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Fluid creep effects on near-wall solute transport for non-isothermal ampoules*

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There is growing practical and theoretical interest in developing accurate macroscopic modelling for flows arising in chemical or physical vapor transport (VT) crystal growth experiments, including those conducted in reduced gravity environments. An example has been given by Debe *et al.*,¹ who reported on experiments performed aboard the Space Shuttle flight in 1985. The authors used physical vapor transport to grow oriented metal-organic thin films of copper phthalocyanine (CuPc) on epitaxially active substrates sealed within non-isothermal ampoules. This particular process is characterized by a fairly low operating pressure (in the Torr range) and very steep gradients of temperature and concentration predominantly in the axial direction (normal to the surfaces of evaporation and deposition). Typical operating conditions and preliminary theoretical investigations regarding the CuPc system have been presented by Rosner and Keyes.² It is noteworthy that, according to the measurements of Debe *et al.*,¹ temperature gradients can reach values as high as 75 K/cm (corresponding to an $O(10^{-3})$ fractional temperature difference over one mean-free-path) in the vicinity of the substrate. Rosner³ first pointed out that, whereas Stefan and buoyancy-driven flows were negligible under the conditions employed, previously neglected rarefied gas dynamics phenomena become rather important sources of convection. In particular, the combination of rarefaction and strong gradients of temperature (and/or concentration) tangential to the side-walls of the ampoule induces convective flows known as thermal (and concentration) "creep" respectively. His order-of-magnitude estimates revealed that thermal creep effects can be non-negligible even at normal gravitational levels.

On the macroscopic level and under the conditions mentioned above, the bulk fluid mechanics can be adequately described by the familiar macroscopic equations as long as the *boundary conditions* are modified to account for the integrated effect of kinetic (Knudsen⁹) boundary layers adjacent to solid boundaries. For example, the most general boundary condition for velocity at a simple gas/solid interface reads⁴:

$$\mathbf{v} = \mathbf{v}_w + \zeta \frac{\partial \mathbf{v}_t}{\partial n} + \omega \left(\frac{2kT}{m} \right)^{1/2} \frac{1}{T} \cdot \left(\frac{\partial T}{\partial \mathbf{x}} - \mathbf{n} \frac{\partial T}{\partial n} \right) \quad (1)$$

*Presented at 3rd Microgravity Fluid Physics Conference, 13-15 June, 1996, Cleveland, Ohio; supported, in part, by NASA Grant NAG-3-1654

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where \mathbf{v} , \mathbf{v}_w refer to the fluid and wall velocity respectively, subscript t denotes the component in the *tangent* plane, \mathbf{n} is the unit vector in the direction locally normal to the surface and \mathbf{x} is a general position vector. The indicated coefficients ζ, ω are *lengths* of the order of magnitude of the gas molecule mean-free-path and depend on the details of the intermolecular and the molecule/surface collision processes. Their values are obtained by solution of the Boltzmann equation or models thereof for idealized geometries. Equation (1) simply states that a velocity slip $\mathbf{v} - \mathbf{v}_w$ is associated with a gradient of tangential velocity in the normal direction and a gradient of temperature *parallel* to the boundary, the latter contribution referred to as *thermal creep*. Similarly, for an isothermal gas mixture :

$$\mathbf{v} - \mathbf{v}_w = \zeta \frac{\partial \mathbf{v}_t}{\partial n} + \sigma D_{12} \left(\frac{\partial x_1}{\partial \mathbf{x}} - \mathbf{n} \frac{\partial x_1}{\partial n} \right). \quad (2)$$

Here, D_{12} is the binary diffusion coefficient and x_1 is the species 1 mole fraction, while the coefficient σ is dimensionless. In analogy to eq. (1), the second contribution is called *concentration creep*.

Motivated by the growing importance of these phenomena, we have embarked on a series of computational studies to elucidate these fundamental creep-induced effects for a rarefied gas in simple, two-dimensional confined geometries. However, unlike previous related studies,^{5,6} we resort to a *microscopic* description of the gas, mathematically expressed by the Boltzmann integro-differential equation. We employ the direct simulation Monte Carlo (DSMC) method of Bird,⁷ the theoretical foundations and several practical applications of which can be found in reference 7. In the case of thermally induced flows, the no-time counter method of Bird⁷ is used, as implemented for a hard-sphere gas. The scheme has been also extended to account for realistic molecular interaction models, an extension necessary if the diffusion physics underlying concentration creep are to be captured.

The results reported herein (see Ref. 4,8,10 for details) pertain to a two-dimensional cartesian cavity, with length L in the x -direction, height H in the y -direction and an aspect ratio $\alpha \equiv L/H$, here taken to be unity. The systems studied consist approximately of a total of 10^5 computational particles, corresponding to an average of several tens of particles in each cell since the average number of computational particles per cell N_c is a simulation parameter which can seriously affect the solution accuracy and associated cost. In addition, an increased value of N_c tends to alleviate possible disparities due to slightly different nonequilibrium collision rate expressions reported in the literature⁷ and obviously represents the flow physics more closely. It is emphasized that axial gradients of temperature and concentration are imposed *via* appropriate microscopic boundary conditions but no creep velocity is specified along the side-walls as done in macroscopic formulations. Therefore, *creep velocities emerge as the problem solution without specifying them a priori*. Symmetry of the computational domain and the imposed boundary conditions allow for a reduction

of computational cost by a factor of two by simply imposing a symmetry boundary condition at the plane $y = H/2$. This is satisfied by requiring specular reflection for molecules ‘impinging’ upon this plane. Further details about the implementation can be found in Papadopoulos.⁸

Figure 1 depicts the velocity vector field together with the accompanying stream-tracer paths computed by our DSMC code for the specific choice of parameters $\Delta T/T_o = 0.66$, $T_o = 600\text{ K}$ and $Kn_T = 5 \cdot 10^{-2}$. The reference velocity u_{ref} chosen is computed by means of one-dimensional, linearized theory for a hard-sphere gas, based on the imposed tangential temperature gradient and other conditions. In figure 2 we show the computed flow field as induced by *concentration creep* for an Ar/He binary mixture. Spatial discretization is $\Delta x = 0.3$ in mean-free-path units. Other relevant parameters take the values $Kn = 2.3 \cdot 10^{-2}$, $Kn_c = 4.8 \cdot 10^{-2}$. Sufficiently far from the end-walls, concentration creep velocity scales increase with decreasing heavy species mole fraction x_1 , in agreement with predictions of one-dimensional theory.

Straightforward order-of-magnitude estimates show that, for comparable gradients and fixed Prandtl number ($Pr \simeq 2/3$), the ratio of thermal to concentration creep scales with the mixture Schmidt number $Sc \equiv \nu/D_{12}$. For typical operating conditions in CuPc/rare gas mixture systems, Rosner & Keyes² estimated $Sc \simeq 3.7$; thus, concentration creep is expected to be less important in these systems. Since thermal creep and isothermal concentration creep flows have been investigated previously on an individual basis, it seems reasonable to follow up with an investigation on their combined effect as a further step towards actual complex systems. Other future plans include the development of a novel computational scheme that will enable calculating fine details of kinetic boundary layer structure. In addition, we are currently assessing the feasibility of various schemes to study these interesting effects in higher density systems. Our long-term goal is to contribute a fairly comprehensive study of creep phenomena in enclosures used in actual crystal growth experiments. We believe we have demonstrated the value of a microscopic approach in revealing the complex nature of microgravity flows within PVT ampoules. One of our main objectives is to guide the implementation of computationally efficient, yet physically realistic, *macroscopic* descriptions of such flows, to anticipate their consequences in crystal growth ampoule experiments. Indeed, microgravity offers a unique environment to study the fundamental and practical aspects of these phenomena without the obscuring effects of gravity.

Acknowledgements

It is a pleasure to acknowledge valuable correspondence and discussions with I.B. Bernstein, M. Loewenberg, P. Garcia-Ybarra and D.W. Mackowski. This work has been supported by National Aeronautics and Space Administration under Grant No. NAG-3-1654.

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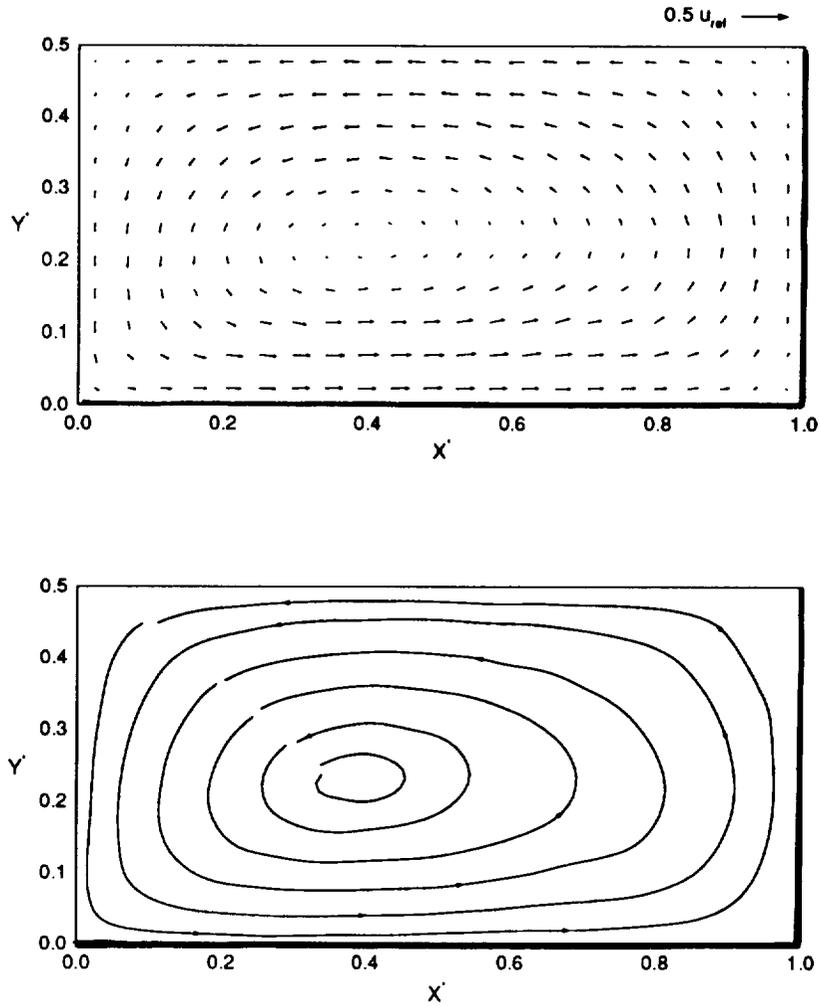


Figure 1: DSMC-calculated gas flow field due to *thermal creep* in a non-isothermal enclosure with $Kn_T = 5 \cdot 10^{-2}$, $T_0 = 600 K$ and $\Delta T/T_0 = 0.66$. A linear variation of wall temperature is imposed along the $y^* = 0$ plane whereas $x^* = 0$, $x^* = 1$ represent isothermal walls kept at temperatures T_1 , T_2 respectively. The $y^* = 1/2$ plane is a symmetry plane (see text for details). The thermal creep velocity predicted by one-dimensional, linearized theory for this specific set of parameters has been used as a reference velocity (u_{ref}). Lower plot shows corresponding streamtraces.

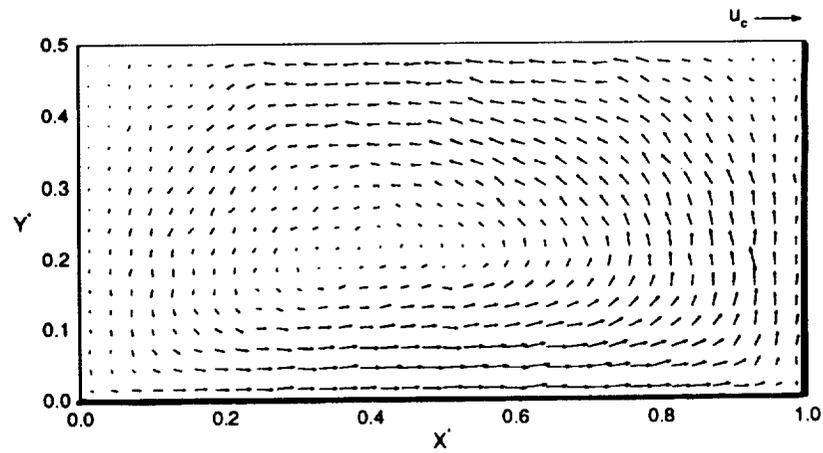


Figure 2: DSMC-calculated flow field induced by *concentration creep* for an Ar/He binary mixture. Relevant parameters take the values $\Delta x = 0.3$, $Kn = 2.3 \cdot 10^{-2}$, $Kn_c = 4.8 \cdot 10^{-2}$. Sufficiently far from the end-walls, concentration creep velocity scales increase with decreasing heavy species mole fraction x_1 , as predicted by existing one-dimensional, linearized theories.