

## LETTERS TO THE EDITOR

### To the Editor:

In the article titled "The Reaction Independence of Mixing Coefficients in Fixed-Bed Reactors," Gunn and Vortmeyer (September 1990, p. 1449) show that the transversely-averaged continuity equation

$$\frac{\partial C}{\partial t} + V \frac{\partial C}{\partial x} = D_L \frac{\partial^2 C}{\partial x^2} - KC \quad (1)$$

for the multicomponent concentration vector  $C$  has the pulse-response solution

$$C = A \exp(-Kt) C_0 \quad (2)$$

in which

$$A = \frac{1}{\sqrt{4\pi D_L t}} \exp \left[ -\frac{(x - Vt)^2}{4D_L t} \right] \quad (3)$$

They claim that this solution requires the dispersion coefficient  $D_L$  to be independent of the kinetic coefficient matrix  $K$ .

This claim merits examination. Equations 1-3 are well behaved as long as  $D_L$  and the eigenvalues of  $K$  are real and positive. Aside from these requirements, Eqs. 1-3 place no constraints on  $D_L$ .

Gunn and Vortmeyer (*loc. cit.*) obtain a constraint by stating an auxiliary relation:

$$C_R = \exp(-Kt) C_{NR} \quad (4)$$

To get this relation from Eqs. 2 and 3, they treat the function  $A$  as independent of  $K$ . But this is equivalent to assuming  $D_L$  to be independent of  $K$ , that is, to assuming the result which was to be proved. Thus, the claimed reaction-invariance of  $D_L$  remains unproven.

Ample evidence is available that dispersion coefficient do depend on chemical kinetics, at least for heterogeneous reaction systems. One should expect such

effects, because surface reactions affect the boundary conditions of the reactor problem. Strong effects of surface kinetics on radial dispersion were found by Schwedock et al. (1989) in experiments on the fixed-bed oxidation of methanol under turbulent flow conditions. Strong effects of surface kinetics on axial dispersion in tubes have been demonstrated and qualitatively explained by Sankarasubramanian and Gill (1973, 1974), DeGance and Johns (1978), Aris (1980), and Wang and Stewart (1988). These results indicate that Fickian dispersion coefficients in chemical reactors are not reliably predictable from values for non-reacting systems, except at small reaction rates. Better models for fixed-bed reactors are needed.

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### To the Editor:

In their article, D. J. Gunn and D. Vortmeyer (September 1990, p. 1449) treat the problem described in the title, apparently unaware of the extensive and definitive literature on this subject. They describe the problem of solute flow and dispersion in porous media at the macroscale or Darcy scale (that is, on a length scale  $L \gg \ell$  greatly exceeding the pore size  $\ell$ ), and purport to show that the inclusion of a first-order irreversible reaction term characterized by a spatially homogeneous rate coefficient ( $\bar{K}$ , say) in the governing equations does not affect the normalized moments of the solute concentration distribution. Accordingly, the authors conclude that the dispersion coefficient, characterizing the second moment of the solute distribution, is unaffected by the chemical reaction, "when all other conditions are the same." Moreover, by failing to state so explicitly, they implicitly suggest that the mean velocity of the reactive solute species is likewise unaffected by the chemical reaction and is simply equal to that of the inert carrier fluid. As we will see, the flaw in their "proof" is that whereas the reaction-velocity constant may be spatially homogeneous at the macroscale  $L$ , it may not be so at the microscale  $\ell$ . And it is the latter scale that is pertinent to the outcome of the problem they address.

First, in circumstances where the reaction-velocity coefficient is truly constant (that is, at the *microscale*), Gunn and Vortmeyer's conclusion has been derived theoretically in several prior studies (Sankarasubramanian et al., 1974; Brenner and Adler, 1982; Shapiro and Brenner, 1986) performed at the more fundamental microscale level—that is, the scale comparable to the size  $\ell$  of the interstitial geometric bed elements: a volumetric first-order irreversible chemical reaction characterized by a position-independent microscale reaction rate con-

stant  $K$ , say, produces no effect on the reactive species transport other than a homogeneously distributed exponential diminution by an amount  $\exp(-Kt)$  in the concentration of solute present at each and every point  $r$  of the fluid continuum. The authors discover a similar effect on the coarser, macroscale  $L$ , which provides no new insight into the transport of chemically reactive species in porous media, since any conclusion true at each point of the microscale medium remains equally true at the macroscale. The converse, however, is not true, and that is the main point of this letter.

Secondly, it has been shown (Shapiro and Brenner, 1986, 1988; Dungan et al., 1990) that a spatially heterogeneous microscale chemical reaction [one characterized by a position-dependent reaction-velocity constant  $K=K(r)$  with  $r$  a microscale position vector] produces an interstitial, microscale reactive solute concentration distribution which is not related in any simple way to that which would exist in the absence of reaction, in particular not by  $\exp(-\bar{K}t)$ , where  $\bar{K}$  is related to  $K$  (and other microscale geometric and phenomenological data) by some coarse-graining averaging scheme. This fact may dramatically affect the macroscale phenomenological coefficients, that is, the macroscale solute velocity and dispersivity. For example, for a catalytic surface chemical reaction, which represents an extreme in spatial inhomogeneity [since  $K(r)$  is then effectively a Dirac delta function distribution—being infinite for those points  $r$  lying on the reactive surface, and zero for those points  $r$  contained in the interior of the interstitial fluid], the above effect is governed by the microscale Damköhler number,  $Da = k\ell/D$ , where  $k$  is (a characteristic value of) the surface reaction constant,  $\ell$  is the characteristic pore-size distance, and  $D$  is the reactive solute's molecular diffusivity (Shapiro and Brenner, 1986, 1988). For large values of  $Da$ , the effective reaction rate is diffusionally-, not kinetically-controlled, in which limiting case the effective solute dispersivity is significantly smaller than that in the absence of the chemical reaction. Moreover, the mean velocity of the reactive species exceeds that of a comparable nonreactive species, since the latter moves at the same mean velocity as the carrier fluid. This increase in solute velocity arises from the fact that

reactive species molecules are selectively removed (via reaction) from the slow-moving streamlines proximate to the no-slip, solid catalytic surfaces.

A chemical reaction which is *inhomogeneous* on the microscale ( $K$  is functionally dependent on  $r$ ), nevertheless, is perceived at the macroscale as being a *homogeneous* chemical reaction, and hence characterized by a position-independent reaction-rate constant  $\bar{K}$  (Shapiro and Brenner, 1988; Dungan et al., 1990). Thus, contrary to the conclusions of Gunn and Vortmeyer (1990), the existence of a macroscopically homogeneous reaction may significantly affect macroscale "mixing" coefficients in fixed-bed chemical reactors due to the inhomogeneous nature of the reaction at the microscale. Dramatic examples of these significant reactive effects are quantified by Dungan et al. (1990), for example.

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#### Reply:

In our article we consider the dispersion coefficient under reaction conditions for random arrangements of fixed particles, making use of a transformation involving the same dispersion coefficient that for consistency describes the field with the term  $KC$  now allowed to approach zero. In the succeeding development, it becomes clear that this dispersion coefficient has the same properties as the coefficient that holds in the absence of chemical reaction. It is our conclusion that if dispersion with re-

action is described by Eq. 1 and dispersion without reaction is described by a consistent simplification of Eq. 1, in which  $KC$  is set to zero, then the dispersion coefficients are the same, a conclusion dictated by the physics of dispersion described by Eq. 1 and its unreactive analog.

There is a substantial basis of experimental validation for the unreactive analog of Eq. 1 that is fundamental to our article. The transformation is, of course, a purely mathematical operation.

It is a surprising assumption expressed in the letters of Brenner and Shapiro, and Stewart that results obtained from studies of dispersion in tubes empty of particles and of dispersion in regular arrays of particles should be applicable without question to dispersion in beds of randomly-fixed particles. There is much evidence that fundamental differences between dispersion in beds of randomly-fixed particles on the one hand, and dispersion in tubes and in regular arrays on the other, are so great that even studies without reaction show major disparities. The differences are particularly large for convection-dominated dispersion.

The concentration profile that develops during mixing in straight tubes empty of particles is not described by Eq. 1 but is two-dimensional. The conditions under which transverse spreading by molecular diffusion is sufficiently rapid to overcome axial spreading by velocity difference have been set forth by Taylor and Aris, and this asymptotic condition is described by Eq. 1. If the Taylor-Aris conditions are met, the concentration distribution is essentially one-dimensional, and we would expect the dispersion coefficients to be independent of linear homogeneous chemical reaction, as has been shown by Shapiro and Brenner (1986). For the chemical reaction at the walls of the tube, the conditions for an effective one-dimensional concentration distribution are probably more restrictive. If the Taylor-Aris conditions are not met because of high velocity or short-bed length, the concentration distribution is not one-dimensional and a dispersion model is not appropriate.

Similar restrictions apply to spatially-periodic porous media; an effective one-dimensional concentration profile in axial flow is only obtained if similar conditions to those of Taylor and Aris hold.

We did not cite the origins of Eq. 1 in our article, but the conditions under

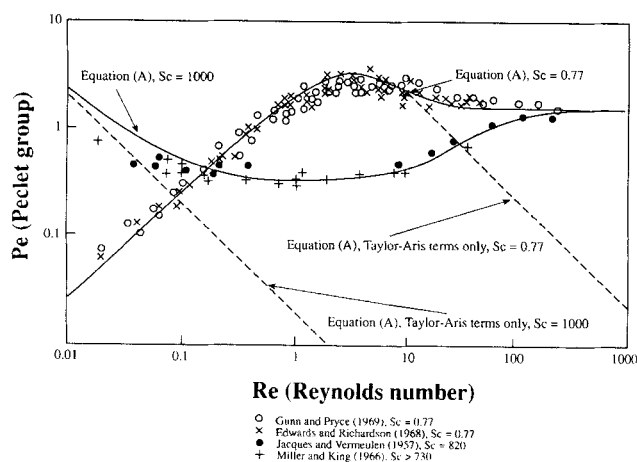


Figure 1.

which Eq. 1 applies are a major point of difference. The fundamental basis of Eq. 1 without the reaction term for randomly-fixed beds of particles is not the Taylor-Aris analysis, but the Central Limit Theorem of the Theory of Probability with the stochastic requirements of the Theorem met by the random placement of the constituent particles of the bed as well as the contribution of molecular diffusion (Gunn, 1969). The velocities and concentrations are mean values taken over volume elements that include several particles yet allow the fluid field distributions of velocity, concentration, and temperature to be portrayed. The formulation of the volume element over a fluid field embedding particles is similar to that used by exponents of the volume-averaging theorem but in other respects the theories are quite different. The validity of this application has been thoroughly tested by the statistical analysis of experimental measurements of mass dispersion and of heat dispersion in randomly-fixed beds mainly for the fluid-phase dispersion model in which the dispersive flux is linearly proportional to gradients in the fluid.

Among the very few measurements of dispersion in spatially-periodic arrays of particles are those of Gunn and Pryce (1969), who measured the dispersion of argon in air during linear flow through face-centered and body-centered arrays of spherical particles. The measurements were made in the range of Reynolds Number from 2 to 200 and were subjected to statistical tests to examine the validity of the dispersion model. The dispersion model did not represent the measurements, and it was concluded that the stochastic requirements of the Cen-

tral Limit Theorem were not met during flow-through, spatially-periodic arrays of particles when dispersion was dominated by convection. The bed lengths were not sufficiently great to satisfy the limiting condition for molecular diffusion to smooth concentration profiles dominated by convection. The validity criteria for the dispersion model were satisfied for similar experiments in randomly-fixed beds of particles.

There is agreement between experiments on mass dispersion and a stochastic theory developed some years ago. The results of an asymptotic analysis based on the Central Limit Theorem are illustrated in Figure 1, a compilation of experimental measurements of both gas-phase and liquid-phase dispersion in randomly-fixed beds of spheres. The experimental measurements are compared in this figure with the following equation (Gunn, 1969) shown as full lines on the graph for Schmidt numbers of 0.77 and 1,000,

$$\frac{D_L}{Ud} = \frac{ReSc}{\epsilon\Gamma} (1-p)^2 + \frac{Re^2Sc^2}{\epsilon^2\Gamma^2} \times p(1-p)^3 \left( \exp \left[ \frac{-\epsilon\Gamma}{p(1-p)ReSc} \right] - 1 \right) + \frac{\epsilon}{\tau ReSc} \quad (A)$$

The first term on the right, with  $D_L$  proportional to  $U^2$  is analogous to Taylor's expression for round tubes, and the last term is analogous to the contribution of molecular diffusion as given by Aris in his extension to Taylor's theory. The second term is not given by the Taylor-Aris theory, but arises from the proposed mechanism of dispersion and in con-

junction with the other two terms gives the correct limiting behavior at low Reynolds Number (diffusive dispersion), and at high Reynolds Number (convective dispersion) (Gunn, 1969). The probability of axial displacement  $p$  is a function of the Reynolds number only and it is clear that the effect of the Schmidt number is accurately predicted by this equation over a thousandfold range even though there are experimental difficulties in measuring liquid-phase dispersion coefficients at low Reynolds number because of disturbance to particles by fluid causing an increase in measured values.

The form of the Taylor-Aris theory from analyses of regular systems and from the first and third terms of Eq. A is shown by dotted lines for the same values of the Schmidt Group, in which it is supposed there is good agreement at low Reynolds Number even though good agreement cannot be established from first principles. However, at high Reynolds Number, the disparity between experiment and theory is very large for gas-phase systems and is even greater for liquid-phase systems. The reason for the disparities is the wrong specification of the asymptotic conditions in the empty tube-regular array theories when applied to beds of randomly-fixed particles. The asymptotic condition of the Central Limit Theorem that is dominated by the random placement of the particles in the fixed bed, as represented in experiment and in Eq. A, is obtained fairly closely in the space of axial flow over the length of a small number of particles (Gunn, 1969). The asymptotic form of the Taylor-Aris theory in contrast is developed by transverse smoothing of concentration profiles influenced by convection. At high velocities, the Taylor-Aris treatment predicts much larger dispersion because mixing is projected over a much greater scale. The dominance of mixing due to random placement of particles, however, prevents the development of the Taylor-Aris form in randomly-fixed beds.

It appears that the analogous upper limit for Taylor-type dispersion is about a Reynolds Number of 10 for gas-phase systems, while the upper limit for liquid-phase systems is off to the left of the graph. These are also the upper limits of representation of the random fixed bed by the analogies of spatially-periodic arrays or empty tubes, but there is no evi-

dence that the analogies are accurate even at low Reynolds number.

Studies of mass dispersion in tubes and in spatially-periodic arrays have no predictive value for dispersion in random-fixed beds, and there can be no confidence in predictions of dispersion with chemical reaction from similar studies. However, in heat transport the validity of the dispersion model for dense regular arrays of particles is extended to intermediate Reynolds numbers as shown by Vortmeyer in his studies with and without chemical reaction. This is because of the dominance of heat conduction in the solid phase, a condition shared with random beds in the same range of Reynolds number. The basis of experimental validation for the dispersion model, on the other hand, includes studies of dispersion combined with diffusion into particles, a better simulation of fluid mass-transport conditions in catalytic reactors.

The reaction term in Eq. 1 appears by material balance that may arise in one of two ways. In the case of homogeneous chemical reaction, the element is taken over a fluid field in which there are random mixing contributions due to both molecular diffusion and convection as established by studies without chemical reaction; the matrix  $K$  with linear elements is that of true kinetic constants. For heterogeneous chemical reaction in a second phase, there is mass exchange between the fluid and boundary surfaces of particles contained within the volume element; if the fluid-phase dispersion model is used and capacitive effects are not considered, Eq. 1 also applies but the matrix  $K$  is not that of the true kinetics, but of effective kinetics in which the elements of the matrix are influenced by intraparticle diffusion and boundary transfer unless the reactions are slow.

More recently, the fluid-phase dispersion model has been shown to provide an accurate description of small-scale heat transport in fixed beds (see, for example, Gunn and de Souza, 1974) and for radial transport in tubes of narrow aspect and of wide aspect, and for particle shapes other than spherical when intraparticle effects are significant. It has been shown that the substantial body of early work on heat and mass transport in fixed beds is consistent in model and transport parameter values with later experimental programs interpreted by the dispersion model (Gunn, 1978). The con-

sistency of a wide range of parameter studies has been shown for mass transport (Gunn, 1987).

Not only is the dispersion model physically consistent for randomly fixed beds of particles, but a wide range of parameter values are now well defined.

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### Reply:

In response to the letter by Stewart, axial and radial dispersion coefficients of packed-bed dispersion models are effective properties, and it cannot be ruled out that they depend on processes such as catalytic reactions and on *a priori* assumptions concerning flow distribution and wall heat-transfer mechanism. Experimental work has to show how significant this interdependence is.

Stewart refers to the articles by Schwedock and coworkers (Schwedock et al., 1989; Windes et al., 1989) to prove his point. These authors conclude from their excellent and detailed experimental work that under the assumption of plug flow, agreement between measurements and model predictions is obtained best if the radial Peclet number is considered as a function of local temperature. This result was obtained by parameter fitting with kinetic and other data also being subjects of the fitting procedure.

Dramatic effects in modeling fixed-bed exothermic reactors were found by Vort-

meyer and coworkers (Kalthoff and Vortmeyer, 1980; Vortmeyer and Winter, 1981) when the plug flow assumption was replaced by the more realistic flow model of a nonuniform flow distribution due to near wall porosity variations. Further improvement was obtained recently (Vortmeyer and Haidegger, 1991) by a modification of the wall heat-transfer mechanism in combination with an effective radial dispersion coefficient depending on the radial flow distribution. In all cases, the chemical reaction had no significant effect on the radial dispersion coefficient. We investigated (Vortmeyer et al., 1992) the interaction between radial temperature distribution and flow in a wall cooled catalytic fixed-bed reactor and have found only minor effects within the degree of experimental accuracy.

Besides that in the presence of a chemical reaction, the effective axial dispersion coefficient is important only for low Reynolds numbers (say  $Re < 70$ ), we have not found it necessary to make it dependent on the chemical reaction for an improved interpretation of measurements. Therefore, we conclude that the effective radial and axial dispersion coefficients are independent of a chemical reaction within the range of experimental accuracy.

Presumably, Schwedock and coworkers (Schwedock et al., 1989; Windes et al., 1989) will find a different Peclet number effect for modified *a priori* assumptions with respect to flow and wall heat-transfer mechanism.

Stewart also pleads for better models. The fundamental aspects of this criticism (Stewart, 1965) of dispersion models are valid still today. On the other hand, "better" models usually include more terms and more coefficients that have to be determined by experiments. We have doubts whether significant values for all coefficients can be obtained from the available experimental material. In this context, I should like to draw attention to an article of Chang and Slattery (1988).

With regard to the rejoinder by Brenner and Shapiro on pp. 1679-1680, there is found no contribution at all to the main issue whether the dispersion coefficient in a particle bed is or is not affected by a chemical reaction. I, therefore, find it difficult to understand what Brenner and Shapiro wish to demonstrate. With respect to their illustration, we disagree on the nature of models

for randomly packed beds.

Brenner and Shapiro can be assured that the experimental findings will not be confused with a theoretical proof. Fortunately, we know from experimental work that there is no dramatic impact of chemical reactions on macroscopic coefficients, if the macroscopic flow is modeled properly. Therefore, from our experience, the macroscopic coefficients of packed beds without reaction are confidently applicable to chemical reactor modeling.

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#### Rejoinder:

As stated in my previous letter, Gunn and Vortmeyer did not prove  $D_L$  to be independent of the kinetic coefficient matrix  $K$ . Their Eq. 9 is obtainable from Eqs. 6 and 7 only by assuming this independence. Their Eq. 6, with their expression for the function  $A$ , is more general and satisfies Eq. 1 whether  $D_L$  is treated as a function of  $K$  or not!

It follows that Eq. 1 of Gunn and Vortmeyer gives no information about the effect, or lack of effect, of first-order reactions on the dispersion coefficient  $D_L$ . This result could have been foreseen because Eq. 1 uses a flat velocity profile, thus omitting the velocity gradients that cause convective dispersion.

Gunn's response ignores these difficulties and digresses by reviewing his well-known experiments, macro-scale theories and correlations of  $D_L$  for nonreactive systems. That work was well done, and its validity was not questioned. Neither was it suggested by Shapiro, Brenner nor me that these results be replaced by

estimates from transport theory for simpler geometries. What we did say is that the interfacial boundary conditions imply a dependence of  $D_L$  on the kinetics in heterogeneous reaction systems, whatever the geometry. Specific calculations of reaction effects on dispersion were cited merely to illustrate this fact.

Vortmeyer acknowledges that dispersion coefficients in fixed beds may depend on the surface kinetics. Experimental evidence on this dependence is limited thus far, and *a priori* computations with micro-scale resolution have not been done, but the results of Schwedock et al. should not be ignored. One also expects that the reaction effects on dispersion could go unnoticed at moderate reaction rates.

This exchange of correspondence has addressed just one of the difficulties of the dispersion model. A fuller discussion is given by Stewart et al. (1991), along with plans for a more realistic packed-bed model.

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#### Rejoinder:

In his letter, Gunn responds to our criticism by attacking the credibility of our spatially periodic model (as well as related geometric models involving tubes devoid of particles), claiming that real beds are (synonymous with and hence) better modeled as randomly packed beds. Whether or not any or all of this is true, Gunn's remarks are wholly irrelevant to our fundamental criticism. Citation of the spatially-periodic and empty-tube model results in our letter refuting Gunn and Vortmeyer's conclusions was merely for the purpose of suggesting the physical implausibility of their conclusions, rather than necessarily laying claim to the quantitative applicability of our idealized theory to real (that is, disordered) systems.

This letter further amplifies our criticism in a wholly different perspective,

by directly demonstrating an elementary and fundamental flaw in the scientific logic of their "proof." We do this by providing a simple counterexample that unequivocally negates their mode of logical inference.

Gunn and Vortmeyer's starting point is the purely empirical phenomenological (macroscale) equation:

$$\frac{\partial C_R}{\partial t} + V \frac{\partial C_R}{\partial x} - K C_R = D_L \frac{\partial^2 C_R}{\partial x^2}, \quad (A)$$

governing the mean reactive solute concentration distribution  $C_R(x, t)$  in a packed-bed reactor (subscript  $R$  refers to a "reactive" system). By the purely mathematical artifice of the following change of dependent variable,

$$C_R(x, t) = C_{NR}(x, t) \exp(-Kt), \quad (B)$$

Gunn and Vortmeyer find that  $C_{NR}$  obeys the relation:

$$\frac{\partial C_{NR}}{\partial t} + V \frac{\partial C_{NR}}{\partial x} = D_L \frac{\partial^2 C_{NR}}{\partial x^2}, \quad (C)$$

in which the reaction term in Eq. A no longer appears (hence, their choice of subscript notation,  $NR$ , referring to a "nonreactive" system). Since the same coefficient  $D_L$  appears in both the reactive and nonreactive transport equations, namely Eqs. A and C, these authors conclude that the longitudinal dispersivity  $D_L$  is unaffected by the chemical reaction.

Drawing this physical conclusion is scientifically illogical; it lies beyond the competence of any purely phenomenological "theory," such as Eq. A, to establish, purely mathematically, the functional dependence of the phenomenological coefficients appearing therein upon any of the physical parameters pertinent to the phenomena. Only experiments or (realistic) microscale models of the pertinent phenomena involved can establish such functional dependence. No purely mathematical operation, such as Gunn and Vortmeyer's transformation of dependent variables, can suffice to establish such dependence.

Our own work (cited in our previous letter) offers a detailed microscale model of the macroscale dispersion-reaction phenomenon described by their Eq. A, and draws the conclusion from the results of our model that the dispersivity

(as well as the mean velocity) is affected by the chemical reaction. Of course, our conclusion is only as good as our model, and it may be that our spatially-periodic model (or the earlier, empty-tube models) are, as Gunn claims, poor microscale models of the macroscale phenomena described by Eq. A. Going further, it may even be true that macroscale experiments and/or a more realistic microscale model, would, in fact, completely confirm Gunn and Vortmeyer's conclusion as to the reaction-independence of  $D_L$ . But none of these facts impacts upon the flawed nature of their original arguments. They have not proved anything!

The following counterexample clearly illustrates the spurious nature of their arguments. In this example, we effect a mathematical transformation of the dependent variable which removes not only the reaction term from Eq. A, as in Gunn and Vortmeyer's Eq. C, but simultaneously the convective term as well, leaving only the dispersive term (see Eq. E). To accomplish this, we introduce the following change of dependent variable in Eq. A:

$$C_R(x, t) = C_{NRF}(x, t) \exp\left(\frac{Vx}{2D_L} - \frac{V^2 t}{4D_L} - Kt\right). \quad (D)$$

Introduction of the latter into Eq. A yields, after some algebra, the following equation governing  $C_{NRF}$ :

$$\frac{\partial C_{NRF}}{\partial t} = D_L \frac{\partial^2 C_{NRF}}{\partial x^2}. \quad (E)$$

Thus, our purely mathematical change of dependent variable has simultaneously removed *both* the reaction and flow terms from Eq. A. [As an aside, this implicitly justifies our subscript notation, since by an obvious extension of Gunn's earlier subscript notation in Eq. C, *NRF* here refers to the "no reaction or flow" case.]

Were we to apply Gunn/Vortmeyer's "logic" to the physical interpretation of Eq. E, we would be led to conclude that the dispersivity  $D_L$  is not only independent of the chemical reaction, as claimed by those authors, but also that it is independent of the mean velocity of flow  $V$ , since Eq. E is formally the same as the equation obtained by setting  $K=0$  and  $V=0$  in Eq. A. This supposed lack

of dependence of  $D_L$  upon  $V$  is at odds with all experiments to date, including that of Gunn himself on nonreactive systems (see the figure accompanying his letter); moreover, this flow-rate independence of  $D_L$  is totally inconsistent with all microscale models of the phenomenon, such as our nonreactive spatially-periodic model (Edwards et al., 1991). The flaw in the Gunn-Vortmeyer argument regarding the  $V$ -independence of  $D_L$  is no different in substance from that which we pointed out in our earlier letter regarding the similar  $K$ -independence of  $D_L$ . In particular, though the velocity is spatially uniform at the macroscale (that is, at the Darcy scale), it is distinctly nonuniform at the micro- or interstitial scale owing to the no-slip microscale velocity boundary condition existing on the bed particles. And it is precisely this microscale velocity inhomogeneity that causes the dispersivity to depend upon mean velocity  $V$ , just as any microscale reaction inhomogeneity (as in the case of catalytic chemical reactions) causes the dispersivity (as well as the mean velocity) to depend upon the chemical reaction. Our *reductio ad absurdum* counterexample constitutes clear and unequivocal evidence of the fact that Gunn and Vortmeyer have not proven what they claim to have proven.

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#### To the Editor:

This letter is motivated by criticism by Lu and Kim in their article titled "Effective Thermal Conductivity of Composites Containing Spheroidal Inclusions," (June 1990, p. 927) of an analytical model proposed by Hatta and Taya (1985) to predict the thermal conductivity of short-fiber composites. The comments of Lu and Kim indicate a misunderstanding of the implicit assumptions of the Hatta-Taya model, which we would like to clarify. In particular, Lu

and Kim state that Hatta and Taya attempted to incorporate pair interactions in the calculation of the effective thermal conductivity of random short-fiber composites and furthermore that Hatta and Taya do not incorporate particle interactions properly. Lu and Kim justify their criticism by noting that: (a) the Hatta-Taya model approximates inclusions (and thus describes pair interactions) by uniformly distributed thermal dipoles when it is known that higher-order multipole moments are required to account for interactions when fibers are close together; (b) the Hatta-Taya model coincides with Maxwell's solution for spherical particle reinforcement.

In the Hatta-Taya model, interactions among short fibers are accounted for in an approximate manner through the Mori-Tanaka (1973) mean field approach, which is one of several well-known effective medium theories, such as the dilute, generalized self-consistent and differential approaches that are commonly used in the composite materials community to predict the effective physical and mechanical properties of composite materials. Like most effective medium theories (EMTs), the Mori-Tanaka theory is based on the solution of the auxiliary problem of a single particle embedded in an infinite matrix and thus configurations of touching or near touching particles are implicitly ignored. Interactions among particles are then considered in an average sense to extend validity to higher particle volume fractions. In the Hatta-Taya model, the Mori-Tanaka mean field approach is incorporated through the equivalent inclusion method proposed by Hatta and Taya (1985, 1986) to parallel Eshelby's (1957) pioneering work in elasticity. The equivalent inclusion method is used as it provides a unified framework to analyze inhomogeneity problems in both steady-state heat conduction and uncoupled thermoelasticity. Thus, contrary to the statements of Lu and Kim, *Hatta and Taya make no attempt to rigorously incorporate pair interactions, but instead utilize the Mori-Tanaka effective medium theory to approximate interactions.*

In the Mori-Tanaka theory, it is assumed that the presence of all fibers and their mutual interactions induces an average field (temperature gradient) in the composite. Upon the random introduction of a single fiber into the composite,

it is assumed that this single fiber "feels" the sum of the applied and average (and as yet unknown) fields. The key assumption is that the exact solution for the *perturbation* of the field in a single fiber with respect to that in the matrix remains valid at finite fiber volume fractions. Finally, the Mori-Tanaka theory assumes that for a finite volume fraction of fibers, the introduction of a single additional fiber does not affect the fiber volume fraction. Since the single additional fiber is randomly inserted, the equation expressing the field in the additional fiber (Eq. 5 in Hatta and Taya, 1985) is assumed to be valid for all fibers in the composite. This is the essence of the Mori-Tanaka theory which has been shown to be on strong theoretical footing for two-phase composites (Weng, 1990). Since the interaction between particles is approximated through the Mori-Tanaka theory, the use of a distribution of thermal dipoles to represent fibers is certainly valid. In fact, the dipole distribution is introduced not to incorporate pair interactions as implied by Lu and Kim, but to provide an exact solution to the auxiliary problem of a single particle in an infinite matrix as required by the Mori-Tanaka theory.

As Lu and Kim state, the Hatta-Taya solution agrees with Maxwell's solution for spherical particles. Although Maxwell claims to ignore particle interaction, since his solution agrees with the dilute approximation (Rocha and Acrivos, 1973) only in the low volume fraction limit, it can be concluded that Maxwell's solution considers interaction in *some* manner, albeit approximate. In fact, we conclude that Maxwell's solution implicitly approximates interaction as each particle feels not only the applied field, but the field due to polarization of the entire domain treated as a continuum although configurations of touching or near-touching particles are clearly ignored. Lu and Kim, however, do not note that the Hatta-Taya solution coincides with Willis' (1977) lower (upper) bound for an aligned short-fiber composite with  $K_f > K_m$  ( $K_f < K_m$ ). The Hatta-Taya solution is thus correct in the dilute limit and also in the high volume fraction ( $f$ ) limit of  $f \rightarrow 1$  and satisfies the Willis bounds for  $0 \leq f \leq 1$ . The practical range of applicability of the Hatta-Taya model (as noted by Hatta and Taya, 1985), though, is  $f \leq 0.5$ . The correct behavior at  $f \rightarrow 1$  is encouraging, though, and sug-

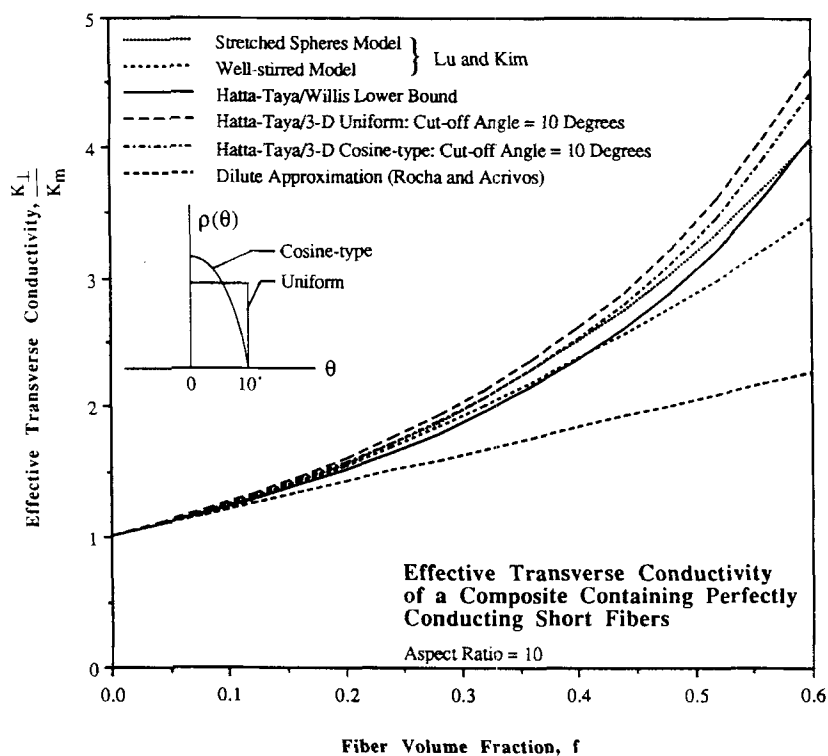


Figure 1.

gests that the approximation may even be reasonable at higher volume fractions.

Finally, we feel that it is important to comment on the practical considerations which favor the use of effective medium theories and in particular the Hatta-Taya model. It is well known that in the processing of a short-fiber composite, fiber alignment is quite difficult (and rarely achieved). Improvements in fiber alignment can be achieved through costly processing routes such as the use of a magnetic field (Taya, 1988); however, this approach is limited to low-volume fractions ( $f < 0.1$ ) to which even the dilute approximation is reasonable. Thus, for short-fiber composites, minor fiber misorientation usually cannot be avoided. The utility of the Hatta-Taya model is in its ability to predict the effective thermal conductivity ( $K^{\text{eff}}$ ) of composites containing *misoriented* short fibers. We have utilized this capability to investigate the effect of fiber misorientation on the effective transverse conductivity ( $K_{\perp}$ ) of the composite containing aligned perfectly conducting short fibers as analyzed by the stretched sphere model of Lu and Kim, the results of which are shown in Figure 1. Figure 1 shows that a small degree of fiber misorientation from the perfectly aligned case (a uniform distribution with a cut-

off angle of  $10^\circ$ ) results in a greater maximum difference in  $K_{\perp}$  (10.1%) than the approximation of the Mori-Tanaka effective medium approach (5.9%) as compared to the more accurate results of Lu and Kim. In fact, these differences are noted to be within the error band typically encountered in experimental data for the measurement of  $K^{\text{eff}}$  for composite materials (Hatta et al., 1991). In addition, the Hatta-Taya model is able to treat the case of composites containing short fibers of finite conductivity to which the rigorous solution of Lu and Kim is not presently applicable. In the case of perfect conductors, however, we feel the conductivity of practical composites where fiber misorientation exists is better modeled by percolation theory as discussed by Taya (1988).

In summary, we have attempted to illuminate the key assumptions of the Hatta-Taya model that were apparently not recognized by Lu and Kim. Furthermore, comparison with the results presented by Lu and Kim seems to strengthen the argument for the use of a mean field approach with regards to composites of practical engineering interest where the effects of fiber misorientation and finite conducting constituents are important. This conclusion has been reached by noting that the



discrepancy obtained by approximating the higher-order terms through a mean field approach seems to be within the typical experimental error band and furthermore, less significant than the effects of parameters related to the composite microstructure such as the misorientation of fibers. These effects, after all, are those toward which the Hatta-Taya model is aimed.

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### Reply:

Taya and Dunn make a valid point in stating that the *wording* of the criticism of the article by Hatta and Taya (1985)

in Lu and Kim (1990) is incorrect. The central points in Lu and Kim (1990), however, are still valid.

It is true that Hatta and Taya (1985) do not consider pair interactions. Instead, a self-consistent, effective mean field theory approach is employed. However, at higher concentrations, it would be desirable to have a theoretical approach that incorporates interactions between near neighbors. The wording in Kim and Lu should be changed from "pair interactions" to "interactions."

An effective medium approach is attractive as a first attempt, but in this era of high-performance computers, the time has come to incorporate the link between microstructure and bulk properties in a rigorous fashion. To the above, we note the following additional points regarding the approach used by Lu and Kim (1990):

1. The pair interactions can be incorporated into an effective medium theory, as in Kim and Russel (1985).
2. The method can be used even when the inclusions have finite conductivities. The singularity solutions are given in Lu and Kim (1987).
3. The method is not restricted to aligned fibers as the letter implies. The BVP can be solved for arbitrary pair orientations.

### Additional literature cited

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### Rejoinder:

We are in agreement with the comments of Lu and Kim that in this era of high-performance computers it is worthwhile to rigorously link the microstructure to the effective properties of a composite. We do not believe, however, that the rigorous numerical solution of such problems should close the door on the practical use of existing, simpler approaches such as effective medium theories. We believe that the rigorous approach should be used to judge the applicability and accuracy of the simpler approaches. When the difference among the approaches is small, especially if it

is inside the error band associated with experiment, it should be so noted. When this occurs, it would seem to favor the practical use of the simpler approach. This appears to be the case here.

Regarding comment 3 of Lu and Kim, we did not mean to imply that their approach was not applicable to composites with misoriented fibers. We have not seen the results of the application of the theory to misoriented fibers in the open literature, though, and clearly their *results* are restricted to the case of aligned fibers. Nevertheless, we look forward to seeing the results of such computations.

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