A Surface Recombination Velocity Model for Liquid Flow in Microchannels

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Extended Abstract

A number of years ago, Eyring introduced the free volume concept to explain why the viscosity of liquids decreased with increasing temperature while at the same time the density for most liquids also decreased (water at O/C being an outstanding and fortunate exception)(1,2). The coefficient of expansion of solids has been reasonably accounted for in terms of the increase in phonon density as the temperature increases. The obvious difference between liquids and solids is the structural order in solids and the general absence of a corresponding long range order in most simple liquids. Eyring's concept of a "free volume" creates space within the liquid as it expands. There is a corresponding concept in solids, namely vacancies.

The presence of vacancies in solids has been used extensively to understand their mechanical, electrical and optical properties. The diffusion of vacancies to and from an interface with their subsequent destruction or creation has been often used to explain the annealing of solids. Vacancies or "holes" also arise in electron transport in semiconductors. Both vacancies and holes arise naturally by thermal activation and exist at thermal equilibrium in solids. However, it is possible to generate excess vacancies and holes over and above their equilibrium value. Given enough time, the holes will recombine with the excess electrons and the excess vacancies will recombine with either with excess interstitial molecules or will diffuse to the surface where they disappear. In the former case, the process is accelerated due to the charge state of holes and electrons while in the latter case, bulk vacancies are generally removed by thermal processes (even though in some instances, stress fields can accelerate the process). What is intriguing about the electron-hole situation is that there is excess current flow so long as the excess carriers exist. The removal of the electron-hole pairs is due to recombination process in the bulk and at the surface. All recombination processes obeys the reaction

$$e+p \rightleftharpoons 0$$

which is identical to the generation recombination process for vacancies (3,

$$V+S \rightleftharpoons 0$$

where e represents the electron, p represents the hole, V is the vacancy and S represents either an interstitial molecule or a surface molecule.

In this paper, we examine this analogy a bit further, following Eyring's original reasoning, by associating the motion of a liquid as a vacancy process. However, the generally accepted view that the flow of liquids is incompressible would imply that vacancy generation cannot occur because of continuity requirements. Our view is that the actual change in density due to excess vacancy generation is sufficiently small so that continuity still applies. By focusing on the vacancy motion rather than the molecular motion, some simplicity is introduced into the problem. It is the presence of excess vacancies due to shearing of the liquid that mediate the flow. What we are interested in is to see if the same approach used in electron-hole recombination can be applied to the flow process, especially in very small channels. The model proposed is greatly simplified. First, we assume that the motion of the liquid is associated with the density of excess vacancies generated by the shearing process in the medium. Second, we assume that the flow is laminar in order to have a simple shear distribution. The justification for the laminar assumption is that we will apply this model to data taken by Urbanek et al. in microchannels that have hydraulic diameters, d, in the 3-10 μm range (4). The flow studied had sufficiently small Reynold numbers so that laminar flow was assured. Third, we assume that a no-slip boundary condition applies to this problem. In a sense, this assumption is somewhat contradictory since the shear is then greatest at the walls, just where the flow is going to zero. However, there already exists a large density of vacancies due to thermal equilibrium in the liquid so that the additional shear induced vacancies are a perturbation on the overall concentration. By increasing the temperature, the equilibrium concentration of vacancies should increase but we would anticipate that the diffusion coefficient of the excess vacancies will also increase. If there is a recombination process at the walls of the channel, the excess density of vacancies should decrease more rapidly not only at the surface, but also in the bulk of the liquid. This, we will examine how temperature enters into the problem with specific reference to the diffusion of the vacancies to the walls.

Using the laminar flow assumption with no-slip boundaries, the velocity profile, U(r), in a plane parallel microchannel is

$$U(z) = U_{d/2}\,[z(d-z)]$$

where $U_{d/2}$ is the maximum velocity at the center of the channel. The reason for choosing the plane parallel channel is for its simplicity. The shear can be written as

$$\frac{\partial U}{\partial z} = U_{d/2}\,(d-2z).$$

Assuming that $\Delta\rho_v(z)$ is the density of excess vacancies, we can write the continuity equation for the vacancies as

$$D_v(T)\frac{\partial^2\Delta\rho_v(z,t)}{\partial z^2} + G(z) - R(z) = \frac{\partial\Delta\rho_v(z,t)}{\partial t}$$

We will only consider the simplified case where the system is stationary in time so that $\Delta\rho_v(z,t) \equiv \Delta\rho_v(z)$. This yields

$$D_v(T)\frac{\partial^2\Delta\rho_v(z)}{\partial z^2} + G(z) - R(z) = 0$$

where the generation rate is

$$G(z) = A\,U_{d/2}\,(d-2z)$$

and the recombination rate is

$$R(z) = \frac{\Delta\rho_v(z)}{\tau_{recom}}$$

The resulting differential equation is then

$$D_v(T)\frac{\partial^2\Delta\rho_v(z)}{\partial z^2} - \frac{\Delta\rho_v(z)}{\tau_{recom}} = -A\,U_{d/2}\,(d-2z)$$

Introducing the dimensionless units: $L_d = \sqrt{D_v(T)\tau_{recom}}$, $\xi = \frac{z}{L_d}$, $\xi_{d/2} = \frac{d}{2L_d}$ and $y(\xi) = \frac{\Delta\rho_v(\xi)}{2\,A\,U_{d/2}}$, we obtain

$$\frac{\partial^2 y(\xi)}{\partial\xi^2} - y(\xi) = \xi - \xi_{d/2}$$

The complete solution to this differential equation has the form

$$y(\xi) = A_1\sinh(\xi) + B_1\cosh(\xi) + \xi_{d/2} - \xi$$

We now introduce the boundary conditions that $y(\xi)$ is symmetric about $\xi = \xi_{d/2}$, i.e.

$$\left.\frac{\partial y(\xi)}{\partial\xi}\right|_{\xi=\xi_{d/2}} = 0$$

and that

$$\left.\frac{\partial y(\xi)}{\partial\xi}\right|_{\xi=0} = \alpha y(0)$$

where $\alpha = \frac{SL_d}{D_v}$ and S is the surface recombination velocity for the vacancies at the wall, $\xi = 0$. It is straightforward to show that

$$y(\xi) = \frac{\cosh(\xi)+\alpha\sinh(\xi)-(1+\alpha\xi_{d/2})\cosh(\xi_{d/2}-\xi)}{\sinh(\xi_{\delta/2})+\alpha\cosh(\xi_{\delta/2})} + \xi_{d/2} - \xi$$

One interesting observation that can be made immediately is that $y(\xi_{\delta/2})$ does not vanish. It has a finite value given by

$$y(\xi_{d/2}) = \frac{\cosh(\xi_{d/2})+\alpha\sinh(\xi_{d/2}) - (1+\alpha\xi_{d/2})}{\sinh(\xi_{\delta/2}) + \alpha\cosh(\xi_{\delta/2})}$$

As $\xi_{d/2}$ becomes large, $y(\xi_{d/2})$ approaches 1. The density of vacancies becomes directly proportional to the maximum velocity of the fluid. However, as $\xi_{d/2} \rightarrow 0$, the bulk generation of vacancies decreases and the result is that $y(\xi_{d/2})$ varies as

$$y(\xi_{d/2}) \rightarrow \frac{\xi_{d/2}^{\;2}}{2\alpha}$$

which is what one expects in the absence of surface recombination. These results are summarized in Figure 1 for a limited range of α and $\xi_{d/2}$.

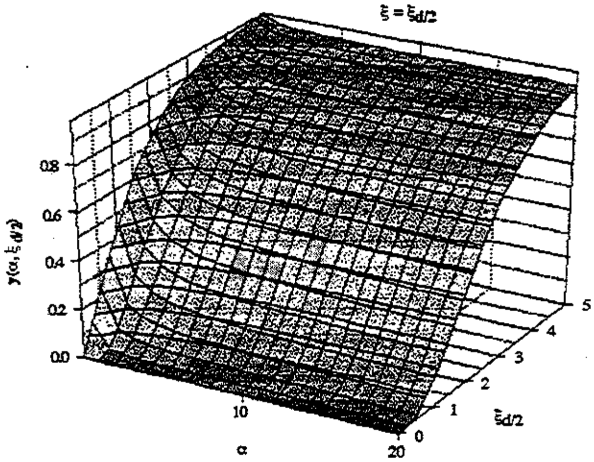

Figure 1. Concentration of vacancies at the midpoint of a parallel plane microchannel as a function of the half height of the channel, $\xi_{d/2}$ and α. The decrease in y as a function of $\xi_{d/2}$ for small α is due to the decreasing shear as $\xi_{d/2} \rightarrow 0$.

The variation of $y(\xi)$ for a fixed value of α and different value of ξ and $\xi_{d/2}$ is also of interest. Consider the three cases where α = 1, 10 and 100 in Figure 2. These data illustrate the rapid decrease in the vacancy density in the vicinity of the surface as α increases. For $\alpha \geq 20$, there is essentially no unrecombined vacancies at the surface.

If we now integrate $y(\xi, \xi_{d/2}, \alpha)$ over $0 \leq \xi \leq \xi_{d/2}$, we obtain

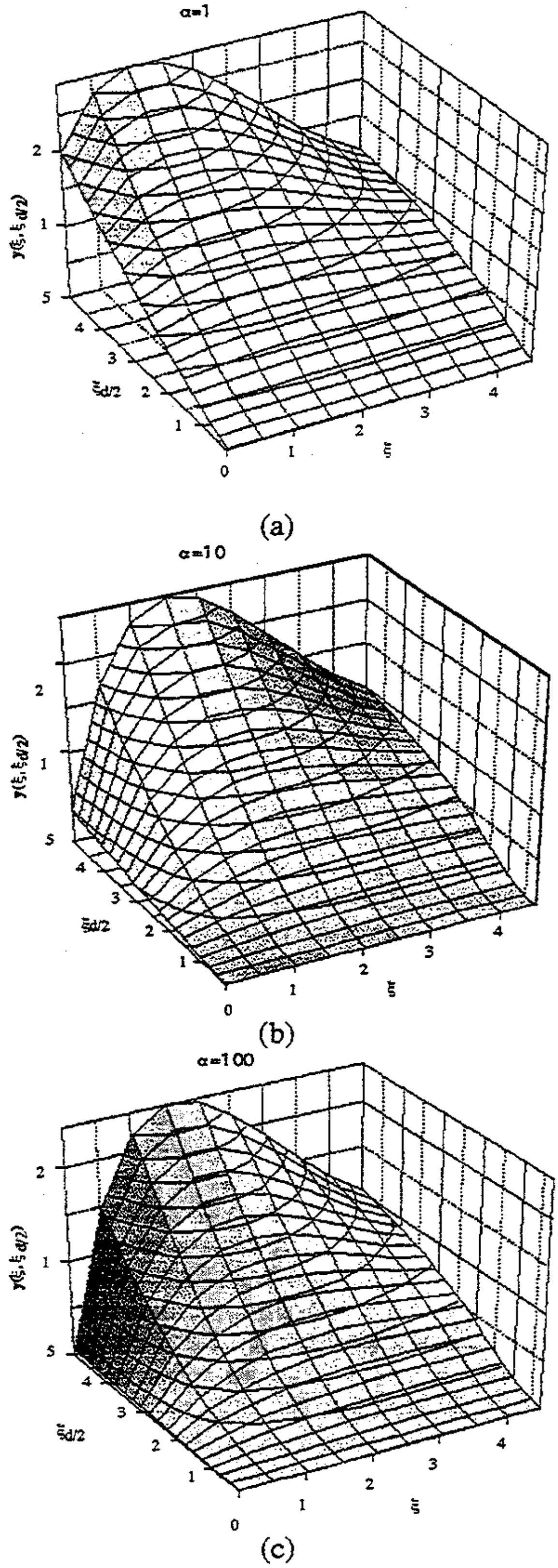

Figure 2: $y(\xi, \xi_{d/2})$ for α = 1, 10 and 100.

$$<y((\xi_{d/2},\alpha)> = 1 + \frac{\xi_{d/2}^{\,2}}{2} - \frac{\alpha + (1+\alpha\xi_{d/2})\sinh(\xi_{d/2})}{\sinh(\xi_{d/2}) + \alpha\cosh(\xi_{d/2})}$$

dividing this by the "bulk" value corresponding to $\alpha = 0$, $\frac{\xi_{d/2}^{\,2}}{2}$, we obtain an expression for the reduced flow through the microchannel, ν.

$$\nu = 1 - \frac{2\alpha}{\xi_{d/2}^{\,2}}\left(\frac{\cosh(\xi_{d/2})-1-\alpha\xi_{d/2}\sinh(\xi_{d/2})}{\sinh(\xi_{d/2}) + \alpha\cosh(\xi_{d/2})}\right)$$

that we will compare to the reciprocal of the reduced Poiseuille number, P* used by Urbanek (6).

P^{*-1} = P(Ideal) /P(Experimental)

The experimental data obtained by Urbanek for 2-propanol is shown in Figure 3 to illustrate the overall behavior of this fluid in a microchannel. The important point to note is that P* increases with temperature.

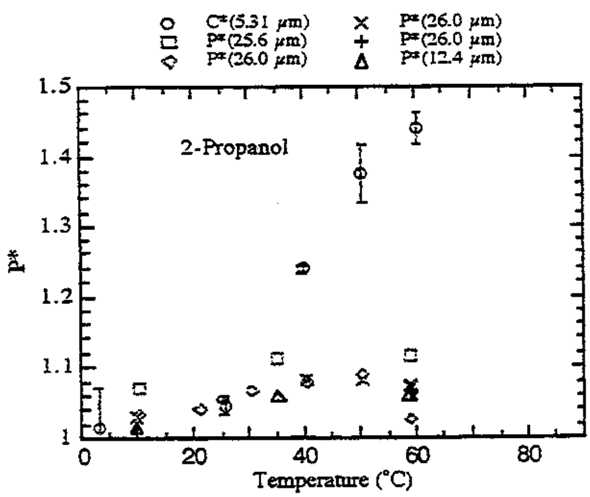

Figure 3. Experimental data on ther temperature dependence of P* of 2-prpanol flow in microchannels of different hydraulic diameter. Multiple data sets taken in the same channel are presented.

$\nu(\alpha,\xi_{d/2})$ is plotted in Figure 4. If ν is unity, the flow is identical to the bulk flow. If ν is less than unity, it correspond to a Poiseulle number greater than unity, i.e. the liquid flow is less than predicted by the Navier-Stokes equations. If $\nu < 1$, the Poiseuille number will be less than unity, i.e. the liquid flows more easily. The former condition is what has been observed by Urbanek et al. for liquids while the latter arises when slip occurs in gas flow

(5). If we allow $\xi_{d/2}$ to become quite small, then ν reduces to a simple expression

$$\nu = \frac{\xi_{d/2}}{\xi_{d/2} + \alpha}$$

Note that if α vanishes, $\nu \rightarrow 1$ but will always be less than unity if α is finite.used by Pfahler et al. (5), Harley et al (6) and Urbanek et al (3). This plot represents the core result since it demonstrates several important characteristics of the data taken by Urbanek et al. (3) First, at large values of $\xi_{d/2}$, the value of $P \rightarrow 1$, as expected from any model. A second and potentially equally important result is that $P \rightarrow 1$ when $\alpha \rightarrow 0$. The significance of this result is that α is likely to be a material dependent parameter and ought to be characteristic of the liquid wall interaction.

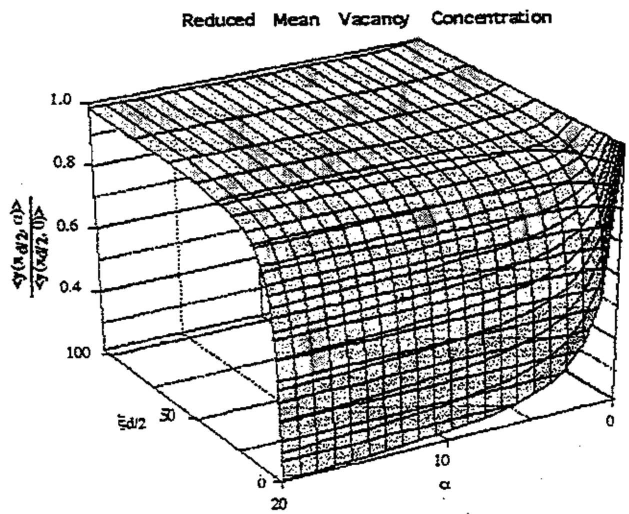

Figure 4. Reduced mean vacancy concentration, ν, as a function of α and $\xi_{d/2}$. Note that ν rapidly approaches unity as $\alpha \rightarrow 0$ for all $\xi_{d/2}$ but becomes quite small for $\alpha \geq 1$ and $\xi_{d/2} \leq 10$.

We emphasize this point because the data for water, perhaps the most extensively studied liquid, suggests that P* is essentially unity down to extremely small $\xi_{d/2}$ values (Anderson and Quinn (7), Beck and Schultz (8), Zemel and Furlan (9)). By contrast, the data of Urbanek et al. (3) suggest that the value of α is non-zero and may be appreciable, especially at elevated temperatures.

Conclusion: The results of this calculation suggest that there may be a useful empirical parameter, the surface recombination velocity of shear generated vacancies in liquids, that might offer insights into the dynamic behavior of liquids in microchannels. Based on the the experimental evidence, the recombination (destruction) of the vacancies at the surface increases with temperature, a result that seems reasonable to us. However, additional experiments on the flow of a variety of liquids in microchannels are needed to confirm the observations of Urbanek as well as experiments that provide more definitive evidence for a vacancy model for flow of fluids.

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