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Royal Institute of Technology, January 1980

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DIFFUSION AND SORPTION IN PARTICLES AND TWO-DIMENSIONAL DISPERSION IN A POROUS MEDIUM

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January 1980

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SUMMARY

A solution of the two-dimensional differential equation of dispersion from a disk source, coupled with a differential equation of diffusion and sorption in particles, is developed. The solution is obtained by the successive use of the Laplace and the Hankel transforms and is given in the form of an infinite double-integral. If the lateral dispersion is negligible, the solution is shown to simplify to a solution presented earlier. Dimensionless quantities are introduced. A steady-state condition is obtained after long times. This is investigated in some detail. An expression is derived for the highest concentration which may be expected at a point in space. An important relation is obtained when longitudinal dispersion is neglected. The solution for any value of the lateral dispersion coefficient and radial distance from the source is then obtained by simple multiplication of a solution for no lateral dispersion with the steady-state value. A method for integrating the infinite double integral is given. Some typical examples are shown.

DIFFUSION AND SORPTION IN PARTICLES AND TWO-DIMENSIONAL DISPERSION IN A POROUS MEDIUM

INTRODUCTION

The problem of disposal of radioactive waste products, and the increased rate of pollution of groundwater by other chemical compounds, have increased the need for mathematical models of the groundwater pollution process. Because of the dangers of contaminants in the water supply, their fate and mode of travel downstream from their sources must be predicted. The fate of a contaminant depends on both the macroscopic and microscopic behavior of the fluid under existing flow conditions, and on physico-chemical conditions within the environment of the granular material. The diffusion of the chemical species into the porous matrix and their sorption comprise the main retarding mechanism. The concentration of the chemical compound in the flowing water is thereby decreased and the migration velocity will be slower than the water velocity. The sorption process is generally considered to occur in three distinct stages :

- diffusion of the component from the flowing water to the external surfaces of particles (external or film diffusion)
- diffusion through the porous network of the particles (internal diffusion)
- the sorption process itself, when the component is bound to some sorption site on the walls of the internal pores.

Only a few analytical studies of the transverse dispersion process have been found in the literature. Because of mathematical difficulties, initial studies of the transverse dispersion process were based on a model which assumed that dispersion parallel to the direction of flow is negligible (e.g., Harleman and Rumer (1962) and Ogata (1961)). A treatment of two-dimensional dispersion from a surface source is available (Ogata, 1969; 1976). However, none of these models consider chemical interactions with the porous material.

In a previous paper by Rasmuson and Neretnieks (1980), a solution of a model for diffusion and sorption in particles and longitudinal dispersion in packed beds was derived. This solution was subsequently used to describe the migration of radionuclides in fissured rock (Rasmuson and Neretnieks, 1981). This is one example of a system where diffusion into the matrix is considered to be very important (Neretnieks, 1980). The assumptions behind the model have been extensively discussed in the chemical engineering literature by e.g. Babcock et al. (1966), Pellet (1966) and Rosen (1952). The main assumptions are:

1 the particle diameter is small in comparison with the overall distance and the porous medium is macroscopically uniform;

2 the sorption equilibrium relationship, describing the intraparticle solute concentration as a function of the external solute concentration, is linear;

3 the attainment of local sorption equilibrium is very rapid;

4 the movement of solute within the particles can be described mathematically by a Fick's law diffusion equation, where the effective intraparticle diffusion coefficient is constant and independent of concentration;

5 the particles may, for the description of internal diffusion, be regarded as spherical.

In this paper the model is extended to include dispersion transverse to the flow direction.

THEORY

A schematic representation of the system is given in Figure 1.

Basic equations and solution

The process is described by the following set of equations:

$$\frac{\partial C}{\partial t} + V\frac{\partial C}{\partial z} - D_L\frac{\partial^2 C}{\partial z^2} - D_T\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right) = -\frac{1}{m}\left(\frac{\partial \overset{\Delta}{q}}{\partial t}\right) \tag{1}$$

$$\frac{\partial q_i}{\partial t} = D_s\left(\frac{\partial^2 q_i}{\partial r'^2} + \frac{2}{r'}\frac{\partial q_i}{\partial r'}\right) \tag{2}$$

The terms in the first equation stand for accumulation in the fluid phase, convective transport, transport by axial dispersion and by radial dispersion, and volume-averaged accumulation in the porous particles. In the second equation the terms give accumulation and radial diffusion in the spherical particles.

It should be noted that the definition of q_i as a local solute concentration includes solute both in the solid and in the intraparticle pores. However, the same mathematical formulation is obtained if one assumes that solid diffusion effects are negligible and that the transport of solutes within the particles may be effectively described by diffusion in the solution phase only. Thus, if it is assumed that the correct driving force for diffusion is the intrapore concentration gradient, $\partial C_p/\partial r'$, an alternate differential equation for intraparticle diffusion can be written:

$$\varepsilon_p \frac{\partial C_p}{\partial t} + \frac{\partial C_s}{\partial t} = \varepsilon_p D_p \left(\frac{\partial^2 C_p}{\partial r'^2} + \frac{2}{r'} \frac{\partial C_p}{\partial r'} \right) \tag{3}$$

The two terms on the left hand side give the accumulation in the pore fluid phase and in the solid phase respectively. On the right hand side, the terms describe diffusion in the pore fluid phase.

It follows from the definition of q_i that:

$$q_i = \varepsilon_p C_p + C_s \tag{4}$$

If it is assumed that local equilibrium always exists in the pores, it follows from the linear adsorption equilibrium that:

$$q_i = KC_p \tag{5}$$

From equations (4) and (5) we obtain for C_s:

$$C_s = (K - \varepsilon_p)\ C_p \tag{6}$$

The minimum value of the equilibrium constant K, defined in this way, is obviously ε_p.

Differentiating (6) to obtain $\frac{\partial C_s}{\partial t}$ and substituting into equation (3) we get:

$$\frac{\partial C_p}{\partial t} = \frac{\varepsilon_p D_p}{K} \left(\frac{\partial^2 C_p}{\partial r'^2} + \frac{2}{r'} \frac{\partial C_p}{\partial r'} \right) \tag{7}$$

It can be seen that when q_i/K is substituted for C_p, equation (7) becomes identical with equation (2) if $D_s = \varepsilon_p D_p/K$. D_s may, in this case, be regarded as an apparent diffusivity.

The following boundary conditions are used:

$$\begin{cases} C(r,0,t) = C_o & ; r \leq a \\ C(r,0,t) = 0 & ; r > a \end{cases} \tag{8}$$

$$C(r,\infty,t) = 0 \tag{9}$$

$$C(0,z,t) \neq \infty \tag{10}$$

$$C(\infty,z,t) = 0 \tag{11}$$

$$C(r,z,0) = 0 \tag{12}$$

$$q_i(0,r,z,t) \neq \infty \tag{13}$$

$$q_i(b,r,z,t) = q_s(r,z,t) \text{ given by } \frac{\partial \overset{\Delta}{q}}{\partial t} = \frac{3k_f}{b} (C - \frac{q_s}{K}) \tag{14}$$

$$q_i(r',r,z,0) = 0 \tag{15}$$

The boundary condition (8) is that of a disk surface source $0 \leq r \leq a$ located at $z = 0$ and maintained at a constant concentration C_o. The boundary condition (14) is the link between the equations (1) and (2). It states mathematically that the mass entering or leaving the particles must equal the flow of mass transported across a stagnant fluid film at the external surface.

The solution of the equations (1) and (2) subject to the boundary conditions (8)-(15) is obtained by the successive use of the Laplace and the Hankel transforms (Appendix). Use is made of an earlier solution for the one-dimensional case (Rasmuson and Neretnieks, 1980). The solution is:

$$u(r,z,t) = \frac{C(r,z,t)}{C_o} =$$

$$\frac{1}{2} \exp\left(\frac{Vz}{2D_L}\right) \int_0^\infty \exp\left(-z\sqrt{\frac{V^2}{4D_L^2} + \frac{D_T}{D_L a^2}\xi^2}\right) J_o\left(\frac{r}{a}\xi\right) J_1(\xi)\, d\xi \; +$$

$$+ \exp\left(\frac{Vz}{2D_L}\right) \frac{2}{\pi} \int_0^\infty J_o\left(\frac{r}{a}\xi\right) J_1(\xi)$$

$$\left[\int_0^\infty \exp\left(-z\sqrt{\frac{\sqrt{x'(\lambda,\xi)^2 + y'(\lambda)^2} + x'(\lambda,\xi)}{2}}\right)\right.$$

$$\left.\sin\left(\sigma\lambda^2 t - z\sqrt{\frac{\sqrt{x'(\lambda,\xi)^2 + y'(\lambda)^2} - x'(\lambda,\xi)}{2}}\right)\frac{d\lambda}{\lambda}\right] d\xi \qquad (16)$$

with:

$$x'(\lambda,\xi) = \frac{V^2}{4D_L^2} + \frac{\gamma}{mD_L} H_1(\lambda) + \frac{D_T}{D_L a^2}\xi^2 \qquad (17)$$

$$y'(\lambda) = \frac{\sigma\lambda^2}{D_L} + \frac{\gamma}{mD_L} H_2(\lambda) \qquad (18)$$

H_1 and H_2 are complicated functions of λ :

$$H_1(\lambda) = \frac{H_{D_1} + \nu(H_{D_1}^2 + H_{D_2}^2)}{(1 + \nu H_{D_1})^2 + (\nu H_{D_2})^2} \qquad (19)$$

$$H_2(\lambda) = \frac{H_{D_2}}{(1 + \nu H_{D_1})^2 + (\nu H_{D_2})^2} \qquad (20)$$

H_{D_1} and H_{D_2} are defined as:

$$H_{D_1}(\lambda) = \lambda \left(\frac{\sinh 2\lambda + \sin 2\lambda}{\cosh 2\lambda - \cos 2\lambda} \right) - 1 \tag{21}$$

$$H_{D_2}(\lambda) = \lambda \left(\frac{\sinh 2\lambda - \sin 2\lambda}{\cosh 2\lambda - \cos 2\lambda} \right) \tag{22}$$

The equations are reduced to a dimensionless form using seven dimensionless quantities:

$\delta = \frac{\gamma z}{mV}$	bed length parameter
$R = \frac{K}{m}$	distribution ratio
$Pe_L = \frac{zV}{D_L}$	longitudinal Peclet number
$Pe_T = \frac{a^2V}{zD_T}$	transverse Peclet number
$y = \sigma t$	contact time parameter
$\zeta = \frac{r}{a}$	dimensionless radial distance
$\nu = \gamma R_F$	external diffusion resistance / internal diffusion resistance

Equation (16) now becomes:

$$u = \frac{1}{2} \exp\left(\frac{1}{2} Pe_L\right) \int_0^\infty \exp\left(- \sqrt{Pe_L \left(\frac{1}{4} Pe_L + \frac{1}{Pe_T} \xi^2\right)}\right) J_o(\zeta\xi)\, J_1(\xi)\, d\xi \; +$$

$$+ \exp\left(\frac{1}{2} Pe_L\right) \frac{2}{\pi} \int_0^\infty J_o(\zeta\xi)\, J_1(\xi) \left[\int_0^\infty \exp\left(- \sqrt{\frac{\sqrt{(z^2x')^2 + (z^2y')^2} + z^2x'}{2}}\right) \sin\left(y\lambda^2 - \sqrt{\frac{\sqrt{(z^2x')^2 + (z^2y')^2} - z^2x'}{2}}\right) \frac{d\lambda}{\lambda}\right] d\xi \qquad (23)$$

with:

$$z^2x' = Pe_L\left(\frac{1}{4} Pe_L + \delta H_1 + \frac{1}{Pe_T} \xi^2\right) \qquad (24)$$

$$z^2y' = \delta Pe_L\left(\frac{2}{3} \frac{\lambda^2}{R} + H_2\right) \qquad (25)$$

For negligible lateral dispersion ($Pe_T \to \infty$) the solution in Rasmuson and Neretnieks (1980) is obtained for $0 \leq \zeta < 1$. This follows from (Abramowitz and Stegun, 1972; p. 487):

$$\int_0^\infty J_o(\zeta\xi) J_1(\xi) d\xi = \begin{cases} 1 & 0 \leq \zeta < 1 \\ \frac{1}{2} & \zeta = 1 \\ 0 & 1 < \zeta \end{cases} \qquad (26)$$

The simplified solution is:

$$u = \frac{1}{2} + \frac{2}{\pi} \int_0^\infty \exp\left(\frac{1}{2} Pe_L - \sqrt{\frac{\sqrt{(z^2x')^2 + (z^2y')^2} + z^2x'}{2}}\right)$$

$$\sin\left(y\lambda^2 - \sqrt{\frac{\sqrt{(z^2x')^2 + (z^2y')^2} - z^2x'}{2}}\right) \frac{d\lambda}{\lambda} \qquad (27)$$

with:

$$z^2x' = Pe_L\left(\frac{1}{4} Pe_L + \delta H_1\right)$$

$$z^2y' = \delta Pe_L\left(\frac{2}{3}\frac{\lambda^2}{R} + H_2\right)$$

If in addition the longitudinal dispersion is negligible ($Pe_L \to \infty$), equation (27) becomes:

$$u = \frac{1}{2} + \frac{2}{\pi} \int_0^\infty \exp(-\delta H_1) \sin(\sigma\theta\lambda^2 - \delta H_2) \frac{d\lambda}{\lambda} \qquad (28)$$

where $\theta = t - \frac{z}{V}$

This solution has previously been given by Rosen (1952).

Steady-state solution

As $t \to \infty$ a steady-state condition is obtained. With a source maintained at constant concentration, this solution also gives the maximum concentration for specific values of Pe_T and Pe_L along ζ = constant .

The equation for the steady-state is found from the Laplace transform of u as:

$$\lim_{t\to\infty} u(r,z,t) = \lim_{s\to 0} s\, \tilde{u}(r,z,s)$$

We get:

$$u_\infty = \lim_{t\to\infty} u = \exp(\tfrac{1}{2}\,Pe_L) \int_0^\infty \exp\left(- \sqrt{Pe_L(\tfrac{1}{4}\,Pe_L + \tfrac{1}{Pe_T}\ \xi^2)}\right) J_o(\zeta\xi)\ J_1(\xi)\ d\xi \qquad (29)$$

It is noted that u_∞ depends on three dimensionless parameters only : Pe_L, Pe_T and ζ .

The steady-state solution, although simpler, cannot be integrated and must in general be evaluated numerically. However, in some special cases the integral can be expressed in terms of elementary functions. In the case of no longitudinal dispersion ($Pe_L \to \infty$) equation (29) simplifies to:

$$u_\infty = \int_0^\infty \exp\,(- \frac{\xi^2}{Pe_T})\quad J_o(\zeta\xi)\ J_1(\xi)\ d\xi \qquad (30)$$

This integral could be analytically solved along the lines $\zeta = 0$ and $\zeta = 1$.

$$\zeta = 0: \qquad u_\infty = 1 - e^{-\frac{Pe_T}{4}} \qquad (31)$$

(Abramowitz and Stegun, 1972; p.486)

$$\zeta = 1: \qquad u_\infty = \frac{1}{2}\left[1 - e^{-\frac{Pe_T}{2}} I_o\left(\frac{Pe_T}{2}\right)\right] \tag{32}$$

(Ogata, 1961; p. B4)

u_∞ along $\zeta = 0$ and $\zeta = 1$ is plotted in Figures 2-3 as function of Pe_T, for different Pe_L.

The limit of equation (29) for constant ζ and Pe_L, and for small values of Pe_T, may be obtained by noting that the integral rapidly converges and:

$$\left.\begin{array}{l} J_o(\zeta\xi) \sim 1 \\ J_1(\xi) \sim \frac{1}{2}\xi \end{array}\right\} \quad \text{as } \xi \to 0$$

Equation (29) then reduces to:

$$u_\infty = \frac{1}{2}\exp\left(\frac{1}{2}Pe_L\right)\int_0^\infty \exp\left(-\sqrt{Pe_L\left(\frac{1}{4}Pe_L + \frac{1}{Pe_T}\xi^2\right)}\right)\xi\, d\xi$$

This integral is easily solved by making the substitution $y^2 = Pe_L\left(\frac{1}{4}Pe_L + \frac{1}{Pe_T}\xi^2\right)$ and we obtain:

$$u_\infty = Pe_T\left(\frac{2 + Pe_L}{4Pe_L}\right); \qquad Pe_T \text{ small} \tag{33}$$

This is a straight line for Pe_L = constant.

u_∞ for $\zeta = 2,3$ and 10 is given in Figures 4 - 6 as a function of Pe_T and for different values of Pe_L. As $\zeta > 1$, the function $u_\infty(Pe_T)$ for constant Pe_L and ζ has a maximum value. This is evident, since for $\zeta > 1$:

$$\lim_{Pe_T \to 0} u_\infty = \lim_{Pe_T \to \infty} u_\infty = 0$$

These limits follow from equation (29), but can also be deduced by physical reasoning. As $Pe_T \to \infty$, no transport of chemicals occur to the region outside $\zeta = 1$. In the case of $Pe_T \to 0$, the radius of the source may be regarded as infinitesimally small, and the input of mass to the system vanishes.

The maximum value of u_∞, when the longitudinal dispersion is neglected, is of great importance. It gives the highest concentration which can be expected at a point in space. This criterion could be very useful in predicting the upper limit of the concentration of a contaminant, without making use of the sometimes unreliable values of the dispersion coefficients. The maximum value can be explicitly derived for small values of Pe_T. For sufficiently small Pe_T, equation (30) simplifies to:

$$u_\infty = \frac{1}{2}\int_0^\infty \xi \exp\left(-\frac{\xi^2}{Pe_T}\right) J_o(\zeta\xi)\, d\xi = \frac{Pe_T}{4} \exp\left(-\frac{\zeta^2 Pe_T}{4}\right) \qquad (34)$$

(Abramowitz and Stegun, 1972; p.486)

The maximum value is obtained by differentiating (34) with respect to Pe_T and setting the resulting expression equal to zero.

We get:

$$Pe_T = \frac{4}{\zeta^2}$$

and (35)

$$(u_\infty)_{max} = e^{-1}\frac{1}{\zeta^2}$$

For $\zeta = 10$, equation (35) predicts $(u_\infty)_{max} = 3.7 \cdot 10^{-3}$ for $Pe_T = 4.0 \cdot 10^{-2}$. The calculated values using equation (30) (Figure 6) are $(u_\infty)_{max} \sim 3.6 \cdot 10^{-3}$ and $Pe_T \sim 3.7 \cdot 10^{-2}$.

Longitudinal dispersion negligible

Refer to equation (23) and let $Pe_L \to \infty$. We find that :

$$u\Big|_{Pe_L \to \infty} = \left[\int_0^\infty \exp\left(-\frac{\xi^2}{Pe_T}\right) J_o(\zeta\xi)\, J_1(\xi)\, d\xi\right]$$

$$\left[\frac{1}{2} + \frac{2}{\pi}\int_0^\infty \exp(-\delta H_1)\sin(\sigma\theta\lambda^2 - \delta H_2)\frac{d\lambda}{\lambda}\right] \tag{36}$$

The first factor in this expression is exactly equation (30), that is, the steady-state solution for the case in which there is no longitudinal dispersion. The second factor has been given previously in equation (28), which yields the breakthrough curve for negligible longitudinal <u>and</u> lateral dispersion ($\zeta < 1$). We can therefore write equation (36) in brief notation as :

$$u\Big|_{Pe_L \to \infty} = u_\infty\Big|_{Pe_L \to \infty} \cdot \; u\Big|_{\substack{Pe_L \to \infty \\ Pe_T \to \infty}} \tag{37}$$

Thus, in the case of negligible longitudinal dispersion, the solution for any Pe_T and ζ is simply obtained by multiplying equation (28) with the steady-state value $u_\infty\Big|_{Pe_L \to \infty} = u_\infty(Pe_T, \zeta)$. Rosen (1954) evaluated equation (28) for many values of the dimensionless parameters δ, $\sigma\theta$ and ν . The evaluation of the steady-state solution for negligible longitudinal dispersion was described in the preceding section.

The importance of this result is that the total solution is reduced to a product of two single integrals, and an evaluation of the double-integral becomes unnecessary. Furthermore, from equations (31) and (32) we get the special cases:

$$u\Big|_{Pe_L \to \infty} = \left(1 - e^{-\frac{Pe_T}{4}}\right) \; u\Big|_{\substack{Pe_L \to \infty \\ Pe_T \to \infty}} \quad ; \zeta = 0 \tag{38}$$

$$u\Big|_{Pe_L \to \infty} = \frac{1}{2}\left[1 - e^{-\frac{Pe_T}{2}}\, I_o\!\left(\frac{Pe_T}{2}\right)\right] \; u\Big|_{\substack{Pe_L \to \infty \\ Pe_T \to \infty}} ; \zeta = 1 \tag{39}$$

Numerical integration

In the general case the integrals in the expression for u, equation (23), must be numerically evaluated. The first integral is easily calculated using standard numerical quadratures. The upper limit of the infinite integral is obtained from the argument of the exponential function. The double-integral is more difficult to handle. A method is used in which numerical integration is performed in one direction at a time. We start by integrating with respect to ξ. For each ξ-value in the grid we have to evaluate:

$$\frac{2}{\pi}\int_0^\infty \exp\left(\frac{1}{2}Pe_L - \sqrt{\frac{\sqrt{(z^2x')^2 + (z^2y')^2} + z^2x'}{2}}\right) \sin\left(y\lambda^2 - \sqrt{\frac{\sqrt{(z^2x')^2 + (z^2y')^2} - z^2x'}{2}}\right)\frac{d\lambda}{\lambda}$$

where z^2x' and z^2y' are given by equations (24) and (25). The integrand in this expression is the product of an exponential decaying function and a periodic sine function. The total function is thus a decaying sine wave in which both the period of oscillation and the degree of decay are functions of the system parameters. A method for integrating this sometimes highly oscillatory function (without the term $\frac{1}{Pe_T}\xi^2$ in z^2x') is described in Rasmuson and Neretnieks (1981). In this method the integration is performed over each half-period of the sine-wave respectively. The convergence of the alternating series obtained is then accelerated by repeated averaging of the partial sums (Dahl-quist and Björck, 1974; p. 72).

Typical examples are given in Figures 7-8 for $\zeta = 0$. It may be seen that, as $Pe_L < \infty$, u/u_∞ lies above the curve produced when the lateral dispersi is neglected ($Pe_T \to \infty$). The relative difference is larger at early times. As follows from equation (37), all the curves coincide as $Pe_L \to \infty$. This curve is also given in Figures 7-8, for comparison.

CONCLUDING REMARKS

A mathematical solution of the two-dimensional differential equation of dispersion from a disk source, coupled with a differential equation of diffusion and sorption in particles, has been derived. Important limiting cases have been obtained. An expression giving the highest possible concentration at a point is developed. It predicts the upper limit of the concentration of a contaminant. For negligible longitudinal dispersion, the solution for any value of the transverse Peclet number and dimensionless radial distance is obtained by multiplication of the solution for no lateral dispersion and $\zeta < 1$ with the steady-state value. A method for integrating the general solution is briefly described.

Mass transfer due to sorption plays an important role in mass transport within natural flow systems. In general, the outcome of any contaminant introduced into the groundwater system is largely dependent on the capacity of the solid matrix material to sorb the dissolved substance. The model takes into account diffusion to the external surfaces, internal diffusion and linear sorption. Furthermore, a solution has been derived which considers the (linear) kinetics of the sorption to the intrapore walls (Rasmuson, 1980). The model and analytical solution presented above can be extended to include radioactive decay (Rasmuson and Neretnieks, 1981). The same general expressions and limiting cases apply, with slight modifications, for these extensions.

The analytical expressions developed herein should prove helpful in making quantitative predictions of the contamination of groundwater supplies from groundwater movement through buried wastes.

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NOTATION

a	radius of disk surface source	L
b	particle radius	L
C	concentration in fluid	M/L^3
C_p	concentration in fluid in intrapores	M/L^3
C_s	concentration in solid material	M/L^3
C_o	inlet concentration in fluid	M/L^3
D_L	longitudinal dispersion coefficient	L^2/T
D_p	diffusivity in fluid in intrapores	L^2/T
D_s	diffusivity in solid phase	L^2/T
D_T	transverse dispersion coefficient	L^2/T
H_1	see equation (19)	
H_2	see equation (20)	
H_{D_1}	see equation (21)	
H_{D_2}	see equation (22)	
I_o	modified Bessel function of the first kind of order zero	
J_o, J_1	Bessel function of the first kind of order zero and one, respectively	
K	volume equilibrium constant	L^3/L^3
k_f	mass transfer coefficient	L/T
m	$= \frac{\varepsilon}{1-\varepsilon}$	
Pe_L	$= \frac{zV}{D_L}$, longitudinal Peclet number	
Pe_T	$= \frac{a^2V}{zD_T}$, transverse Peclet number	
p	Hankel transform variable	

$\overset{\Delta}{q}$	volume averaged concentration in particles	M/L^3
q_i	internal concentration in particles	M/L^3
q_s	$= q_i(b,r,z,t)$	M/L^3
R	$= \frac{K}{m}$, distribution ratio	
R_F	$= \frac{b}{3k_f}$, film resistance	T
r	radial distance	L
r'	radial distance from center of spherical particle	L
s	Laplace transform variable	
t	time	T
u	$= C/C_o$, dimensionless concentration in fluid	
$u\|_{Pe_L \to \infty}$	dimensionless concentration in fluid when the longitudinal dispersion is negligible	
$u\|_{Pe_L \to \infty, Pe_T \to \infty}$	dimensionless concentration in fluid when the longitudinal and lateral dispersion are negligible ($\zeta < 1$)	
u_∞	steady-state value of u	
$u_\infty\|_{Pe_L \to \infty}$	steady-state value of u for negligible longitudinal dispersion	
V	average linear pore velocity	L/T
x'	see equation (17)	L^{-2}
y	$= \sigma t$, contact time parameter	
y'	see equation (18)	L^{-2}
z	distance in flow direction	L

Greek letters

γ	$= \frac{3D_s K}{b^2}$	T^{-1}
δ	$= \frac{\gamma z}{mV}$, bed length parameter	
ε	void fraction of bed	L^3/L^3
ε_p	void fraction of particle	L^3/L^3
θ	$= t - \frac{z}{V}$	T
ζ	$= \frac{r}{a}$, dimensionless radial distance	
λ	variable of integration	
ν	$= \gamma R_F$	
ξ	variable of integration	
σ	$= \frac{2D_s}{b^2}$	T^{-1}

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APPENDIX

Differential equations:

$$\frac{\partial C}{\partial t} + V\frac{\partial C}{\partial z} - D_L\frac{\partial^2 C}{\partial z^2} - D_T\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right) = -\frac{1}{m}\left(\frac{\partial \overset{\Delta}{q}}{\partial t}\right) \quad (1)$$

$$\frac{\partial q_i}{\partial t} = D_s\left(\frac{\partial^2 q_i}{\partial r'^2} + \frac{2}{r'}\frac{\partial q_i}{\partial r'}\right) \quad (2)$$

Boundary conditions:

$$\begin{cases} C(r,0,t) = C_o & ; \quad r \leq a \\ C(r,0,t) = 0 & ; \quad r > a \end{cases} \quad (3)$$

$$C(r,\infty,t) = 0 \quad (4)$$

$$C(0,z,t) \neq \infty \quad (5)$$

$$C(\infty,z,t) = 0 \quad (6)$$

$$C(r,z,0) = 0 \quad (7)$$

$$q_i(0,r,z,t) \neq \infty \quad (8)$$

$$q_i(b,r,z,t) = q_s(r,z,t) \text{ given by } \frac{\partial \overset{\Delta}{q}}{\partial t} = \frac{3k_f}{b}\left(C - \frac{q_s}{K}\right) \quad (9)$$

$$q_i(r',r,z,0) = 0 \quad (10)$$

The boundary condition (9) is the linking equation between equations (1) and (2).

The solution of the equations (1) and (2) subject to the boundary conditions (3)-(10) is obtained by the successive use of the Laplace and the Hankel transforms. The Laplace transform of equation (1) with $D_T = 0$ is given in Rasmuson and Neretnieks (1980) as:

$$\frac{\partial^2 \tilde{C}}{\partial z^2} - \frac{V}{D_L}\frac{\partial \tilde{C}}{\partial z} - \left(\frac{s}{D_L} + \frac{Y_T(s)}{mD_L}\right)\tilde{C} = 0$$

where:

$$Y_T(s) = \frac{Y_D(s)}{R_F Y_D(s) + 1}$$

$$Y_D(s) = 2\gamma \sum_{n=1}^{\infty} \frac{s}{s + D_s \sigma_n^2}$$

$$R_f = \frac{b}{3k_f}$$

$$\gamma = \frac{3D_s K}{b^2}$$

$$\sigma_n = n\pi/b$$

For $D_T > 0$ the transformed equation becomes:

$$\frac{\partial^2 \tilde{C}}{\partial z^2} - \frac{V}{D_L}\frac{\partial \tilde{C}}{\partial z} - \left(\frac{s}{D_L} + \frac{Y_T(s)}{m\,D_L}\right)\tilde{C} + \frac{D_T}{D_L}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \tilde{C}}{\partial r}\right) = 0 \tag{11}$$

with the boundary conditions:

$$\begin{cases} \tilde{C}(r,0,s) = \dfrac{C_o}{s} & ; r \leq a \\ \tilde{C}(r,0,s) = 0 & ; r > a \end{cases} \tag{12}$$

$$\tilde{C}(r,\infty,s) = 0 \tag{13}$$

$$\tilde{C}(0,z,s) \neq \infty \tag{14}$$

$$\tilde{C}(\infty,z,s) = 0 \tag{15}$$

The solution of this partial differential equation in r and z is obtained by applying the Hankel transform of order zero with respect to r:

$$\frac{\partial^2 \hat{\tilde{C}}}{\partial z^2} - \frac{V}{D_L}\frac{\partial \hat{\tilde{C}}}{\partial z} - \left(\frac{s}{D_L} + \frac{Y_T(s)}{m\, D_L} + \frac{D_T}{D_L} p^2\right) \hat{\tilde{C}} = 0 \qquad (16)$$

Equation (16) may be treated as an ordinary second-order, linear differential equation in z whose solution after applying the boundary condition for $z \to \infty$ is:

$$\hat{\tilde{C}} = A \exp\left[\left(\frac{V}{2D_L} - \sqrt{\frac{V^2}{4D_L^2} + \frac{s}{D_L} + \frac{Y_T(s)}{mD_L} + \frac{D_T}{D_L} p^2}\right) z\right] \qquad (17)$$

The inversion formula for the Hankel transform gives:

$$\tilde{C} = \int_0^\infty A(p) \exp\left[\left(\frac{V}{2D_L} - \sqrt{\frac{V^2}{4D_L^2} + \frac{s}{D_L} + \frac{Y_T(s)}{m\, D_L} + \frac{D_T}{D_L} p^2}\right) z\right] p\, J_o(r\, p)\, dp \qquad (18)$$

where we have written $A = A(p)$ to indicate that it depends on p.

A(p) is determined from the "dual" integral equations obtained by inserting (18) in the boundary condition (12). These are:

$$\int_0^\infty A(p)\, p\, J_o\,(rp)\, dp = \frac{C_o}{s} \quad ; r \leq a$$

$$\int_0^\infty A(p)\, p\, J_o\,(rp)\, dp = 0 \quad ; r > a \qquad (19)$$

The solution of this problem is given in e.g. Sneddon (1951, p. 528) as:

$$A(p) = \frac{C_o}{s} \frac{a}{p} J_1 (ap) \tag{20}$$

Inserting in (18) and making the substitution ξ = ap gives the required solution of (11) as:

$$\tilde{u}(r,z,s) = \frac{\tilde{C}}{C_o} = \frac{1}{s} \int_0^\infty \exp \left[\left(\frac{V}{2D_L} - \sqrt{\frac{V^2}{4D_L^2} + \frac{s}{D_L} + \frac{Y_T(s)}{m\, D_L} + \frac{D_T}{D_L a^2} \xi^2} \right) z \right] J_o(\frac{r}{a} \xi)\; J_1(\xi)\; d\xi \tag{21}$$

The desired result u(r,z,t) is given by the contour integral representing the inverse Laplace transform of $\tilde{u}(r,z,s)$:

$$u(r,z,t) = \frac{C(r,z,t)}{C_o} = \exp\left(\frac{Vz}{2D_L}\right) \frac{1}{2\pi i} \int_{\alpha-i\infty}^{\alpha+i\infty} \frac{1}{s} \exp(st) \left[\int_0^\infty \exp \left(-z \sqrt{\frac{V^2}{4D_L^2} + \frac{s}{D_L} + \frac{Y_T(s)}{m\, D_L} + \frac{D_T}{D_L a^2} \xi^2} \right) J_o(\frac{r}{a} \xi)\; J_1(\xi)\; d\xi \right] ds$$

{changing the order of integration} =

$$\exp\left(\frac{Vz}{2D_L}\right) \int_0^\infty J_o(\frac{r}{a} \xi) \quad J_1(\xi) \underbrace{\left[\frac{1}{2\pi i} \int_{\alpha-i\infty}^{\alpha+i\infty} \frac{1}{s} \exp\left(st - z \sqrt{\frac{V^2}{4D_L^2} + \frac{s}{D_L} + \frac{Y_T(s)}{m\, D_L} + \frac{D_T}{D_L a^2} \xi^2} \right) ds \right]}_{I} d\xi \quad ($$

The integral I when $D_T = 0$ has been evaluated in Rasmuson and Neretnieks (1980). Putting $\frac{V^2}{4D_L^2} = \frac{V^2}{4D_L^2} + \frac{D_T}{D_L a^2}\xi^2$ (=constant for constant ξ)

everywhere in that solution we obtain I for $D_T > 0$ as:

$$I = \frac{1}{2} \exp\left(-z\sqrt{\frac{V^2}{4D_L^2} + \frac{D_T}{D_L a^2}\xi^2}\right) +$$

$$\frac{2}{\pi}\int_0^\infty \exp\left(-z\sqrt{\frac{\sqrt{x'(\lambda,\xi)^2 + y'(\lambda)^2} + x'(\lambda,\xi)}{2}}\right)$$

$$\sin\left(\sigma\lambda^2 t - z\sqrt{\frac{\sqrt{x'(\lambda,\xi)^2 + y'(\lambda)^2} - x'(\lambda,\xi)}{2}}\right)\frac{d\lambda}{\lambda} \tag{23}$$

with:

$$x'(\lambda,\xi) = \frac{V^2}{4D_L^2} + \frac{\gamma}{mD_L} H_1(\lambda) + \frac{D_T}{D_L a^2}\xi^2 \tag{24}$$

$$y'(\lambda) = \frac{\sigma\lambda^2}{D_L} + \frac{\gamma}{mD_L} H_2(\lambda) \tag{25}$$

H_1 and H_2 are complicated functions of λ:

$$H_1(\lambda) = \frac{H_{D_1} + \nu(H_{D_1}^2 + H_{D_2}^2)}{(1 + \nu H_{D_1})^2 + (\nu H_{D_2})^2} \tag{26}$$

$$H_2(\lambda) = \frac{H_{D_2}}{(1 + \nu H_{D_1})^2 + (\nu H_{D_2})^2} \tag{27}$$

H_{D_1} and H_{D_2} are defined as:

$$H_{D_1}(\lambda) = \lambda \left(\frac{\sinh 2\lambda + \sin 2\lambda}{\cosh 2\lambda - \cos 2\lambda}\right) - 1 \tag{28}$$

$$H_{D_2}(\lambda) = \lambda \left(\frac{\sinh 2\lambda - \sin 2\lambda}{\cosh 2\lambda - \cos 2\lambda}\right) \tag{29}$$

From equations (22) and (23) we finally obtain u(r,z,t) as:

$$u(r,z,t) = \frac{1}{2} \exp\left(\frac{Vz}{2D_L}\right) \int_0^\infty \exp\left(-z\sqrt{\frac{V^2}{4D_L^2} + \frac{D_T}{D_L a^2}\ \xi^2}\right)$$

$$J_o\left(\frac{r}{a}\xi\right) J_1(\xi)\, d\xi \quad +$$

$$+ \quad \exp\left(\frac{Vz}{2D_L}\right) \frac{2}{\pi} \int_0^\infty J_o\left(\frac{r}{a}\ \xi\right) \ J_1(\xi)$$

$$\left[\int_0^\infty \exp\left(-\ z \sqrt{\frac{\sqrt{x'(\lambda,\xi)^2 + y'(\lambda)^2} + x'(\lambda,\xi)}{2}}\right)\right.$$

$$\left.\sin\left(\sigma\lambda^2 t - \ z \sqrt{\frac{\sqrt{x'(\lambda,\xi)^2 + y'(\lambda)^2} - x'(\lambda,\xi)}{2}}\right)\frac{d\lambda}{\lambda}\right] d\xi \tag{30}$$

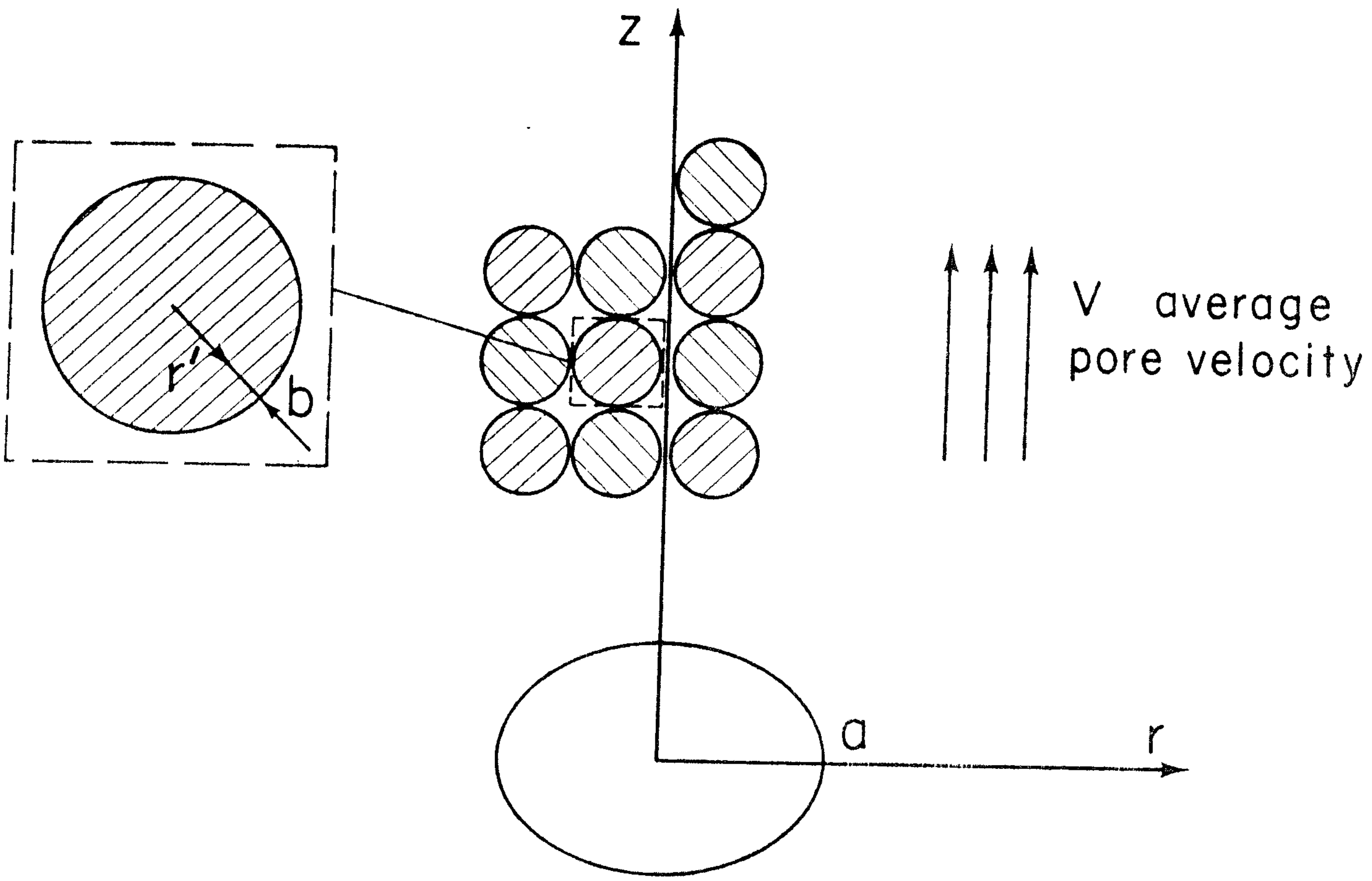
FIGURE CAPTIONS

Figure 1 Definition sketch of the modeled system

Figures 2-6 Steady-state value of u, u_∞, as a function of Pe_T for $\zeta = 0, 1, 2, 3, 10$. $Pe_L = 0.1, 1.0, \infty$.

Figures 7-8 Dimensionless breakthrough curves divided by the steady-state values.

FIGURE 1



Disk surface source

$C(r,o,t)=C_0\ (0 \le r \le a)$

XBL 801-6724

FIGURE 2

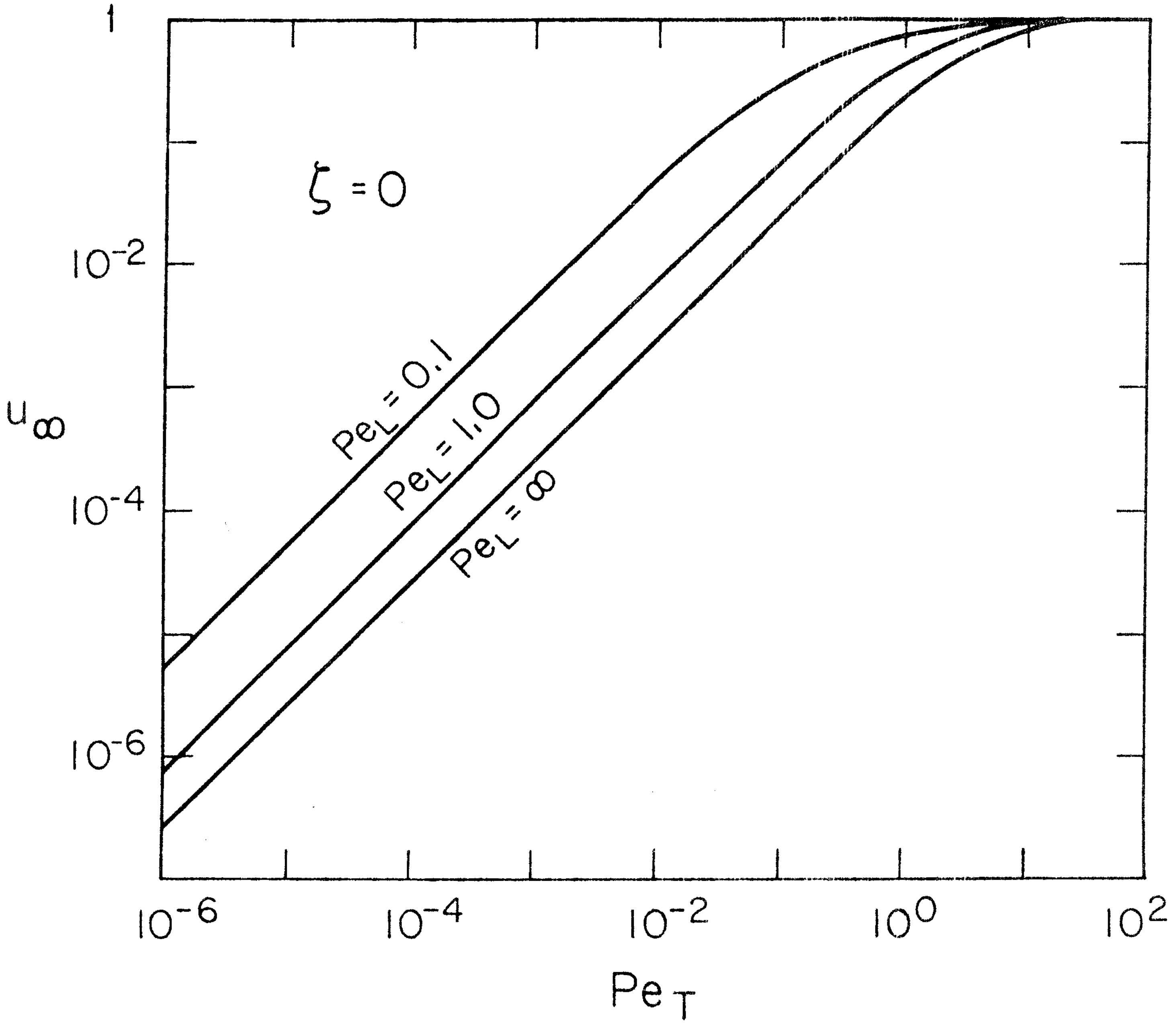


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FIGURE 3

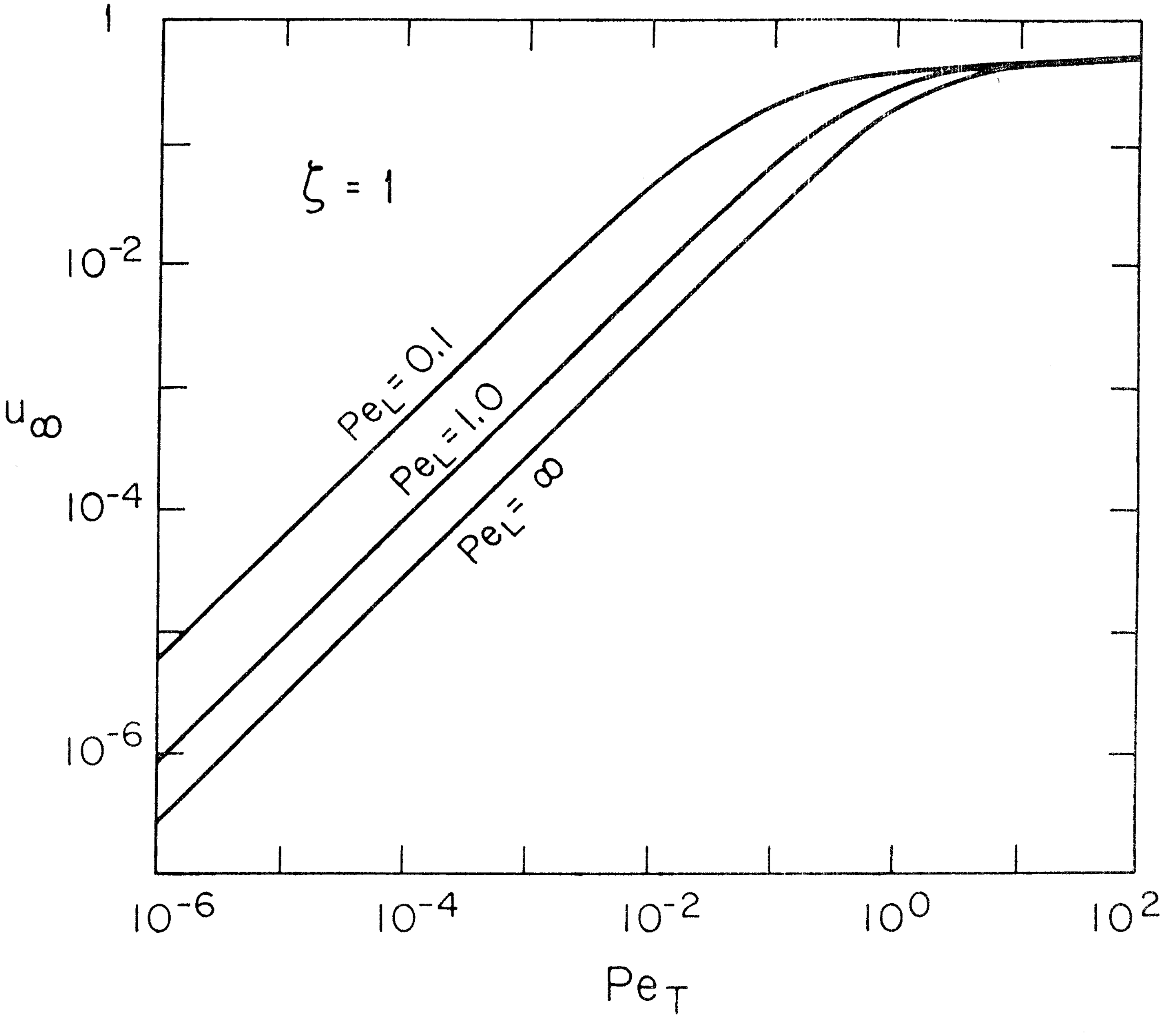

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FIGURE 4

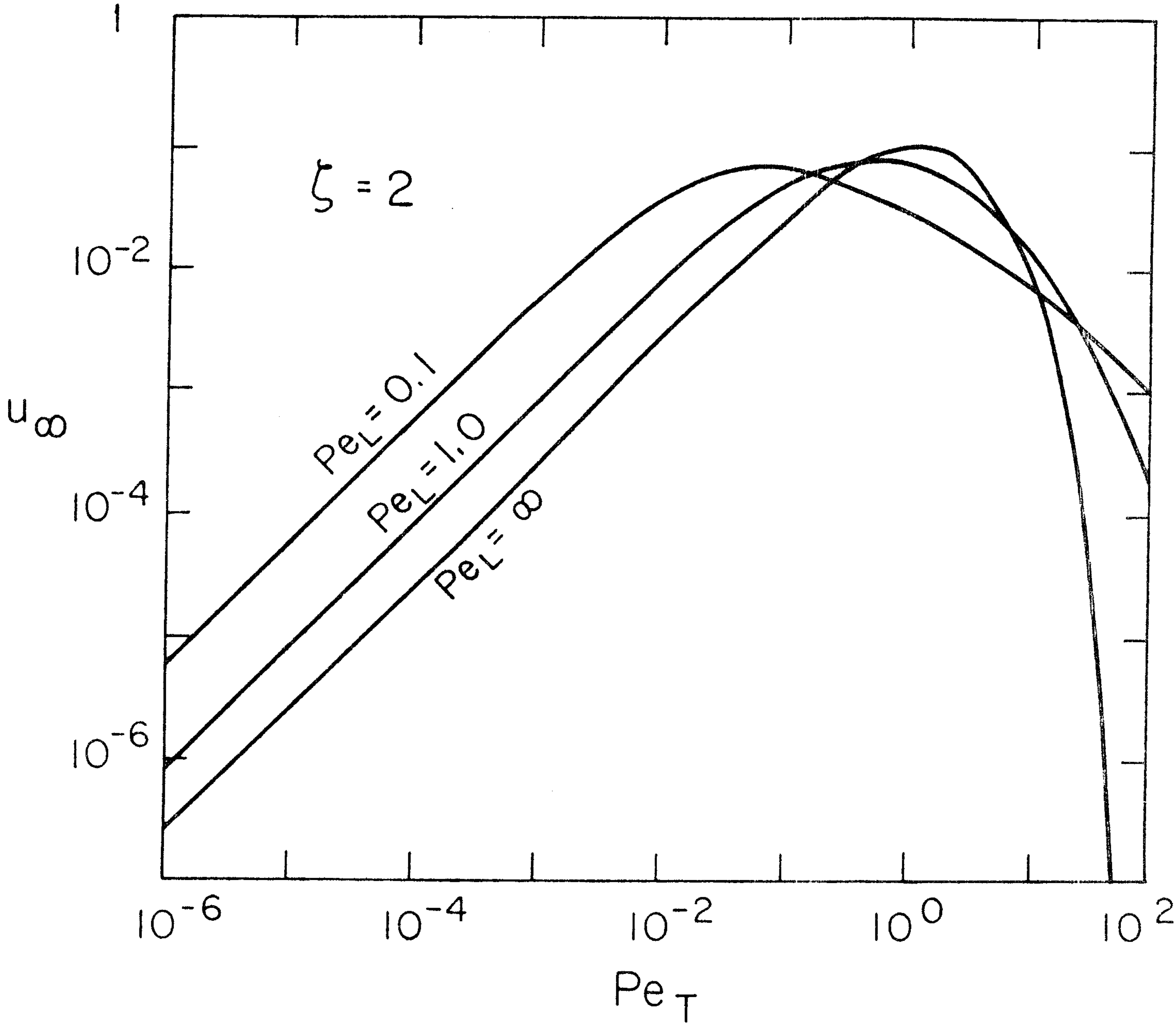

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FIGURE 5

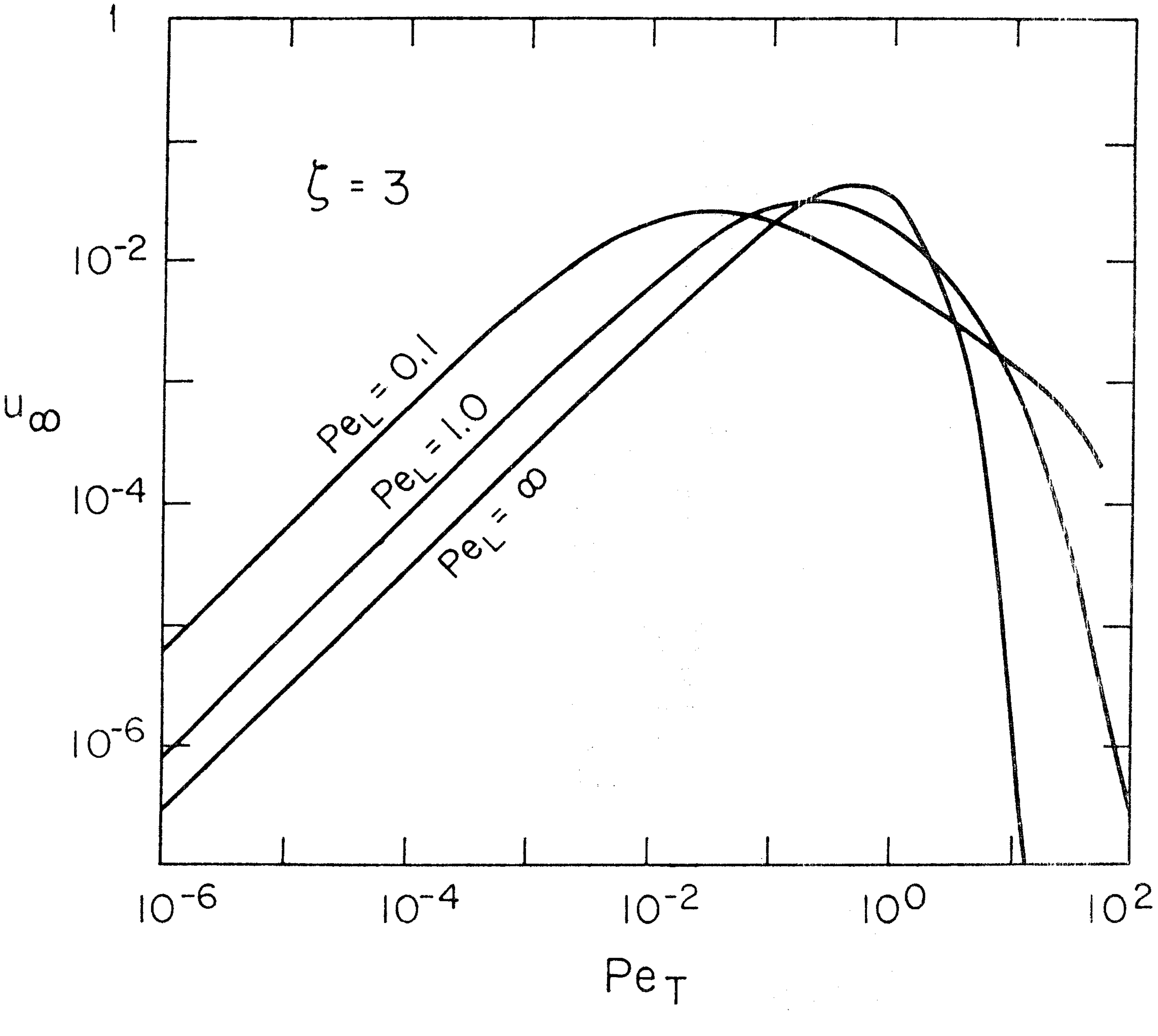

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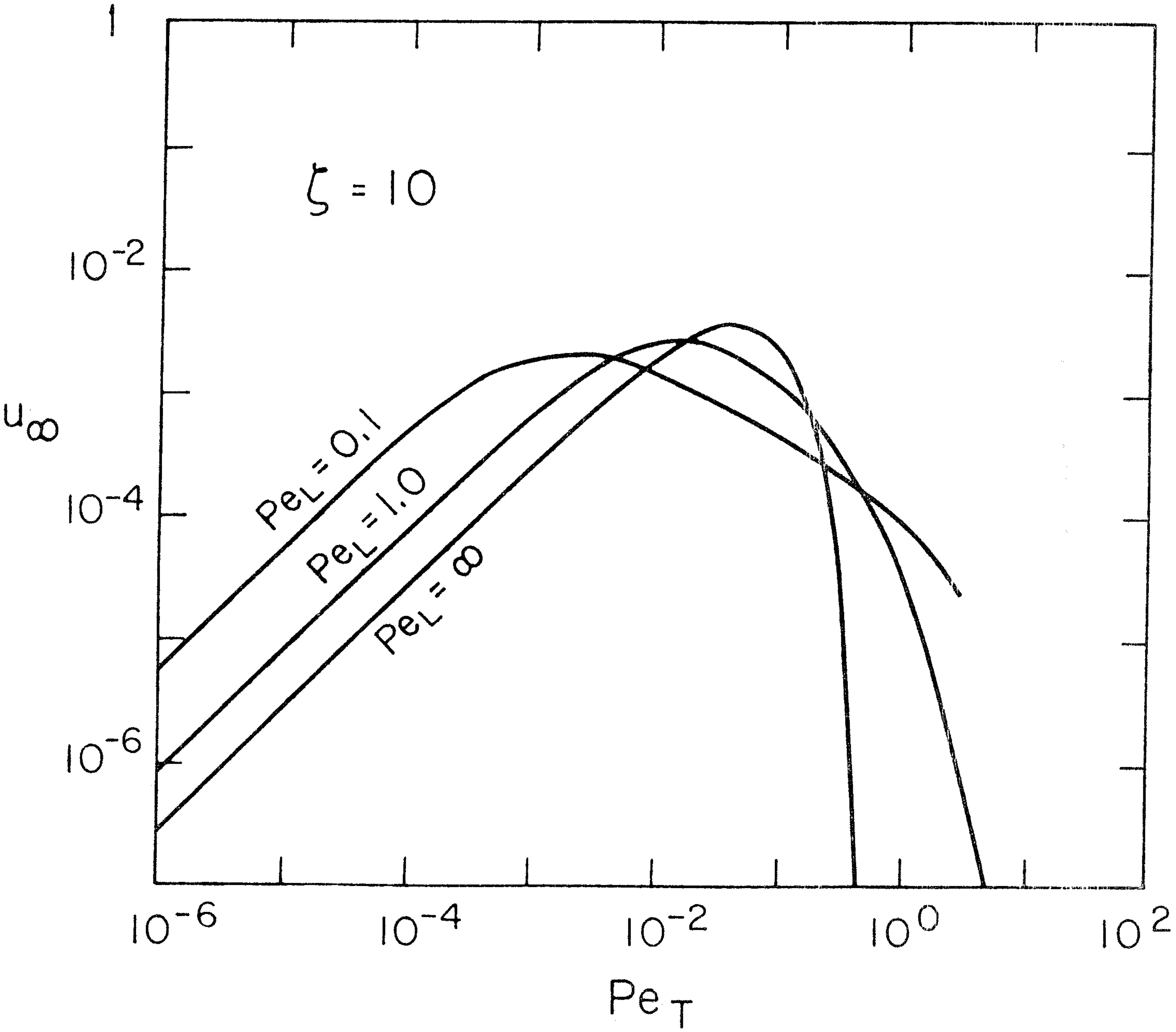
FIGURE 6



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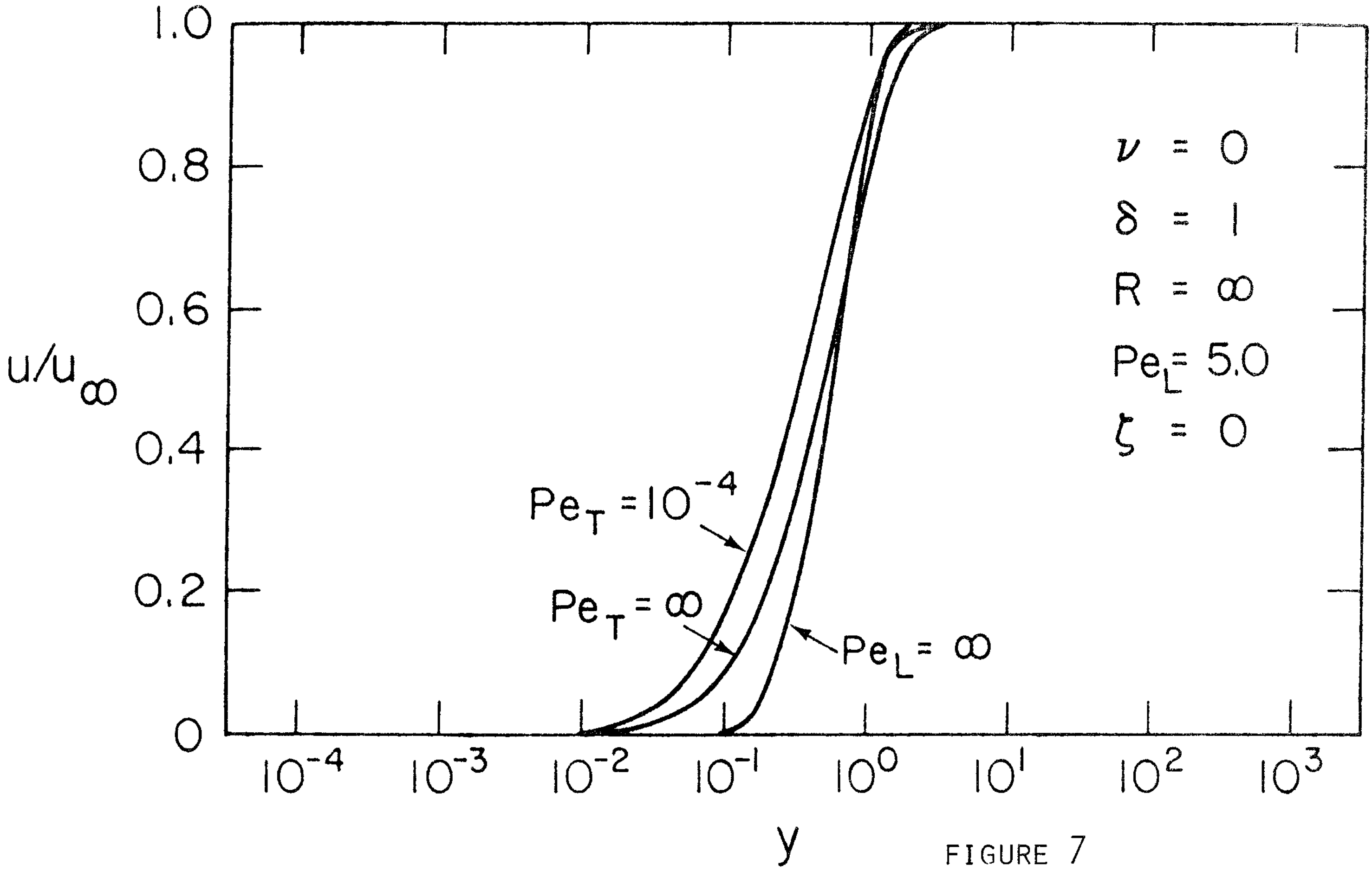
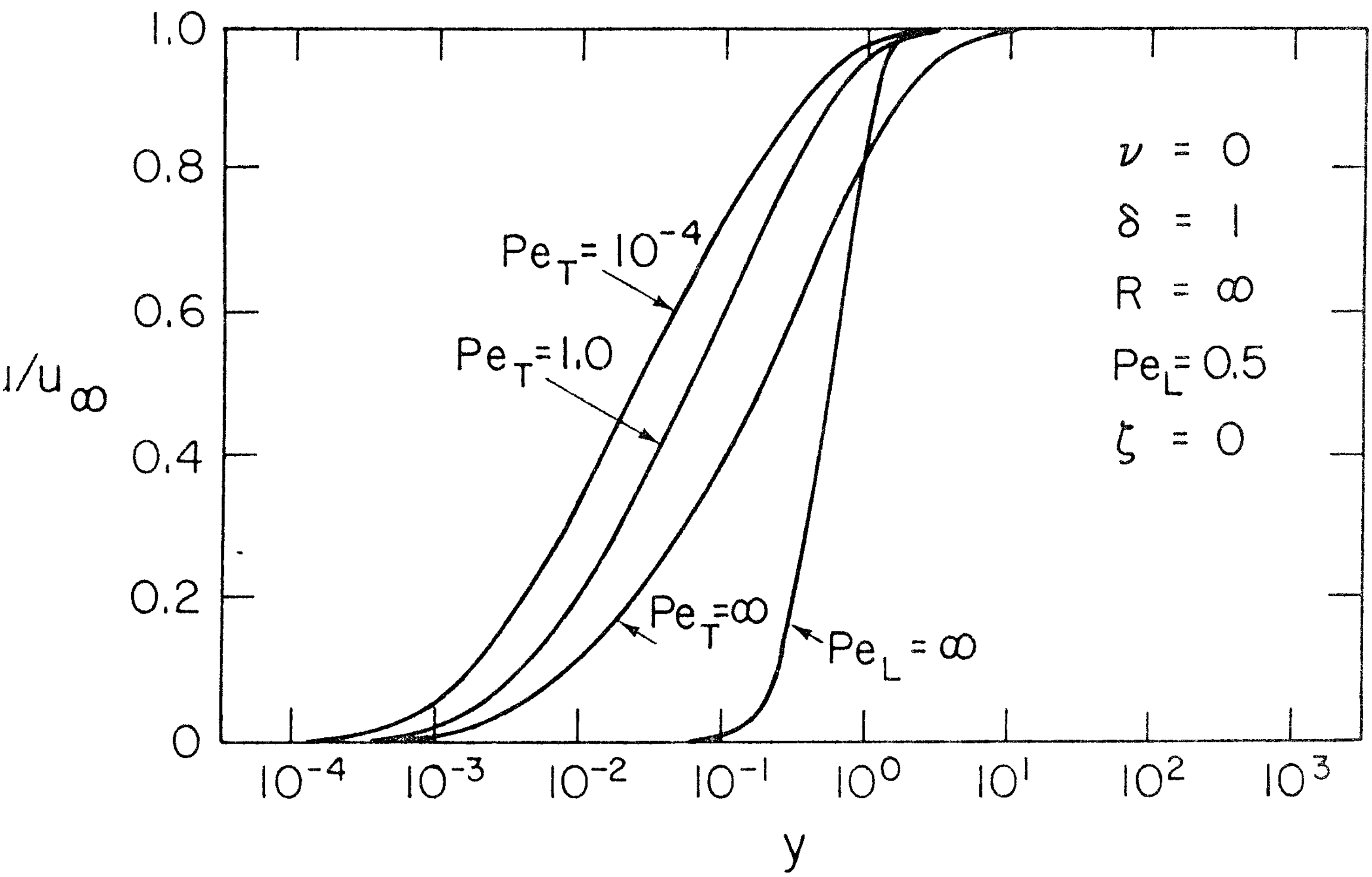


FIGURE 7

FIGURE 8



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