

Fluid/Solid Boundary Conditions in Non-Isothermal Systems

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1. Introduction, background and objectives

In a short paper (*Phys. Fluids A* 1 (11) 1761-1763 (1989)) the PI pointed out for the first time that vapor-filled nonisothermal ampoules operating in micro-gravity will experience convection *driven* by both "wall-induced thermal creep"* as well as thermal stresses (in the bulk vapor). But, as emphasized in our subsequent review of thermally-induced *particle phoresis* (Rosner *et.al.*, 1992) these "thermal creep" boundary condition (BC-) phenomena also determine the readily observed migration rates ("phoresis") of suspended "small" solid particles in suspension. This led us to the idea that careful phoresis measurements in a suitably designed microgravity environment (to preclude complications such as 'sedimentation' for particles large enough both to sustain large temperature differences and avoid appreciable Brownian motion) could be used to obtain unambiguous information about the nature of the tangential momentum transfer boundary condition over a broad range of Newtonian fluid densities. This would be especially interesting since present *theoretical* methods are really valid only in the low density ("ideal"-) gas limit. As noted below, we recently carried out numerical simulations of the "low-density" Boltzmann equation which not only clarified the wall ("creep") BC, but also thermal stress (non-Newton-Stokes-) effects within such crystal-growth ampoule flows. However, to clarify the nature of the BC transition from the Enskog-Chapman regime to the technologically important but theoretically less tractable case of *liquid-like densities* (including supercritical polyatomic vapors) it is inevitable that high-quality *experimental* data for carefully selected fluid/solid interfaces will be required. The best environment for obtaining these data appears to be the *microgravity* environment, as spelled out in Section 2 below.

Previous theoretical work on "thermal creep" at fluid/solid interfaces (going back to J.C. Maxwell[1879]) has been understandably focused on "structureless", single component *low density gas* motion adjacent to a non-isothermal smooth flat solid surface, usually exploiting an approximate (*eg.* linearized) model of the Boltzmann equation and a "diffuse reflection" molecule/surface interaction model. However, since many applications are multi-dimensional and involve non-dilute mixtures of disparate mass polyatomic molecules, frequently well outside of the domain of "ideal" gas behavior, many generalizations are urgently needed to understand and ultimately predict such flows, whether in micro-gravity or in ground-based laboratories. Progress will be slow in the absence of reliable *experimental data* on the

dimensionless thermal creep (or wall 'slip') coefficient, C_{tc} , appearing in the relevant tangential momentum BC:

$$(v_{t,w})_{tc} = C_{tc} \cdot n \cdot (\cdot \ln T_{fluid,w} / \cdot x) \quad (1)$$

Here $(v_{t,w})_{tc}$ is the thermal creep contribution to the *tangential* component (x-direction) of the

*It is rather remarkable that, despite the small Knudsen numbers typically associated with these flows, one cannot apply "no-slip" boundary conditions along the non-isothermal ampoule walls-*ie.* the walls *drive* a significant amount of convection!

fluid *velocity* relative to the solid surface, n is the momentum diffusivity ("kinematic viscosity", m^2/r) of the fluid, and $T_{fluid,w}$ is the *fluid* temperature evaluated at the fluid/solid interface. One sees from Eq.(1) that such wall-induced creep flow is subtle since for solids in gases, if $C_{tc} = O(1)$ (as appears to be the case from the limited available experiments) then the Mach number associated with the wall creep flow is of the same order of magnitude as the fractional change of gas temperature over one mean-free-path.

In our view, the ultimate goal of this line of research is a rational molecular level theory which predicts the dependence of C_{tc} on relevant dimensionless parameters describing the way fluid molecules interact with the solid surface, and how they interact among themselves (see, *eg.*, Rosner and Papadopoulos,1996). Accordingly, microgravity-based experimental data (Section 2 below) will be an important step forward.

2. Photophoretic "space race" experiments

It might be thought that the best way to experimentally obtain this rather important dimensionless coefficient would be the "direct" one of measuring fluid velocities near non-isothermal solid surfaces using, say, laser velocimetry on very small (negligible inertia) particles immersed in the local fluid. However, even if the microgravity environment were used to preclude any confusion from bouyancy-driven convection, the phenomenon of *thermophoresis* (*eg.*, Rosner *et.al.*, 1992, Gomez and Rosner,1993) would inevitably cause the local motion of small "tracer" particles to depart systematically from that of the non-isothermal host fluid!

To avoid this dilemma we suggest exploiting the closely related phenomenon of *photophoresis* under *microgravity* conditions. This phenomenon (in which the intraparticle temperature nonuniformity which causes the thermal creep in the surrounding fluid is induced by the absorption of incident radiation) is quite sensitive to the momentum transfer boundary condition of interest (Eq.(1)) and becomes rather important at particle sizes at which sedimentation phenomena would normally set in for ground-based experiments (Castillo *et.al.*,1990, Mackowski 1989,1990). Thus, microgravity experiments involving deliberately suspended *supermicron* spherical solid particles of low thermal conductivity but with known "optical" properties (over a wide range of transparent fluid densities) could prove to be

extremely valuable in defining the nature of the momentum transfer boundary condition "transition" (*ie.*, C_{1c} -trends) from the low density (ideal gas-) limit to the *bona-fide* "liquid" limit.

One simple realization of this basic idea, would, in effect, be a "space-race" of illuminated, absorbing spheres, each immersed and simultaneously released in a different pure, transparent Newtonian fluid (including dense as well as low density polyatomic gases, and certain transparent Newtonian liquids). These low thermal conductivity spheres would be illuminated by a common non-polarized, omni-directional radiation source, and each would be large enough to sustain a significant temperature difference across its diameter (despite the isothermal environment far from each sphere). Moreover, as mentioned above, in the microgravity environment 'sedimentation' or 'bouyant rise' would be eliminated as a complication, broadening considerably the choice of informative fluid/solid combinations. Therefore, from the "photo-phoretic" drift velocity of these spheres, (recorded "from above" *via* a TV camera) and the relevant theory (see, *eg.*, Rosner *et.al.*, 1992, and Mackowski, 1989), it should be possible to extract the tangential momentum thermal creep coefficient, C_{1c} , operative at each fluid/solid interface.

We have already identified most of the basic requirements for such experiments (to extract the *dimensionless thermal creep coefficient*, C_{1c} , from measurements of photophoretic drift velocities in different Newtonian fluids). Indeed, we are currently evaluating the possible construction/use of *composite* test spheres to amplify the effects sought---*ie.*, opaque thin shells containing a thermally insulating rigid "core" of small mass. As a part of this research program we are currently working out the (asymptotic) theory of photophoresis for such test-spheres.

3. Thermophoresis of isolated solid spheres and aggregates in gases

A little-noticed but potentially very important feature (see below) of the existing theory of solid sphere thermophoresis in ideal gases is that for sphere thermal conductivities less than about 2.3 times that of the background gas, the sphere thermophoretic diffusivity can actually exceed that in the free-molecule limit! This remarkable feature, which translates to larger spheres moving faster than their smaller counterparts, may be partially 'rationalized' by noticing that, whereas the (Waldmann-) free-molecule limit calculation (see, *eg.*, Rosner, 1980, Garcia-Ybarra and Rosner, 1989, or Loyalka, 1992) does not involve either the abovementioned creep coefficient, or the sphere thermal conductivity, the near-continuum value *does* contain both C_{1c} , and sphere thermal conductivity. We mention this behavior here because, in related studies, we have been clarifying the effects of intrinsic thermal conductivity, particle morphology, and Knudsen number on the thermophoretic properties of suspended particles (in ideal gases), and 'coagulation-aged' populations thereof (Rosner and Khalil, 1998). While a comprehensive theory for *aggregate* thermophoresis as a function of Knudsen number is not yet available (see, *eg.*, Rosner *et.al.*, 1991), and outside the scope of the present program, we have proposed that a rational estimate can be obtained by imagining that an aggregate behaves like a homogeneous sphere with an effective mobility diameter about equal to the gyration diameter but with an *effective thermal conductivity* equal to that expected for the 'granular medium' (of spherules) existing at the gyration radius (for some details, see Tandon and Rosner, 1995). Results of this plausible model indicate that the thermophoretic transport rates of aggregates of even intrinsically conductive materials (like carbonaceous soot, for which $k_p/k_g \cdot 1000$ in *ca.* 1200K

combustion products) will remain high at *all* Knudsen numbers due to the poor *effective thermal conductivity* of such aggregates. We have shown (Rosner *et al.*,1998) that this leads to the following interesting conclusions about soot thermophoretic transport rates at very high pressures: 1. Actual soot *aggregate* transport rates at very high pressures are now expected to be perceptibly (but not appreciably) different from the rates formally expected using the *free-molecule* isolated sphere thermophoretic diffusivity; and: 2. If soot aggregates could be prevented from forming, or broken up prior to thermophoretic deposition, then appreciable transport rate *reductions* could be realized at very high pressures due to their high intrinsic thermal conductivity. The implications for soot *deposition* to cooled surfaces (Rosner,1986, Garcia-Ybarra and Castillo, 1997, Rosner and Khalil,1998) are immediate and potentially important.

4. Solid sphere thermophoresis in liquids and dense vapors

Dr. J. Walz and the PI have initiated a critical evaluation of the "thermal field-flow fractionation" (ThFFF-) data on apparent thermophoretic diffusivity coefficients for colloidal particles in liquids (see Shiundu *et.al.* (1995), and one ancillary theoretical treatment (Giddings, *et.al.*,1995)). We suspect these ThFFF *data* are 'falsified' by electrostatic interactions between the colder channel wall and the suspended particles whose retention behavior is reported. Moreover, the abovementioned "theory", which attributes the apparent thermophoresis to distorted double layers in an ionically conducting liquid rather than to the fluid/solid *thermal creep boundary condition* of primary interest to this program, cannot be general since (contrary to available experiments (McNab and Meisen,1973) it would predict *no* thermophoresis in the *absence* of mobile ions in solution---*ie.*, in *electrically non-conducting* fluids. Nevertheless, some variant of the ThFFF technique *could* prove to be a fruitful source of particle or macro-molecule thermophoretic coefficient data and thereby shed light on the fluid/solid thermal creep boundary condition) but *only if such electrostatic artifacts are eliminated or systematically corrected for.*

Particle *thermal* conductivity appears to play a role in the thermophoretic properties of suspended particles in non-(electrically) conducting liquids, but there is no current *theory* to predict such thermophoretic behavior. These considerations are expected to have important implications for the abovementioned photophoretic "space-race" experiment on macroscopic ("non-colloidal") suspended spheres in dense vapors and true liquids. One route to a theoretical understanding of in such systems may be hard-sphere vapor DSMC Knudsen layer simulations (see Part 6) in which the molecular volume fraction $f = (p/6) \cdot n s^3$ is non-negligible.

5. Thermophoresis of small immiscible *liquid* droplets

It does not seem to be generally appreciated that thermal creep should also influence (and ultimately dominate) the phoresis of immiscible *liquid* droplets if they are sufficiently small yet much larger than the mean-free-path in the prevailing Newtonian fluid. As is well known, the phoresis of large droplets is often adequately described exclusively in terms of Marangoni-driven flow associated with a temperature-dependent surface tension (with negligible interfacial 'slip'). (In contrast to ordinary thermophoresis this usually leads to droplet migration towards *hotter* regions of the host fluid). However, we find (Castillo *et.al.*,1998) that,

contrary to the statement of Ruckenstein (1981), the droplet phoretic velocity is *not* simply the (algebraic) sum of the abovementioned two effects reckoned separately. Moreover, the thermophoresis of sufficiently small droplets (*eg.*, organic fuel droplets in a "spray flame", or alkali sulfate "mist" nucleated in a thermal boundary layer (Liang, *et.al.*,1989) may be appreciable for the reasons mentioned above (*ie.*, small effective thermal conductivity ratio, $k_{p,eff}/k_g$). Not surprisingly, there is little available information on the magnitude of the thermal creep coefficient, C_{1c} , for such fluid/fluid (or vitreous 'solid') interfaces.

6. Applications of Direct Simulation Monte Carlo (DSMC)

In the low density ("ideal gas"-) limit many interesting "Knudsen sublayer" questions are now being answered with the help of a *Direct Simulation Monte Carlo* (DSMC-) method of the type originally developed for rarefied external gas flows (Bird,1994)) . A preliminary account of our results was contained in the paper by Papadopoulos and Rosner, 1996, and is updated here.

The DSMC code originally written by D. Papadopoulos as part of his NASA-MSAD-supported PhD dissertation research (see, *eg.*, Papadopoulos, 1996) is being used to provide predictions against which Burnett(-level) continuum predictions can be tested. In collaboration with Prof. D.W. Mackowski (Auburn U.) we have begun to critically assess the ability of Burnett-type ("higher-order") *continuum* methods to simulate gas flows within non-isothermal enclosures. In such cases, the 'meter-stick' for accuracy is the flow-field predicted by our DSMC (ideal gas) code. Whether it would be attractive to generalize such (near-) continuum methods to apply to the dense vapor regime remains to be seen.

DSMC has now also been adapted/used to study how well the Fuchs' 2-layer model can predict variable property† Knudsen transition regime *energy transfer* from a highly overheated spherical particle (Filippov and Rosner (1998)). Variable thermophysical property corrections will

†Of the available 'semi-theoretical interpolation methods, the Fuchs' 2-layer model appears to be the only one able to adequately capture the observed *non-monotonic* variable properties correction at intermediate Knudsen numbers.

be one (of many) correction(s) which will have to be understood to properly interpret solid particle thermophoretic and photophoretic velocities in terms of the more fundamental *thermal creep fluid/solid boundary condition* . Another motivation for this particular exercise of DSMC is the interpretation of signals produced using the promising soot diagnostic technique called "laser-induced incandescence"(LII) (Filippov *et.al.*(1998)) for both ground-based and micro-gravity combustion experiments .

Extensions of DSMC to provide solutions of the Enskog-Boltzmann equation for *dense* hard-sphere (HS-) vapors far from solid surfaces have recently been reported by Santos *et.al.* (1996). We have now taken steps to apply this extended (dense gas) methodology to examine the behavior of such a fluid in the immediate vicinity of a solid with a *tangential* temperature

gradient. In this way we hope to gain a better theoretical understanding of tangential momentum transfer between non-isothermal solids and *dense* fluids--- both *supercritical vapors* and true *liquids*, albeit restricted to the 'hard-sphere' case. This will have an immediate bearing on the expected phoretic velocities of solid particles or small immiscible viscous droplets suspended in such fluids (*cf.* Section 2, above).

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