volume of gas and the stress tensor $\boldsymbol{\tau}$ is the sum of the Newtonian stress tensor and the Burnett thermal stresses, $\boldsymbol{\tau}_3$ and $\boldsymbol{\tau}_5$.

We note that the term associated with viscous dissipation, $\boldsymbol{\tau} : \boldsymbol{\nabla} \mathbf{v}$, is no longer a quadratic form. However, there is no violation of the Second Law of Thermodynamics, as Bobylev [12] has proved that the analogue of the H-theorem still exists, and a nonequilibrium entropy may be defined, having a non-negative rate of production, and which, in the absence of temperature gradients, is identical to the equilibrium definition of entropy with a vanishing rate of production.

The boundary condition on the gas velocity takes the general form

$$\mathbf{v} = \beta \boldsymbol{\nabla} T \cdot (\mathbf{I} - \mathbf{nn}) \qquad (5)$$

on the solid surface adjoining the gas, where the slip coefficient β is a constant determined by the nature of the gas and the solid. The slip coefficient derived by Maxwell has the value

$$\beta = \frac{3}{4} \frac{\nu}{T}. \qquad (6)$$

In general, an inverse relation exists between the density ρ and the temperature, so that $\rho T =$ constant, and as a result, the slip coefficient is constant. A review of various derivations of the slip coefficient for different models of molecular interactions among the molecules of the gas and the solid consti-tuting the wall, based on models of the Boltzmann equation, the moment method and Monte Carlo simulations is provided in [5].

Thermal stresses and Onsager symmetry

We denote by $\boldsymbol{\xi}$ the set of thermodynamic variables $(\rho, \epsilon, \mathbf{p})^T$, where ϵ is the internal energy density and $\mathbf{p} = \rho \mathbf{v}$ the momentum density, with $\mathbf{v}$ the velocity of the gas. The variables $\boldsymbol{\chi}$ denote the variables thermodynamically conjugate to $\boldsymbol{\xi}$. In other words,

$$\boldsymbol{\chi} = -\frac{\partial S}{\partial \boldsymbol{\xi}}, \qquad (7)$$

where S is the entropy. The generalized thermodynamic forces conjugate to the fluxes of mass, energy and momentum are given by

$$\delta \chi(\rho) = \frac{1}{\rho T} \delta P - \frac{h}{\rho T^2} \delta T, \qquad (8)$$

$$\delta \chi(\epsilon) = \frac{1}{T^2} \delta T, \qquad (9)$$

$$\delta \chi(\mathbf{p}) = \frac{1}{T} \delta \mathbf{v}, \qquad (10)$$

where P denotes the thermodynamic pressure, $h = \epsilon + P$ is the enthalpy per unit volume of gas and δ represents a small deviation from the equilibrium state of $\mathbf{v} = 0$ and constant ρ, T and ϵ. For small deviations from equilibrium, the deviations $\delta \boldsymbol{\xi}$ satisfy the linear equations

$$\frac{\partial}{\partial t}\delta\boldsymbol{\xi} = -L\delta\boldsymbol{\chi}. \tag{11}$$

Onsager's symmetry theorem [13] states that the matrix L has the symmetry property $L^{\dagger} = \tau L \tau$, where $\dagger$ denotes the Hermitian conjugate of a matrix, and τ is the matrix with 1 or -1 along the diagonal, according as $\boldsymbol{\xi}_i$ is even or odd under time reversal.

It has been found by McLennan [14] that the higher order hydrodynamic equations, such as the Burnett equations, do not satisfy Onsager's symmetry theorem. However, under slow, non-isothermal flow conditions, the Burnett thermal stresses known to reduce to the order of the Navier-Stokes equations must be included alongside the Navier-Stokes stress tensor, and the loss of Onsager symmetry becomes manifest even at the modified Navier-Stokes level. This is proved as follows. After linearization about the equilibrium state, the hydrodynamic equations, eqs. (2)-(4), become

$$\frac{\partial}{\partial t}\delta\rho = -\rho\boldsymbol{\nabla}\cdot\delta\mathbf{v}, \tag{12}$$

$$\frac{\partial}{\partial t}\delta\epsilon = k\nabla^2\delta T - h\boldsymbol{\nabla}\cdot\delta\mathbf{v}, \tag{13}$$

$$\frac{\partial}{\partial t}(\rho\delta\mathbf{v}) = -\boldsymbol{\nabla}(\delta P) + \mu\nabla^2\delta\mathbf{v} - \omega_3\frac{\mu^2}{\rho T}\nabla^2\boldsymbol{\nabla}\delta T. \tag{14}$$

The above equations are cast in the form of eq. (11) by expressing the deviations $\delta\mathbf{v}$, δT and δP in terms of the thermodynamic forces with the aid of eqs. (8)-(10), resulting in the matrix of coefficients

$$L = \begin{bmatrix} 0 & 0 & \rho T\boldsymbol{\nabla}\cdot \\ 0 & -kT^2\nabla^2 & hT\boldsymbol{\nabla}\cdot \\ \rho T\boldsymbol{\nabla} & \left(hT + \omega_3\mu^2\frac{T}{\rho}\nabla^2\right)\boldsymbol{\nabla} & -\mu T\nabla^2 \end{bmatrix}. \tag{15}$$

The matrix L does not possess the Onsager symmetry property (whereas the matrix obtained from the Navier-Stokes equations in the absence of the Burnett thermal stresses does in fact possess such a symmetry). The origin of this symmetry violation was attributed by McLennan to initial slip, namely, the difference between the actual initial values of the local thermodynamic variables $\boldsymbol{\xi}$, and the values obtained by extrapolating to zero time the solutions to the hydrodynamic equations, which are valid only after an initial aging period. The effect of initial slip is now manifest at the level of the modified Navier-Stokes equations.

A resolution of this symmetry violation by the Burnett equations has been proposed based on Grad's 13-moment approximation [15]. However, Grad has also observed that nonuniform heat flow, as described by Fourier's law, gives rise to thermal stresses [7]. The method of Grad does not suggest a resolution of the symmetry violation that occurs at the first order, corresponding to the modified Navier-Stokes and Fourier constitutive relations, with the inclusion of the thermal stresses alongside the Navier-Stokes viscous stress tensor.

Under steady, slow or unidirectional flow conditions, the temperature satisfies the Laplace equation, and as noted by Maxwell [2], there is no contribution from the thermal stress terms to the momentum equation. However, the cross-sectionally averaged flux of gas also depends on the boundary condition imposed on the gas velocity. We next provide an example of a steady-state situation in which, owing to the inertial effects being negligible, there is no contribution from the thermal stresses, and yet, due to the thermal slip boundary condition, the global Onsager reciprocal relations fail to hold.

Thermal slip and the global Onsager reciprocal relations in porous media

A periodic bundle of identical capillaries arranged parallel to each other constitutes a simple model of a consolidated porous medium, each periodically repeating unit of which is a single capillary tube in a rectangular matrix. When a temperature gradient is imposed across the porous medium, each individual capillary acts as a thermal transpiration capillary. At steady state, there is no heat exchange between the fluid in the capillary and the matrix, so that the capillary walls are effectively insulated.

A derivation of the thermomolecular pressure gradient in a laterally insulated thermal transpiration capillary tube through which a net flow of gas takes place was provided by Maxwell [2]. Here, we calculate the cross-sectionally averaged fluxes of gas volume and heat through the capillary tube. The two ends of the capillary at $(L, -L)$ are maintained at respective temperatures of (T_h, T_c), with $T_h > T_c$, and the corresponding gas densities are ρ_h and ρ_c, with $\rho_h < \rho_c$. The radius of the capillary tube, denoted by a, is much smaller that its half-length L.

Since we have that $a/L \ll 1$, we make the unidirectional flow assumption, from which it follows that

$$\mathbf{v} = v_z(r)\mathbf{e_z}, \tag{16}$$

where $\mathbf{e_z}$ is the unit vector directed along the capillary axis from the cold to the hot end, and that the pressure, temperature, and hence density, vary in the axial direction alone, or in other words,

$$P = P(z), \; T = T(z), \; \rho = \rho(z). \tag{17}$$

The boundary conditions to be applied are the no-penetration boundary condition on $\mathbf{v}$ at the capillary wall, i.e., $v_r = 0$ at $r = a$, which is consistent with the unidirectional flow assumption, and the thermal slip condition, which is most generally given by the expression

$$v_z = \beta \frac{dT}{dz} \text{ at } r = a, \tag{18}$$

where β is the coefficient determined by the model of interactions between the gas molecules and the wall. The momentum equation yields

$$\frac{\mu}{r} \frac{d}{dr} \left(r \frac{dv_z}{dr} \right) = \frac{dp}{dz}. \tag{19}$$

On integrating eq. (19) and imposing the thermal slip boundary condition, eq. (18), together with the finiteness of the velocity field along the axis of the capillary at $r = 0$, we obtain

$$v_z = -\frac{1}{4} \frac{a^2}{\mu} \frac{dP}{dz} \left(1 - \frac{r^2}{a^2} \right) + \beta \frac{dT}{dz}. \tag{20}$$

The net mass flow rate of gas Q_g across any cross-section is given by

$$Q_g = \int_0^a \rho \mathbf{v} \cdot d\mathbf{S}, \tag{21}$$

where the surface element $d\mathbf{S}$ in cylindrical coordinates is given by $2\pi r dr \mathbf{e_z}$. On substituting eq. (20) into the above and integrating, we obtain

$$Q_g = -\frac{\pi}{8} \frac{\rho}{\mu} a^4 \frac{dP}{dz} + \pi a^2 \rho \beta \frac{dT}{dz}. \tag{22}$$

This expression is similar in form to that obtained by Maxwell [2]. However, the coefficient of the temperature gradient in Maxwell's expression corresponds to the approximate slip condition derived by him for a gas of Maxwellian molecules, i.e., eq. (6).

The thermal energy equation

$$\frac{d^2T}{dz^2} = 0 \tag{23}$$

leads to a linear temperature profile given by

$$T = T_c + \frac{T_h - T_c}{2L}(z + L). \tag{24}$$

On integrating the dissipative heat flux as given by Fourier's law over the capillary cross-section, we obtain the rate of flow of heat,

$$Q_h = \int \mathbf{q} \cdot d\mathbf{S} = -\pi a^2 k \frac{dT}{dz}. \tag{25}$$

The corresponding cross-sectionally averaged fluxes of gas volume and heat are thus

$$\frac{Q_g}{\rho \pi a^2} = -\frac{1}{8}\frac{a^2}{\mu}\frac{dP}{dz} + \beta\frac{dT}{dz}, \tag{26}$$

$$\frac{Q_h}{\pi a^2} = -k\frac{dT}{dz}. \tag{27}$$

While the flux of gas through the tube depends on the pressure gradient as well as the temperature gradient, no analogous pressure gradient-induced contribution exists for the dissipative heat flux, the sole driving force for which is the temperature gradient. As a result, these fluxes do not satisfy the global Onsager reciprocal relations.

In fact, the application of the Onsager reciprocal relations to this problem leads to the conclusion that there can be no thermomolecular pressure gradient in a capillary whose radius is large compared with the mean free path of the molecules [11, 16, 17], or in other words, that a gradient in temperature cannot induce a pressure gradient or flow of gas under continuum conditions. This is contrary to experimental findings [18, 19, 20], which reveal that a thermomolecular pressure gradient is in fact induced under continuum conditions.

Conclusions

We have found that the existence of thermal stresses and thermal slip, or even the existence of thermal slip alone, leads to a violation of the Onsager reciprocal relations by the resulting hydrodynamic fluxes.

The reduction in order of Burnett stress terms previously supposed to be $O(\mathrm{Kn})$ higher than the Navier-Stokes equations has also been found to take place in the presence of concentration gradients, resulting in concentration-stress convection and the concomitant concentration gradient-induced slip condition [21]. The inclusion of concentration stresses in the momentum equation again leads to the loss of Onsager's symmetry, analogous to the thermally inhomogeneous situation. Analogous to thermal transpiration, the existence of concentration gradient-induced slip leads to the development of a pressure gradient in a capillary tube in which a steady state of binary diffusion is established [22].

While the inclusion of thermal and concentration stresses in the stress tensor and the use of the slip condition in the presence of temperature or concentration gradients are rigorously justified by kinetic theory for the case of gases, no similar justification is known to exist for the presence of thermal or concentration stresses in liquids. However, Semenov and Schimpf [23] provide an expression for the thermophoretic mobility of a solvent contained in a closed cell, such as a field flow fractionation channel, based on the asymmetry of molecular interactions in the presence of temperature gradients, leading to the development of a macroscopic pressure gradient in the channel. This situation is analogous to the development of a thermomolecular pressure gradient in a gas contained in a capillary under nonisothermal conditions, and follows from the solution of the Navier-Stokes equations in conjunction with an appropriate slip condition. The Onsager reciprocal relations at the global scale have been used to model the simultaneous flow of water and heat in porous media [24]. However, the existence of thermal slip in liquids, if established experimentally, would invalidate the use of the Onsager reciprocal relations for modeling the nonisothermal flow of liquids.

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