Multicomponent gas diffusion and an appropriate momentum boundary condition

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Multicomponent gas diffusion is reviewed with particular emphasis on gas flows near solid boundaries--the so-called Kramers-Kistemaker effect. The aim is to derive an appropriate momentum boundary condition which governs many gaseous species diffusing together. The many species' generalization of the traditional single gas condition, either as slip or stick (no-slip), is not obvious, particularly for technologically important cases of lower gas pressures and very dissimilar molecular weight gases. No convincing theoretical case exists for why two gases should interact with solid boundaries equally but in opposite flow directions, such that the total gas flow exactly vanishes. In this way, the multicomponent no-slip boundary condition requires careful treatment. The approaches discussed here generally adopt a microscopic model for gas-solid contact. The method has the advantage that the mathematics remain tractable and hence experimentally testable. Two new proposals are put forward, the first building in some molecular collision physics, the second drawing on a detailed view of surface diffusion which does not unphysically extrapolate bulk gas properties to govern the adsorbed molecules. The outcome is a better accounting of previously anomalous experiments. Models predict novel slip conditions appearing even for the case of equal molecular weight components. These approaches become particularly significant in view of a conceptual contradiction found to arise in previous derivations of the appropriate boundary conditions. The analogous case of three gases, one of which is uniformly distributed and hence non-diffusing, presents a further refinement which gives unexpected flow reversals near solid boundaries. This case is investigated alone and for aggregating gas species near their condensation point. In addition to predicting new physics, this investigation carries practical implications for controlling vapor diffusion in the growth of crystals used in medical diagnosis (e.g. mercuric iodide) and semiconductors.

History and Problem Statement

In 1943, Kramers and his student Kistemaker [1] undertook a novel study of gas-solid interactions. Their initial aim was to examine the isothermal, counterdiffusion of two

gases, one having low molecular weight, the other having high molecular weight. The diffusion problem for the binary case was the simplest configuration which carried significance for many timely technological difficulties—most notably, isotope separation using gas diffusion.

Their experiment was straightforward: place two glass bulbs having equal volumes on opposing ends of a small capillary. Keep the capillary blocked initially and fill each glass bulb with a gas of either low or high molecular weight. (Nitrogen and helium were typical examples). Connect a second larger tube between the two bulbs to measure both the pressure differential and absolute pressure as a function of time. This "dumbbell" configuration represents one of the most versatile set-ups for studying gas behavior. The final step in the Kramers-Kistemaker experiment was to unplug the capillary tube, to initiate the counterflow exchange of gases between the two bulbs and to monitor the resulting pressure difference (Fig. 1).

What one might predict is a transient pressure increase, namely a local gas buildup or accumulation of the lighter component within the bulb initially rich in the heavier component. The explanation seemed simple: at the same temperature, the molecular velocity scales as the inverse square root of molecular weight, so the heavy component (nitrogen) travels down the capillary slower than the lighter gas (helium). Thus a resulting buildup of pressure arises locally in the bulb initially filled with heavy gas (nitrogen-rich end).

Over time, this transient pressure increase must tend to an equal pressure state or equilibrium. The observed finding therefore follows a predictable sequence: initially equal pressures, leading to a pressure difference driven
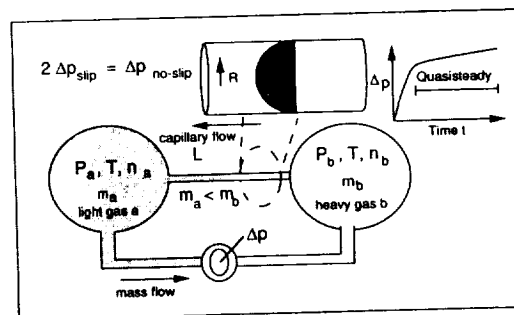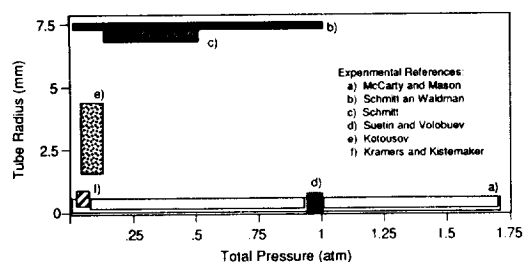

Figure 1. The baroeffect experiment. The stoppered sidearm measures the pressure difference between the two bulbs; pressure p, temperature T, and molecular weight m as shown.

by the differing molecular weights and velocities, finally ending with a backflow of both gases which stream out of the high pressure bulb towards the low pressure bulb. The predictable sequence was monitored simply using a manometer and pressure readings were reported as a function of time. The actual results of the experiment, however, proved most surprising.

As they predicted, Kramers and Kistemaker did see the back and forth flow of gases with time and a large pressure buildup amounting to about 10 percent of the total pressure. However, what they could not have predicted was that the pressure buildup was too low, about a third to a half as much as traditional kinetic theory might warrant. By varying the capillary size and absolute pressure, they found that the pressure difference changed accordingly (Table I). Both capillary size and absolute pressure, of course, combine to make the usual dimensionless number, the Knudsen number, which gives a measure of the importance of gas-gas collisions

Table I. The R-P Parameters for Diffusive Slip.

relative to gas-wall (capillary) collisions [2]. In this way, the Knudsen number, or equivalently the ratio between the mean free path in the bulk gas (a pressure-dependent term) and the capillary radius, could be used together to characterize the low pressure gas flow.

What remained to be explained, however, was not so much the changing pressure differences with Knudsen number, but the anomalously low readings reported for all sizes of capillaries and many different absolute pressures between 1-100 mm Hg. To solve the quandary, they had to look more closely at the particulars of gas-wall collisions. Their work began a serious reexamination of the momentum boundary condition, its multicomponent generalization and its implications for calculating gas transport properties. The remainder of this review will present the central issues in formulating a new boundary condition, propose a number of solutions to anomalous cases and finally suggest future directions for overcoming related problems in crystal growth from the vapor and other gas exchange technologies.

A new boundary condition. Dating back to Maxwell's original formulations of kinetic theory [3], numerous assumptions were built into the modern understanding of gas dynamics. The gas was assumed to collide with a solid surface, to randomize its outgoing direction and subsequently to attain instantaneous thermal equilibrium with the wall. Gas and wall temperatures were set to be equal everywhere, fixed at a single value and attained in an instant. The randomized direction was assumed to fit a familiar $sin^2\psi$ distribution for outgoing velocities (where ψ is the angle) and became known as the definition of diffusive or randomly directed reflection. This diffusive reflection was contradistinct from its alternative, mirror or specular reflection, which preserved the forward scattering but reversed or reflected its direction upon collision with a wall.

As for the solid itself, it was pictured by Maxwell as an infinite heat source or sink with some surface texture or roughness. Close to the wall, this roughness provided for the randomizing component to the outgoing gas velocity. On average, then, Maxwell used this picture to generalize the gas velocity to be exactly zero at the rough wall and the usual (and now standard) case of no-slip between gases in solid contact was born.

Kramers and Kistemaker took these Maxwellian arguments concerning gas-wall collisions and in their own experiment, built a rather convincing case for some novel physics. Maxwell's argument for no-slip holds particularly well for most cases of a single gas component hitting a wall. As confirmed subsequently using a host of observation techniques (direct flow visualization, pressure readings, etc.) and simulations (direct solution of Navier-Stokes equations), no-slip was then and remains today the experimental and theoretical

benchmark [2]. However, the multicomponent case, in particular the result for binary gases, is not so straightforward. It is not clear that all gases should collide with walls to give identical outgoing velocity and direction. For counterdiffusing gases, the result proved particularly perplexing: why should two gases (one heavy, one light or one monatomic, one diatomic with different rotational and vibrational modes) exactly cancel upon wall-collision and thus give no-slip? In fact, modern quantum mechanics says much to the opposite.

In 1943, Kramers and Kistemaker built into Maxwell's picture one additional corollary. Their binary gas diffusion experiments could be explained if they assumed that the average gas velocity did not tend to zero at the capillary wall. Rather some net slip velocity must arise from the different molecular weights of the component gases. They called this effect, diffusive slip, a finite mass-averaged velocity of two gases which counterdiffuse near a solid surface or wall.

Subsequent workers [4-13] have reported and confirmed these results using a variety of different setups and drawing on a more modern view of momentum transfer between gases and solids. Thus in general, the slip velocity can be thought to occur in isothermal fluids when a concentration gradient exists parallel to a solid boundary. The gradient drives diffusive flow and the boundary interacts differently with the two species. In multicomponent gases, the magnitude of the resulting flow depends critically on the inverse pressure and the molecular weight difference between the diffusing components. Low pressures favor higher slip velocities, as do higher molecular weight differences. The extremes of low pressure (P<100 mm Hg) and one very heavy gas drive a

maximum wall velocity (~1-10 mm/s).

Authors subsequent to Kramers have used different names to describe this same boundary effect: hydrodynamic flows, mass flow, non-diffusional flow, viscous bulk flow, the gas Kirkendall effect and the Kramers-Kistemaker effect. In industrial growth of crystals from their vapor, it has most recently been called, concentration creep [14]. The Soviet literature [6-11] uniformly refers to the accompanying experimental details as the baroeffect, a term which will be used interchangeably with the other terms in this literature. At all levels the fundamental modelling depends most centrally on simple mass and momentum conservation of gas molecules which diffuse near a wall.

An unsolved theoretical issue: the role of molecular weight. While the experimental procedure which accompanies the baroeffect is now well-established, a number of theoretical issues remain unsolved [14-19]. A recent review [20] acknowledged in passing that the multicomponent generalizaton of no-slip presents somewhat of a continuing mystery in fluid mechanics. The research thrust thus undertaken in the present literature has been to answer the fundamental question: how generalizable is the baroeffect experiment and should one expect no-slip to hold universally in all counter-diffusing gases? In the generalizations which follow, notable exceptions in kinetic theory are presented. Their consequences are discussed with particular attention paid to how future experiments might highlight or take advantage of exceptional gas behavior. Finally the practical significance of solving the baroeffect problem is remarked upon in reference to such diverse fields as vapor-crystal growth [16] and laser gas pumping.

The baroeffect problem for equal molecular weight gases. The first and most obvious question in generalizing the baroeffect is this: does a pressure buildup occur for *equal* molecular weight gases? A case in point is the common gas combination of carbon dioxide with nitrogen. Kramers and Kistemaker's theory predicts no baroeffect in this situation. Equal molecular weights should yield equal molecular velocities and thus no pressure difference. The actual experiment [17], however, indicates that sizable pressure differences arise for many equal molecular weight components. How can this be so?

Apparently gas-wall collisions must depend on some factor in addition to molecular weight. In this way, each gas interacts differently with the wall, thus some surface-sensitive property of molecular collisions must be identified and incorporated. In the spirit of Kramers and Kistemaker, the first several Generalizations thus undertake to preserve the basic form of the governing equations--mass and momentum conservation of gas molecules near the wall-- while including some physical parameters which are surface-sensitive.

Generalization 1: Specular reflection and the baroeffect for equal molecular weight gases Several candidate factors can be analyzed for plausiblity as the surface-sensitive parameter (Fig. 2). The first generalization of the baroeffect takes Maxwell's original definition of no-slip, the result of totally randomizing (diffusive) collisions, and considers the alternative consequences of a small fraction of collisions which cannot reach instantaneous equilibrium [15]. Recent molecular dynamics results by Koplik, et al. [18] suggest that this approach appears promising, since "algorithms (which
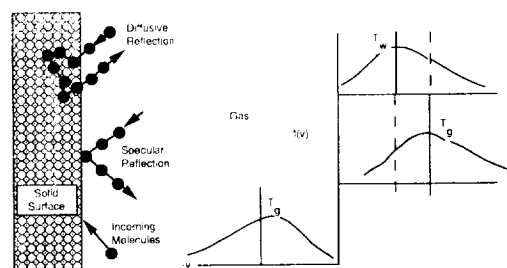

Figure 2. Typical velocity distributions in transition layer near the wall.

assume total diffusive reflection) do not apply to the problem of elucidating the boundary condition, because they essentially assume the answer."

Including a few percent of mirror reflection allows higher values for slip velocities, predicts faster buildup of light molecules in the high pressure bulb and thus can readily account for the anomalous baroeffect results even in the case of equal molecular weight species [15]. The most important consequence of the analysis, thus, is the beginning outline of a plausible and (self-) consistent way of looking at the otherwise unexplainable, equal-molecular-weight experiments. The baroeffect occurs in equal molecular weight gases because the gases reflect differently from the boundary. In this way, the Generalization condenses the complex interactions of two gases into one parameter, the fraction of specularly reflected molecules. This fraction carries historical significance in kinetic theory [3] and now appears summarily as an important parameter in molecular beam experiments. The first task of finding a surface-sensitive parameter is the central outcome of Generalization 1.

Generalization 2: Surface diffusion and the

baroeffect for equal molecular weight gases
Generalization 2 continues the previous line of analysis, namely it seeks to find a more general and scientifically appealing picture of how different gases can transfer momentum to a surface. The work [16] takes up the same question as Generalization 1 (does the baroeffect generalize theoretically to equal molecular weight gases?), but aims for a broader parameter for measuring surface sensitivity. It proposes a more sophisticated picture of gas-wall collisions as interactions between potential energy wells (Fig. 2). No longer does the Maxwellian view of colliding hard spheres, mirror reflection or rough walls play a dominant role. Rather, each gas is considered as having a characteristic interaction or relaxation time upon wall contact. This relaxation time differs according to the gas molecular weight and its self-diffusion coefficient. The result is a fundamentally different view of the baroeffect experiment. In this new picture, equal molecular weight gases differ not so much in their outgoing direction upon wall collision, but in their depths of penetration and relaxation times to move *within a potential well* on the surface. Because one gas may spend more time on the surface (higher potential for desorption), its viscous interaction with the wall will differ from one gas to another in a way consistent with experiment. The finding is thus that residence times carry five-fold more significance compared to molecular weight in regulating gas-wall flows. In other words, a doubling of residence time has an equivalent effect on predicted slip velocities of an order-of-magnitude increase in molecular weight. In the baroeffect experiment, this finding would argue for a more careful consideration of

atomic interaction potentials relative to their coarser and somewhat anomalous dependence on molecular weight as a control parameter alone.

Generalization 3: Is the baroeffect generalizable to steady-state conditions? This brief analysis [17] examines the transient behavior of the baroeffect pressure buildup and its evolution as a function of time. The baroeffect is always transient, a short-term pressure increase which drives a compensatory backflow of gases. No true steady-state exists. However, the theory's historical development has abandoned this recognition of transiency and rather assumed steady-state diffusion as a governing assumption. Kramers and Kistemaker's original treatment [1] relied on an assumption of steady-state diffusion or equivalently no net molecular flux between the two bulbs. In steady state, each heavy gas molecule moving in one direction was accompanied by a compensating light molecule moving in the reverse direction. However, such a steady-state assumption cannot be supported for a transient baroeffect, either experimentally or theoretically. The experimental evidence is the most convincing.

One key rule for binary counterdiffusion is found to hold across all pressure regimes and goes by the name of Graham's law [19]. Grahams' law maintains that the molar flux ratio scales as the inverse square root of molecular velocities, $(nm)_1/(nm)_2 = (v_2/v_1)^{1/2}$. Implicit however within baroeffect results is the assumption that in steady state diffusion, the molecular flux must compensate and balance, namely that $(nm)_1/(nm)_2 = (v_2/v_1)$. This difference in velocity exponents, either as first-order or a square-root, is neither experimentally supportable, nor consistent with any kind of no-slip condition at

the wall [17]. In fact, no-slip cannot hold for such steady-state counterdiffusion, a general result which reaches beyond the particulars of any baroeffect experiment to include most examples of multicomponent diffusion setups (such as crystal growth from vapor). This inconsistency appears in at least six derivations in the baroeffect literature [4,7-9,11-12] including Kramers-Kistemakers original development. No longer can diffusive slip be thought of simply as a parametric excursion which fits experiment to theory. Rather diffusive slip is the consistent framework for treating multicomponent diffusion, more the rule than the exception. Elsewhere Kucherov [10] has expressed similar arguments in favor of developing a more rigorous kinetic theory to underpin the no-slip condition.

Generalization 4: Is the baroeffect generalizable beyond the binary case to 3 gases? Generalizations 1-3 have posed some novel physics in binary counterdiffusion. Their main purpose has been to characterize the surface physics of binary gas collisions with a wall. The case of three gases or the ternary baroeffect not only builds on these previous generalizations, but presents an appealing set of new interactions. Generalization 4 examines the possibilities of an experimenter actively controlling the counterdiffusion of two gases [18]. Experimental control depends on adding a third gas to counterweight or mitigate between the usual binary exchanges. This third gas can be thought to correspond best to a buffer gas typically included in crystal growth ampoules.

For an advantageous selection of the third gas (i.e. high molecular weight), the analysis finds that counterflow can be slowed, halted or finally

reversed entirely. The prospect is introduced to amend the usual baroeffect result, namely to cause the gas to flow in a counterdirection in the bulk and near the wall [17]. In other words, while bulk flow goes from heavy towards light gas, the wall flow goes opposite, from light to heavy (Fig. 1).

The all-important boundary interaction drives the new phenomenon and depends on the heaviness of the third gas. The result is called negative slip, suggesting that the wall gas velocity flows contrary to the bulk flow from heavy towards light gas. The wall flow instead can be either made to stop or move from light to heavy gas. Negative slip arises most prominently for very different molecular weights betwen the two principal gas components, in particular when coupled with a heavy, third gas which buffers their exchanges. Since these results hinge on the assumption that the third gas is equally distributed initially in the two bulbs (i.e., no initial concentration gradient in gas 3), then experimental confirmation of negative slip would be the next logical and most welcome step.

The analysis more generally explores the use of a buffer gas as an independent control parameter. Through its successful manipulation, a new experimental handle is given. Now baroeffect theories can be tested more completely. Novel gas recipes can be generalized using a standard diffusion apparatus. Finally, preliminary contact can be made with a host of intriguing applications in vapor-crystal growth and laser pumping [21-29]. These technological issues will be briefly taken up in the conclusion.

Generalization 5: Is the baroeffect generalizable to two self-aggregating gases? An allied problem to the 3-gas baroeffect is the

standand case of two gases counterdiffusing as before, but now with one or both components capable of irreversible aggregation [19]. Gas aggregation, itself, is an important event in low-temperature applications near a gas's condensation point. A host of aggregated states appear routinely (even in otherwise inert species such as argon) and range in complexity from dimeric to higher oligomeric combinations. The appearance of such states is known to complicate interpretation of other diffusion experiments [25].

No previous work has looked to the baroeffect as a way to monitor the aggregation process, despite the sensitive molecular weight determinations that the experiment typically can yield. Generalization 5 therefore treats the simplest possible example of a single gas, unaggregated in one bulb as monomeric, but aggregated in the second bulb into higher order oligomers. For a single species in different states of aggregation (equivalently, polymers or j-mers) pressure predictions are found as a function of the aggregation state alone. In sum, this Generalization reports pressure differentials for more or less aggregated gases.

As expected, the more highly aggregated species has higher overall molecular weight and thus can drive larger pressure differences when contacted with its monomers. The principal limit of this analysis is the assumption that aggregation is irreversible. A given oligomeric state must persist despite interpenetration with its monomeric building blocks. Unfortunately on this point there exists little experimental guidance. However, large potential barriers are known to provide a steeply rising free energy curve for disaggregation and thus effectively to separate aggregated species at appropriate

temperatures [28,29]. Much more experimental work here is required.

To initiate such investigations, one preliminary case is presented to conclude the baroeffect analysis [19]. In the case of a pressure-sensitive aggregation state, very novel (and possibly oscillatory) states can be derived from the usual baroeffect picture. Namely as two monomeric gases flow down the capillary tube, the expected pressure increase in one bulb will customarily lower the free energy for its aggregation. But more aggregation must necessarily reduce the relative driving force for further diffusion (i.e. push the system towards its equal molecular weight limit). This interesting circumstance suggests that as the driving force of aggregation increases (i.e. pressure buildup), then the corresponding driving force for diffusion must decrease (i.e. more equal molecular weights for pressure-sensitive aggregation). The feedback circuit is a classic recipe for non-linear behavior which deserves further examination and a concerted search for oscillatory or chaotic states. The principal result of this generalization derives from its formal analysis of the aggregation effect on pressure differences, velocities, and direction of flow. The baroeffect's dependence on molecular weight logically suggests the experiment as a means to follow aggregation with time.

Technological implications of the baroeffect
The central point of the analysis has been to generalize the baroeffect. The baroeffect experiment was originally designed as a simple test for finding diffusion coefficients. The need for an accurate understanding of binary counterdiffusion and in particular, its molecular weight dependence, arose directly from the war-

time needs of isotope separations. Even this simple experiment, however, proved to yield forth a multifaceted set of new questions. Subsequent workers have used the general picture of binary counterdiffusion for aerosol research, crystal growth and laser pumping. The crystal growth literature [21-23, 30]] is most relevent presently.

Like the baroeffect, crystal growth from vapor typically employs more than one gas which diffuses along a concentration gradient from some source (uncrystallized solid) to some sink (the crystal). To regulate or control the speed of this transport is the primary aim and challenge of crystal growth.

To manipulate the rate of crystal growth, a buffer gas of different molecular weight is often added to the growth ampoule [30]. When the detailed computer modelling of such gas flows is undertaken, however, the relation between a valid boundary condition and subsequent vapor transport becomes important. For example, if the mass-averaged velocity is chosen to be zero at the ampoule's boundary (i.e. no-slip), then the simulation will show large recirculation loops of flowing buffer gas [21,30].

The explanation turns out to be simple: near the walls, the crystallizing component must travel from source to sink for crystal gorwth to occur uniformly across the crystal's face. However if no-slip or zero mass-averaged velocity is applied at the wall, this requirement of a net flux of the crystallizing component necessarily demands a compensating back circulation of buffer gas. Large crystal growth rates thus drive fast recirculation of buffer and non-uniform diffusion is caused simply by the *assumption* of no-slip. Gravity, temperature gradients or chemical kinetics play no role in this

flow, since the backflux of buffer gases follows from the assumed no-slip condition alone.

Clearly, a deeper experimental understanding of crystal growth will require both accurate diffusion coeffficients between mixed components and also the kind of physical intuition of gas exchanges found from a detailed look at the various baroeffect results. This research thrust motivates the current review and will dominate work in future baroeffect investigations.

To summarize, the control parameters for understanding the baroeffect are the total pressure, molecular weight and gas aggregation state. The measurable parameters are the slip velocity and the pressure differential between the two gas bulbs. The question is how general is the kinetic theory for solid-gas interactions. To construct a general theory, a model must explain the molecular weight behavior for counterdiffusion, identify a surface sensitive parameter either for molecular reflection or for residence times within a potential well, and account for transient effects in the time evolution of the pressure. As an outcome of this analysis, new physics arises in cases of a very heavy buffer gas and aggregating gas diffusing near its condensation point. The application of this unique phenomenon plays a role in a host of technologically advanced crystal growth setups and controls recirculation of gas driven by the boundary condition itself.

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