

Comment on “No-Slip Condition for a Mixture of Two Liquids”

Koplik and Banavar [1] in a recent paper make the broad generic claim that the classical no-slip mass-average velocity boundary condition at solid walls applies equally well to the individual *species* velocities in a diffusing binary mixture subjected to a concentration gradient parallel to the direction of flow. However, their conclusion cannot be correct. The question of whether, in fact, $\mathbf{v}_i = \mathbf{0}$ ($i = 1, 2$) at the wall is crucial in the context of the *volume-average* velocity, the importance of which has been elucidated in [2]. It is important to recall in what follows that the continuum-mechanical definition of the vector species flux relative to the fixed walls is $\mathbf{n}_i = c_i \mathbf{v}_i$, and that this flux consists of a convective contribution $c_i \mathbf{v}$ together with a molecular diffusive contribution $\mathbf{j}_i = c_i(\mathbf{v}_i - \mathbf{v})$, where c_i is the mass of species i per unit volume and \mathbf{v} the mass-average velocity.

The very concept of specifying both species velocity *vectors* at the wall—*whether zero or otherwise*—as boundary conditions to be imposed on the governing species transport equations at the continuum length scale (e.g., the distance L , say, between the flat plates in the two-dimensional Poiseuille flow case considered in [1]) for the case of constant diffusivity is mathematically flawed. Specification of two such *vector* boundary conditions overspecifies the data required to assure a uniquely posed pair of scalar convective-diffusion equations governing the species transport process. As such, no solution of the boundary-value problem will exist. One is free to specify only that the *normal* components of the species velocities vanish at the wall (and even then, only if no surface adsorption, surface chemical reaction, or other species-depleting continuum-level process occurs at the wall) [2]. The corresponding *tangential* species velocity components are then determined *a posteriori* from the solution of the convective-diffusion equations and cannot be specified *a priori*—either as being zero or anything else. For the sake of definiteness, below we make our point explicit for the particular case where Fick’s law, $\mathbf{j}_i(x, y) = -D\nabla c_i(x, y)$, describes the diffusive species flux; however, our generic arguments transcend use of this particular constitutive equation. The claim that the species velocities vanish at the wall $y = 0$ automatically assures the same for the mass-average velocity. As such, these jointly require that the molecular diffusion fluxes vanish at the wall: $j_{ix}(x, 0) = 0$. However, according to Fick’s law, $j_{ix}(x, 0) = -Ddc_i(x, 0)/dx$. Therefore, the vanishing of the species velocities requires that $c_1(x, 0) = \text{const}$, a result which is inconsistent with the fact that $c_1(1, 0) = 0.75$ and $c_1(21, 0) = 0.25$. Thus, the argument that $\mathbf{v}_i(x, 0) = \mathbf{0}$ contradicts Fick’s law.

How can the authors’ apparently accurate microscale numerics, presumably demonstrating that $v_{ix}(x, 0) = 0$, be reconciled with our statement that this is impossible?

Only relatively small differences exist between the respective magnitudes of the mass-average velocity \mathbf{v} and the species velocities \mathbf{v}_i . Estimates of the respective orders of magnitude of the convective and diffusive velocities can easily be effected as follows: $v_x \sim |dp/dx|R^2/8\eta$, and $(v_x - |v_{ix}|) \sim D\Delta c_i/L$. From the values provided in [1] we can estimate $(v_x - |v_{ix}|)/v_x \sim 0.01$. Given the noisiness of the results of the simulation in relation to the smallness of the latter, together with the uncertainties introduced when asymptotically extrapolating the discrete “bin” results to the wall, $y = 0$, it could easily have been (numerically) incorrectly concluded that $\mathbf{v}_i(x, 0) = \mathbf{0}$ since $\mathbf{v}(x, 0) = \mathbf{0}$. Had the authors, for example, studied the limiting case of pure diffusion, where $\mathbf{v} = \mathbf{0}$, the small *but nonzero* value of \mathbf{v}_i would perhaps then have been discerned without being masked by the numerically dominant \mathbf{v} term.

While our arguments exclude the possibility of species adherence at the usual Navier-Stokes, convective-diffusion, continuum level of description (the L scale), where one needs to confront Fick’s law, our arguments do not exclude the possibility of species adherence at a finer continuum length scale [the l scale ($l \ll L$), which from the scaling used in [1] constitutes the intermolecular length scale σ]. Indeed, it is well known in a variety of contexts (see, e.g., [3,4]) that the boundary conditions can depend explicitly upon the choice of continuum length scale at which the physical phenomenon is being viewed. But this difference arises because the more detailed view embodies novel features and concepts not present in the coarser-scale view (e.g., the existence of short-range, l -scale forces, resulting in species-specific “surface adsorption” at the L scale [3]—or boundary roughness present on the scale l but absent on the “smooth”-appearing L -scale surface [4]). From the background context provided in [1], it seems that they intended their results to be interpreted as applying at the usual continuum level. And at this level of description, species adherence is not a viable physical possibility.

We thank Professor R.F. Sekerka and Professor R. Jackson for useful discussions.

Venkat Ganesan and Howard Brenner
Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139-4307

Received 30 June 1998 [S0031-9007(98)08361-6]
PACS numbers: 47.10.+g, 47.11.+j, 47.55.Kf, 83.20.Lr

- [1] J. Koplik and J.R. Banavar, Phys. Rev. Lett. **80**, 5125 (1998).
- [2] J. Camacho and H. Brenner, Ind. Eng. Chem. Res. **34**, 3326 (1995).
- [3] M. Shapiro, H. Brenner, and D.C. Guell, J. Colloid Interface Sci. **136**, 552 (1990).
- [4] S. Richardson, J. Fluid Mech. **59**, 707 (1973).