PATH-INTEGRAL VARIATIONAL METHODS FOR FLOW THROUGH POROUS MEDIA

by

MICHAEL A. TANKSLEY

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Date

Chairman of Examining Committee

5/1/95
Date

Joseph B. Kruger
Executive Officer

Andreas Acrivos

Ronald Dickman

Frederick W. Smith

David Wilkinson

Supervisory Committee

THE CITY UNIVERSITY OF NEW YORK

Abstract

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by

Michael A. Tanksley

Advisor: Professor Joel Koplik

We characterise a porous medium as a statistically homogeneous continuum with local fluctuations in physical parameters. We consider the steady-state flow of a single incompressible fluid through an infinite medium, the dissipation of a passive tracer in such a flow, and the first passage problem for tracer transport in a stratified medium. For each problem we average a path-integral expression for the Green function over parameter fluctuations, and obtain large-distance, long-time effective parameters via Feynman's variational method. For the permeability problem, and the tracer problem at small Peclet number P, the variational results are consistent with results obtained by first-order perturbation theory. For the tracer problem at large P, the variational method predicts the expected linear dependence of the effective dispersion tensor on P, which perturbation theory does not. This indicates that, for these problems and others like them, a first-order perturbation expansion can be of limited utility. For the first passage problem, we assume that the medium is infinite in the direction normal to the layering but finite (of length $2L$) in the direction parallel to the layering. We calculate the exit time distribution and the mean first passage time. The latter is proportional to $L^{4/3}$, consistent with previous work.

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Chapter 1

Introduction

1.1 Flow in porous media

The flow of a single fluid through a porous medium is of great practical interest in several fields of applied physics, including chromatography, filtration processes, and groundwater hydrology (see, for example, Scheidegger (1974)). The problem is often well understood over regions typically of the order of centimetres, where the medium is treated as a homogeneous continuum with certain bulk properties, and where laws governing transport through the medium are known. The problem is not so well understood over regions typically of the order of metres, where we do not know the large-scale transport laws. To find these laws, we treat a large region as an aggregation of smaller sub-regions, i.e., a heterogeneous continuum. Transport through the large region can be described by a local version of the smaller-scale transport equation. Averaging over the heterogeneities results in an equivalent homogeneous description good over large length scales.

The general problem can be thought of as three more specific problems, depending on the length scale at which the medium is examined. Over "microscopic" scales, of the order of microns, the medium is grainy and highly irregular. Flow is governed by the Stokes equations, which are solved in the pores with the conditions that flow is incompressible and that

velocity is zero at the pore walls. Due to the microscopic irregularity, it is impractical to obtain the exact flow field. One can get bulk properties instead, by averaging over a volume large enough to contain a statistically representative selection of pores. Such a volume is said to be of "mesoscopic" extent. Over mesoscopic scales, of the order of centimetres, the medium appears to be a homogeneous continuum, and flow of a single fluid is governed by Darcy's law. "Macroscopic" lengths are of the order of geological irregularity, i.e., metres and up. Over macroscopic length scales, the medium appears to be a heterogeneous continuum, and flow of a single fluid is governed by a local version of Darcy's law.

Suppose a passive tracer is released into a single fluid flowing through the medium. Dispersion of this tracer is governed at microscopic scales by a convection-diffusion equation (CDE), in which the diffusion constant is the molecular diffusion constant of the tracer in the fluid, and the drift velocity is the Stokes flow field. It is impractical to obtain an exact microscopic solution in this case, as in the previous case; however, bulk properties can again be obtained by averaging over the irregularities. The equation governing dispersion of a passive tracer at mesoscopic scales is also a CDE. The velocity comes from Darcy's law. The dispersion tensor has an isotropic part due to molecular diffusion, and an anisotropic part due to convective dispersion. Transport is governed by competition between convection and diffusion. For a typical length L, $\tau_D \equiv L^2/D$ is a characteristic transport time for diffusion, where D is a diffusion coefficient (usually the transverse). Likewise, $\tau_C \equiv L/u$ is a characteristic transport time for convection, where u is the velocity. Their ratio τ_D/τ_C is called the Peclet number P. The convective dispersion is a function of this Peclet number (Koch and Brady (1985)). If diffusion is more important than convection in moving a tracer particle around the medium, meaning P is small, then convective dispersion is proportional to P^2. If convection is more important than diffusion, meaning P is large, convective dispersion is proportional to P, and is due primarily to mechanical effects, i.e., to splitting (for compressible flow) and twisting of

streamlines. For very large P, convective dispersion parallel to $\mathbf{u}$ is proportional to $P\ln P$, although convective dispersion normal to $\mathbf{u}$ is still proportional to P. Over macroscopic scales, dispersion of a passive tracer is governed by a local CDE, in which the velocity and (therefore) the convective dispersion vary with position. Fried and Combarnous (1971) present a review of the early experimental work done on the tracer problem.

When averaging over heterogeneities in the tracer problem, it is usually assumed that the central limit theorem (CLT) holds, i.e., that if in the limit of long times a tracer particle samples a statistically representative set of the fluctuating values, then the distribution of particle displacements is Gaussian, and the particle's mean square displacement increases as the first power of time t (diffusion) (van Kampen (1981)). If for some reason the CLT does not hold, then the distribution is not generally Gaussian, and furthermore the mean square displacement increases as t^{α}, where α may be less than one (subdiffusion) or greater than one (superdiffusion) (Fisher (1966), Bouchaud and Georges (1990)).

Interest in groundwater flow leads quite naturally to interest in flow through layered media, given that rock and sediment are so often found to be layered. Generally, theoretical investigations assume that the medium is of infinite extent, and consider the mean tracer concentration to be the prime object of interest. This is mathematically convenient in that one is not obliged to work with boundaries which are a finite distance from the source, but it is unusual for an experiment to be so arranged. A more common experimental practice is to inject tracer into the medium at one point, and then to measure the time interval necessary for the tracer to reach the boundary of the medium. This "first passage time" problem has been well studied in one dimension (Weiss (1967), van Kampen (1981), Gardiner (1983)), and is now being studied in more complex media (Lee and Koplik (1995)). We will examine the first passage time problem for flow through a layered medium. Transport normal to the layering is governed by diffusion alone; transport parallel to the velocity is governed by both

diffusion and convection, with the velocity a random function of transverse position; and transport parallel to the layering but normal to the velocity is simple diffusion, which we shall ignore. This model is of theoretical interest because the average concentration profile in unbounded space is superdiffusive (Matheron and de Marsily (1980)).

1.2 Statement of problem

The flow of a single fluid through an isotropic porous medium is governed at macroscopic scales by Darcy's law,

$$\mathbf{u}(\mathbf{r})=-\frac{\kappa(\mathbf{r})}{\mu}\nabla\phi(\mathbf{r}) \tag{1.2.1}$$

where $\mathbf{u}(\mathbf{r})$ is the local velocity, $\kappa(\mathbf{r})$ is the local permeability, μ is the viscosity, and $\phi(\mathbf{r})$ is the local pressure. The flow is assumed to be incompressible, i.e.,

$$\nabla\cdot\mathbf{u}(\mathbf{r})=0 \tag{1.2.2}$$

We suppose that $\kappa(\mathbf{r})$ is a random variable, and discuss its probability distribution in Sec. 2.2. Combination of Darcy's law and the incompressibility condition gives

$$\nabla\cdot\kappa(\mathbf{r})\nabla\phi(\mathbf{r})=0 \tag{1.2.3}$$

We wish to average the Green function for this equation over fluctuations in permeability.

The transport of a tracer by an incompressible fluid is governed at macroscopic length scales by a CDE,

$$\left[\frac{\partial}{\partial t}+\mathbf{u}(\mathbf{r})\cdot\nabla-\nabla\cdot\mathbf{D}(\mathbf{r})\cdot\nabla\right]c(\mathbf{r},t)=0 \tag{1.2.4}$$

where $\mathbf{u}(\mathbf{r})$ is the local velocity, $\mathbf{D}(\mathbf{r})$ is the local dispersion tensor, and $c(\mathbf{r},t)$ is the mass concentration of tracer in the fluid. We suppose that $\mathbf{u}(\mathbf{r})$ is a random variable, and discuss its probability distribution in Sec. 2.2. Since convective dispersion is a function of velocity, we expect in general that the former will be a random variable like the latter, and that the fluctuations of the two will be correlated. We wish to average the Green function for (1.2.4) over

fluctuations in velocity and dispersion.

Although mesoscopic dispersion is known to be anisotropic, with principal directions parallel to and normal to flow, the model of Matheron and de Marsily (1980) takes the parallel and transverse dispersion coefficients to be numerically equal. This is possible because convection dominates diffusion parallel to bulk flow in the limit of long times; in addition, doing this simplifies the equations somewhat. If $D\mathbf{I}$ is taken to be the mesoscopic dispersion tensor, then the CDE for the first passage problem becomes

$$\left[\frac{\partial}{\partial t}+\mathbf{u}(\mathbf{r})\cdot\nabla-D\nabla^2\right]c(\mathbf{r},t)=0 \tag{1.2.5}$$

The Green function for Eq. (1.2.5) is essentially the probability that a tracer particle starting at $(\mathbf{r}_0,t_0)$ will be found at $(\mathbf{r},t)$. The exit time distribution $p(\mathbf{r}_0,t-t_0)$ is defined as the probability per unit time that the particle leaves the region of interest at time t, and is given in terms of the Green function $G(\mathbf{r},\mathbf{r}_0,t-t_0)$ by

$$p(\mathbf{r}_0,t-t_0)=-\frac{\partial}{\partial t}\int_V d\mathbf{r}G(\mathbf{r},\mathbf{r}_0,t-t_0) \tag{1.2.6}$$

where the integration is taken over the region of interest. From $p(\mathbf{r}_0,t-t_0)$, we can obtain whatever moments we desire of the first passage time distribution. Therefore, we wish to average the Green function for (1.2.5) over fluctuations in velocity, and then obtain the exit time distribution from the result via Eq. (1.2.6).

1.3 Plan of dissertation

In Chapter 2, we will present some background material concerning statistics in general and the specific statistical models employed here in particular. Chapter 3 will be a discussion of some particularly relevant aspects of the work already done on these problems: specifically, methods of obtaining the mesoscopic equations which serve as our starting point, methods of deriving the mesoscopic equations from the microscopic equations via statistical arguments,

and two well-known techniques used to average over fluctuations in the macroscopic equations. In Chapter 4, we first develop a path-integral formulation for the problems considered here, and then present the variational method which we shall apply to the path integrals. In Chapter 5, we present the results of applying this method to three problems: the permeability problem in an infinite medium, the tracer problem in an infinite medium, and the first passage problem in a layered medium. Chapter 6 contains a summary and conclusions.

Chapter 2

Statistical preliminaries

2.1 General considerations

A random variable X is defined by (1) a set or ensemble of possible values $\{x\}$, and (2) a set of corresponding numbers $\{P(x)\}$, where $P(x)$ gives the probability for x to occur (Beran (1968), van Kampen (1981)). Since they are probabilities, the $\{P(x)\}$ are non-negative and their sum is 1. A standard example is the throw of a die, the outcome of interest being the number of dots showing. Here, x may assume any integer value from 1 to 6 with probability 1/6, assuming the die to be honest. Another example is the throw of two dice. If the outcome of interest is the total number of dots showing, x may assume any integer value from 2 to 12. Some outcomes are more likely than others, with $P(2)=P(12)=1/36$ the least likely, and $P(7)=1/6$ the most likely. X may have a continuous set of possible values, as for example if X is the displacement of a Brownian particle. In this case $P(x)\Delta x$ is the probability that X has a value between x and $x+\Delta x$, and $P(x)$ itself becomes a probability density. A probability density function (PDF) that is seen quite often is the Gaussian or normal PDF

$$P_G(x)=\frac{1}{(2\pi)^{1/2}\sigma}\exp\left[-\frac{(x-\mu)^2}{2\sigma^2}\right] \tag{2.1.1}$$

which has been normalised via $\int_{-\infty}^{\infty} dx P_G(x)=1$. This is the familiar "bell curve", with μ the

location of the distribution's peak and σ related to its width.

The conditional probability $P(x\,|\,y)$ for two variables X and Y is defined as the probability that X will assume value x given that Y assumes value y. If $P(x\,|\,y)=P(x)$, than X and Y are statistically independent. A simple example is a coin which is tossed twice. Let Y be the first toss, and let X be the second; then $P(x\,|\,y)=P(x)$ states merely that the first toss has no effect on the second. A more complex example is a pot with six marbles in it, three red and three blue. Let Y be the drawing of a marble without replacement, with $y=r$ or b. Let X be the subsequent drawing of a second marble, with $x=r$ or b. Now, $P(y=r)=P(y=b)=1/2$: this merely states that the probability of first drawing a red marble is the same as the probability of first drawing a blue marble. But if $y=r$, there are two red marbles remaining in the pot and three blue. Thus $P(r\,|\,r)=2/5$ and $P(b\,|\,r)=3/5$. Likewise, if $y=b$, $P(r\,|\,b)=3/5$ and $P(b\,|\,b)=2/5$. $P(x\,|\,y)\neq P(x)$ in this case, since $P(r\,|\,r)\neq P(r\,|\,b)$. It follows that X and Y are not statistically independent.

A distribution $P(x)$ is characterised by its moments $\langle X^n\rangle\equiv\sum_x x^n P(x)$. This is especially convenient for distributions which are peaked, because often knowing the first few moments of the distribution is approximately as good as knowing the distribution itself. The zero-order moment is the normalisation condition $\langle X^0\rangle=1$. The first moment is the average or mean $\mu\equiv\langle X\rangle$; in distributions which are peaked, μ gives a rough measure of the position of the peak. The second moment $\langle X^2\rangle$ is combined with the first moment to define the variance $\sigma^2\equiv\langle X^2\rangle-\langle X\rangle^2$; in distributions which are peaked, σ gives a rough measure of the width of the peak. The Gaussian distribution is very simple, in the sense that all moments higher than the second are functions of μ and σ.

To solve the permeability problem exactly, we need to know the permeability everywhere in the medium. What we actually know is the permeability at only a few sites, and we must guess the remainder. There are a great many guesses that agree with the data in our

possession, and some guesses are physically more likely than others. We are thus naturally led to treat the permeability as a random variable. The ensemble here is the set of all possible realisations of the permeability field, each element $\kappa(\mathbf{r})$ of this set being correct with probability $P(\kappa(\mathbf{r}))$. Typically, our direct knowledge of the velocity fluctuations in the tracer problem is even more sketchy. Even knowing the permeability at some point, we do not know the velocity, since we do not know the corresponding pressure fluctuation. Even more so than for the permeability, we are led to treat the velocity as a random variable.

The "average" of some quantity F usually refers to an average over elements of the ensemble, $\langle F\rangle \equiv \sum_{\kappa(\mathbf{r})} FP(\kappa(\mathbf{r}))$. The ensemble average can be a useful tool for classifying the system. Consider the second moment of the fluctuations $\langle\kappa(\mathbf{r}_1)\kappa(\mathbf{r}_2)\rangle$. If this quantity is a function of the difference $\mathbf{r}_1-\mathbf{r}_2$ alone, then the fluctuations are homogeneous, meaning that they have no preferred point in space. Though we will not employ time-dependent fluctuations in this dissertation, such fluctuations $f(t)$ are homogeneous if $\langle f(t_1)f(t_2)\rangle$ is a function of t_1-t_2 alone, meaning that the fluctuations have no preferred point in time. If $\langle\kappa(\mathbf{r}_1)\kappa(\mathbf{r}_2)\rangle$ is a function of the distance $|\mathbf{r}_1-\mathbf{r}_2|$ alone, then the fluctuations are isotropic, meaning that they have no preferred direction in space.

In addition to an ensemble average, we can average F over a particular volume V' in the medium $\langle F\rangle_{V'} \equiv \frac{1}{V'}\int_{V'} d\mathbf{r}F$, or, if F is time-dependent, we can average F over a period of time T, $\langle F\rangle_T \equiv \frac{1}{T}\int_0^T dtF$. Space and time averages are of some importance, because a given fluid flows not through an ensemble, but through a particular porous medium. This presents something of a difficulty, since ensemble averages are what we can compute theoretically, while space and time averages are what we obtain by experiment. The difficulty arises because our ultimate aim is usually to predict from theory the result of experiment. To resolve matters, we

often invoke the ergodic hypothesis, first advanced by Boltzmann (1887), which states that for large enough volumes or long enough time intervals, the space and time averages are the same as the ensemble average (Huang (1963)). A quantity for which the ergodic hypothesis holds is said to be self-averaging (le Doussal and Machta (1989)), in the sense that for large enough volumes or long enough time intervals the space or time average of that quantity is independent of the configuration. Self-averaging is not understood in this sense by everybody. For many, self-averaging is the convergence of finite-sample averages to the ensemble average as the size of the sample increases. This is not so different from what we have here, if we suppose that the configuration-independent limit of the first formulation is in fact the ensemble average. On the other hand, Sposito et al. (1986) point out for the tracer problem that such a supposition requires justification.

The central limit theorem (CLT) says this of the sum of n random variables: if the variables are statistically independent, then the distribution of the sum is Gaussian, and the variance of the sum is proportional to n, in the limit that n becomes indefinitely large. The usefulness of this theorem can be seen by considering the random variables to be n displacements of a tracer particle, each over time period Δt. The sum of the n displacements is just the total displacement after time $n\Delta t \equiv t$. The CLT states that if each displacement is independent of the others, then the distribution of the total displacement is Gaussian, with a variance proportional to t, or in other words, the tracer diffuses like a Brownian particle. If by (say) calculation of the moments we find that the distribution is not Gaussian, or that the variance is not proportional to t, the CLT allows us to conclude that the displacements are not mutually independent.

Van Kampen (1981) makes an excellent observation concerning the use of statistical methods in physics. We are led to introduce statistical methods because of some lack of information on our part. Perhaps we do not know the permeability at every point in the medium,

and have to guess from a range of values for what we don't know, even though each point has a particular value in a given medium. Or consider the toss of a coin. We treat it as a random event, saying it will come up either heads or tails, with probability 1/2 each. From the point of view of Newtonian physics, the tossing of a coin is a perfectly deterministic event, governed by the appropriate equations; but, from the motion of the hand tossing the coin, to the motion of the air through which the coin travels, the thousand things that determine what will happen are unknown to us. But *why* we are led to treat certain processes as random, is a question very different from why we *can* treat certain processes as random. Nature did not have to be set up in such a way that statistical methods yield intelligible and useful results. The latter question is one dealing with the foundations of statistical physics, and is beyond the range of our discussion. We must be satisfied by observing that such methods work well for us.

2.2 Statistical models

Law (1944) was the first to analyse statistically the variation in permeability of a region of macroscopic extent. He deduced from core data that the horizontal fluctuations of permeability in a stratified bed are log-normally distributed. Although there are some differences on the matter (Jensen et al. (1987)), several subsequent studies generally agree with Law, while in some respects refining his model: for example, the vertical fluctuations in a stratified bed are also thought to be log-normally distributed, with a vertical correlation length shorter than the horizontal (Mackay et al. (1986), Sudicky (1986)). As a starting point for calculations, we shall assume that the medium is isotropic and that the permeability fluctuations are log-normally distributed. In other words, if $\kappa(\mathbf{r})$ is the permeability, with κ_0 its most probable value, then

$$f(\mathbf{r}) \equiv \ln\left[\frac{\kappa(\mathbf{r})}{\kappa_0}\right] \tag{2.2.1}$$

is a Gaussian random variable of mean zero, the correlation function of which in Fourier space is

$$\langle f(\mathbf{q}_1)f(\mathbf{q}_2)\rangle=(2\pi)^3\delta(\mathbf{q}_1+\mathbf{q}_2)\rho(q_1^2) \tag{2.2.2}$$

We cannot rely on direct experimental measurement for our model of the velocity field, because there is little information of that kind available. (The better part of that which is available can be found in Mackay et al. (1986) and Freyberg (1986)). Instead, we will obtain velocity as a function of permeability, using the condition of incompressibility to eliminate the pressure from Darcy's law. Expanding velocity, permeability, and pressure in powers of f,

$$\mathbf{u}(r)=\mathbf{u}_0+\mathbf{u}_1(\mathbf{r})+{}^1\!/_2\mathbf{u}_2(\mathbf{r})+\cdots \tag{2.2.3a}$$

$$\kappa(\mathbf{r})=\kappa_0+\kappa_0 f(\mathbf{r})+{}^1\!/_2\kappa_0 f^2(\mathbf{r})+\cdots \tag{2.2.3b}$$

$$p(\mathbf{r})=p_0(\mathbf{r})+p_1(\mathbf{r})+{}^1\!/_2p_2(\mathbf{r})+\cdots \tag{2.2.3c}$$

we obtain from Darcy's law one equation for each order in the expansion:

$$\mathbf{u}_0=-\frac{\kappa_0}{\mu}\nabla p_0(\mathbf{r}) \tag{2.2.4a}$$

$$\mathbf{u}_1(\mathbf{r})=-\frac{\kappa_0}{\mu}f(\mathbf{r})\nabla p_0(\mathbf{r})-\frac{\kappa_0}{\mu}\nabla p_1(\mathbf{r}) \tag{2.2.4b}$$

$$\mathbf{u}_2(\mathbf{r})=-\frac{\kappa_0}{\mu}\nabla p_2(\mathbf{r})-2\frac{\kappa_0}{\mu}f(\mathbf{r})\nabla p_1(\mathbf{r})-f^2(\mathbf{r})\frac{\kappa_0}{\mu}\nabla p_0(\mathbf{r}) \tag{2.2.4c}$$

and so on. The pressure can be eliminated order by order, if we suppose that the flow is incompressible at each order in the expansion. This is most easily done in Fourier space. Consider for example the first order term of Eq. (2.2.4b). Defining

$$g(\mathbf{r})\equiv\int\frac{d\mathbf{q}}{(2\pi)^3}e^{i\mathbf{q}\cdot\mathbf{r}}g(\mathbf{q})$$

with $\mathbf{r}$ a position variable and $\mathbf{q}$ a momentum variable, Eqs. (2.2.4a) and (2.2.4b) can be combined to give

$$\mathbf{u}_1(\mathbf{q})=\mathbf{u}_0 f(\mathbf{q})-\frac{\kappa_0}{\mu}i\mathbf{q}p_1(\mathbf{q}) \tag{2.2.5}$$

In Fourier space, the incompressibility condition at each order is $\mathbf{q}\cdot\mathbf{u}_i(\mathbf{q})=0$, so that

$$\mathbf{u}_0\cdot\mathbf{q}f(\mathbf{q})-\frac{\kappa_0}{\mu}iq^2p_1(\mathbf{q})=0 \tag{2.2.6}$$

This can be substituted back into (2.2.5) to get

$$\mathbf{u}_1(\mathbf{q})=\mathbf{u}_0f(\mathbf{q})-\mathbf{q}\frac{\mathbf{u}_0\cdot\mathbf{q}}{q^2}f(\mathbf{q}) \tag{2.2.7}$$

Although the higher orders become more calculationally involved, the basic procedure is the same. Once the pressure is eliminated from the velocity at each order, the velocity terms such as (2.2.7) can be substituted back into (2.2.3a) and simplified to give

$$\mathbf{u}(\mathbf{r})=\mathbf{u}_0+\int\frac{d\mathbf{q}}{(2\pi)^3}e^{i\mathbf{q}\cdot\mathbf{r}}\mathbf{u}_0\cdot[\mathbf{I}f(\mathbf{q})+\cdots]\cdot(\mathbf{I}-\hat{\mathbf{q}}\hat{\mathbf{q}}) \tag{2.2.8}$$

It follows that the correlation function in Fourier space is

$$<u_{1i}(\mathbf{q}_1)u_{1j}(\mathbf{q}_2)>=(2\pi)^3\delta(\mathbf{q}_1+\mathbf{q}_2)\rho(q_1{}^2)[\mathbf{u}_0\cdot(\mathbf{I}-\hat{\mathbf{q}}_1\hat{\mathbf{q}}_1)]_i[(\mathbf{I}-\hat{\mathbf{q}}_1\hat{\mathbf{q}}_1)\cdot\mathbf{u}_0]_j \tag{2.2.9}$$

plus terms of higher order in $\rho(q^2)$ (for a similar derivation see Gelhar and Axness (1983)).

$$<u_{1i}(\mathbf{q}_1)u_{1j}(\mathbf{q}_2)>=(2\pi)^3\delta(\mathbf{q}_1+\mathbf{q}_2)\rho(q_1{}^2)[\mathbf{u}_0\cdot(\mathbf{I}-\hat{\mathbf{q}}_1\hat{\mathbf{q}}_1)]_i[(\mathbf{I}-\hat{\mathbf{q}}_1\hat{\mathbf{q}}_1)\cdot\mathbf{u}_0]_j \tag{2.2.9}$$

plus terms of higher order in $\rho(q^2)$ (for a similar derivation see Gelhar and Axness (1983)).

general form for the velocity fluctuation. The tensor $\mathbf{I}-\hat{\mathbf{q}}\hat{\mathbf{q}}$ ensures that the fluctuation is incompressible, and $\mathbf{u}_0$ appears because the problem's only preferred direction is that of bulk flow. The tensor in the square brackets determines the statistical properties of the fluctuation. The form of this tensor could be determined theoretically, for example, by expanding Darcy's law as we have done here, or by assuming Gaussian fluctuations, i.e., keeping only the first term in (2.2.8). Its form could also be measured experimentally, at least in principle. While an expansion of Darcy's law implicitly assumes that the fluctuations are small, neither Gaussian fluctuations nor experiment are limited in this way. In the calculations which follow, we will assume that the velocity fluctuations are Gaussian, because doing so gives us more tractable equations, and because of a lack of experimental data saying we cannot.

For the first passage problem, the medium is perfectly stratified; with no loss of generality, we can take the layering to be parallel to $\hat{\mathbf{x}}$. If we apply a pressure gradient parallel to the

layering, then the velocity $\mathbf{u}(\mathbf{r})$ is parallel to $\hat{\mathbf{x}}$ and a random function of y alone, $\mathbf{u}(\mathbf{r})=u(y)\hat{\mathbf{x}}$, which follows from Darcy's law (Scheidegger (1974)). We assume that the velocity fluctuations can be characterised as Gaussian white noise, with the statistics of $u(y)$ completely determined by $<u(y)>=0$ and $<u(y)u(y')>=\rho(|y-y'|)=\sigma^2\delta(y-y')$.

Chapter 3

Review of the literature

3.1 Obtaining mesoscopic transport laws

Low-velocity steady state flow of a single liquid through a porous medium was first studied experimentally by Darcy (1856). Although the Euler equations were well known at this time, Darcy knew that solving them would be a hopeless task. He chose instead to deduce an empirical law directly from experimental data. The apparatus is roughly as follows. A homogeneous filter bed of height h is bounded by two horizontal planes, and an incompressible liquid flows slowly through it. Open manometer tubes are attached to the upper and lower boundaries of the filter bed. During flow, liquid will rise to heights h_2 and h_1 respectively in the manometer tubes. By varying the quantities involved, one can deduce

$$Q=-KA(h_2-h_1)/h, \tag{3.1.1}$$

where Q is the total volume of liquid percolating in unit time, A is the cross-sectional area of the bed, and K is some constant depending on the properties of both the fluid and the filter bed. This, properly speaking, is Darcy's law. Eq. (3.1.1) can be restated in terms of the pressure p and the density ρ of the liquid. Suppose the upper and lower boundaries of the filter bed are at z_2 and z_1 respectively, with $z_2-z_1=h$. Then the pressure at the upper boundary is $p_2=\rho g(h_2-z_2)$, and the pressure at the lower boundary is $p_1=\rho g(h_1-z_1)$. From these,

$$Q=-\frac{K'A}{h}(p_2-p_1+\rho gh). \tag{3.1.2}$$

To separate the effects of the fluid from those of the medium, Nutting (1930) and Wyckoff et al. (1934) proposed

$$K'=\frac{\kappa}{\mu} \tag{3.1.3}$$

where μ is the viscosity of the fluid and κ is a property of the medium alone. Hubbert (1940) gives statistical and physical arguments as to why K' can be decomposed in this way. This κ we call the permeability. In natural formations, the permeability is often found to be anisotropic, which is to say that if a cube of material is cut out of a porous medium, and the permeability across opposite faces of the cube is measured, then the three different pairs of faces will give differing values. This leads to the possibility that the velocity of fluid in the medium will not always be in the same direction as the pressure drop.

Darcy's law can be generalised to a differential form by letting $h\rightarrow 0$ (Hubbert (1940))

$$\mathbf{q}\equiv\frac{\mathbf{Q}}{A}=-\frac{\kappa}{\mu}\cdot\nabla p \tag{3.1.4}$$

where $\mathbf{q}$ is the specific discharge, p has been redefined so as to swallow up the gravitational component, and κ is a tensor. Often, the velocity in Darcy's law is represented by $\mathbf{u}$. This can lead to some confusion, since $\mathbf{u}$ is commonly used in the engineering literature to represent the pore velocity $\mathbf{u}\equiv\frac{\mathbf{q}}{n}$, where n is the porosity. It should not be a problem as long as we keep in mind that the velocity in Darcy's law is the specific discharge, or filtration velocity. Our final differential anisotropic version of Darcy's law,

$$\mathbf{u}(\mathbf{r})=-\frac{\kappa(\mathbf{r})}{\mu}\cdot\nabla p(\mathbf{r}) \tag{3.1.5}$$

is not the only version possible that would duplicate the results of Eq. (3.1.1); but the competing version, which would bring the $\kappa(\mathbf{r})$ inside the gradient, gives the wrong physics (Hubbert (1940)).

The dispersion of a passive tracer in a fluid is time dependent, and so can be much more involved than the permeability problem. For this reason, theoretical considerations played a much more prominent role in the early study of the tracer problem. Fick (1855), in his study of molecular transport by a fluid, established by simple statistical arguments that the flux J of molecules across a planar surface is proportional to the negative gradient of the molecular concentration c,

$$J=-D\frac{\partial c}{\partial x} \tag{3.1.6}$$

where D is some constant. Eq. (3.1.6) is called Fick's first law. When it is combined with an equation of continuity

$$\frac{\partial c}{\partial t}=-\frac{\partial J}{\partial x} \tag{3.1.7}$$

to account for cases of time-varying flux, it yields Fick's second law

$$\frac{\partial c}{\partial t}=D\frac{\partial^2 c}{\partial x^2} \tag{3.1.8}$$

This is merely the standard diffusion equation for the concentration, which had been widely used before Fick's time in the study of heat transport. It can be shown that a group of particles initially concentrated at one spot, whose concentration obeys this law, will spread in such a way that the mean square displacement (equal in this case to the second moment of x) increases in direct proportion to the first power of time. Similar equations have been used to describe Brownian movement. Brown (1828) observed that when one suspends in a liquid particles which are large and heavy in relation to the liquid molecules, e.g., pollen in water, the particles will move about in an irregular manner. If the particles are initially localised in the liquid, then they will spread through the liquid over time. Einstein (1905, 1906) examined an idealised system wherein masses are randomly struck by many relatively very small projectiles. Although Einstein did not claim to prove that his idealised system gave the microscopic physics which cause Brownian movement, he did note the similarities between his system on

the one hand, and both Brownian movement and solute transport on the other. Starting from the concept of osmotic pressure, Einstein derived a diffusion equation for the solute concentration, and formulas for the diffusion constant and molecular dimensions in terms of large-scale quantities. Smoluchowski (1906) obtained Einstein's results without using the concept of osmotic pressure, by using an approach relying more closely on statistical and molecular concepts. It is now agreed that Brownian movement is caused by random collisions between the large particles and the much smaller liquid molecules. Similar transport laws are quite common in nature, and have been recognised in many other physical systems. The reason follows from the CLT. No matter what the distribution of the fluctuations is in a system, as long as the fluctuations can be considered independent, the limiting distribution of their sum will be Gaussian.

Einstein derived the diffusion equation by assuming that the time interval between consecutive observations of position was long enough so that what happened in a given time interval was independent of what happened in the prevous time interval. Rayleigh (1891) had earlier examined the same sort of system, but on a time scale fine enough so that velocity no longer appears to vary instantaneously in a random manner. For the distribution f of velocities u among the large particles, he obtained

$$\frac{\partial f}{\partial t}=\gamma\frac{\partial}{\partial u}(uf)+\frac{A}{2}\frac{\partial^2 f}{\partial u^2} \tag{3.1.9}$$

where γu represents the drag force due to the viscosity of the liquid, and A is a measure of the strength of the force exerted by molecular collisions. In the equilibrium state, for which f is independent of t, it can be shown (van Kampen (1981)) that the mean square displacement is given by

$$<x^2(t)>\sim\gamma t+e^{-\gamma t}-1 \tag{3.1.10}$$

This is one example of diffusion for which the mean square displacement is not directly pro-

portional to t. Richardson (1926) noted, in the case of dispersion of a passive tracer in the atmosphere, that the diffusion "constant" of Fick's law increases as the length or time scale of the measurement is increased. The dependence of the diffusion parameter on characteristic length scales is also familiar in the dispersion of a passive tracer in flow through a porous medium: as Dagan (1987) notes, this phenomenon shows that Fick's law, the constant-parameter CDE, is not suitable for describing transport in large natural formations. Both Richardson and Dagan deal with cases for which the mean square displacement increases faster than t, which is obscured by the fact that the standard definition of diffusivity D

$$D \sim \frac{<x^2>}{t} \tag{3.1.11}$$

implicitly assumes normal diffusion, i.e., that D is constant. If one insists on applying (3.1.11) to processes for which $<x^2>$ increases faster than t, one will see that D increases as the volume over which the average is taken increases, or, equivalently, as the time of travel increases. This phenomenon has been called "megadispersion", and has received much attention (cf. Dagan (1987) and references therein). Bouchaud and Georges (1990) reviewed the literature on all manner of anomalous (non-Brownian) diffusion. They examined subdiffusion, for which $<x^2>$ increases more slowly than t, as well as superdiffusion, for which $<x^2>$ increases more quickly than t. They note that the usual laws of Brownian motion result from the CLT, and that the usual form of the CLT must fail whenever anomalous diffusion is found. This failure "can be due to the presence of either 'broad distributions' (with diverging first or second moments), or of 'long range' correlations. These statistical mechanisms can be present a priori in the problem at hand for some underlying physical reason (e.g. long range correlations in the velocity field of turbulent flow) or, most interestingly, they can be induced by the dynamics itself" (Bouchaud and Georges (1990)). One example of the latter, which has received much study, is the stratified porous medium with flow parallel to the layers, which is associated with Matheron and de Marsily (1980). Supposing that the velocity is a random

function of vertical position, they found that for large times $\langle x^2 \rangle$ is proportional to $t^{3/2}$. Gelhar et al. (1979) would have found the same thing, but instead of looking at $\langle x^2(t) \rangle$ for large t, they looked at $\langle x^2(t) \rangle / t$ for infinite t, assuming the latter would be constant (cf. the discussion of this matter in Dagan (1987)). They found that $\lim_{t \to +\infty} \langle x^2(t) \rangle / t$ will not be constant unless severe restrictions are imposed on the velocity correlation. Recent studies (Redner (1989), Bouchaud et al. (1990), Bouchaud and Georges (1990)) have shown that the interplay between convection and diffusion induces long-range time correlations in the velocity fluctuations. Thus, while more and more of the velocity distribution is sampled as time increases, the distribution is never sampled completely, so that the sampled velocity values are not independent and the CLT does not hold.

3.2 Deriving mesoscopic transport laws from microscopic laws

Although the mesoscopic equations governing the problems studied here were developed from mesoscopic experiments and theories, they can also be derived by averaging the microscopic equations. Since our problems are closely related to many similar problems involving transport in heterogeneous media (Batchelor (1974)), techniques developed elsewhere can often be applied here. For example, Maxwell (1873) developed a method for calculating the effective conductivity of a disordered dielectrical system. The technique is known generally as an "effective medium" approximation; attention is fixed on one element of disorder, while the detailed interactions of all other elements of disorder with it are approximated by a homogeneous effective interaction. For the permeability problem, Brinkman (1947) used a method similar to Maxwell's method. Assuming the medium to be a fixed bed of spheres, Brinkman modelled this medium as a single sphere embedded in a porous mass. He next calculated the drag exerted by an isotropic medium on the fluid. The drag force can be calculated on a

mesoscopic scale by using Darcy's law

$$\nabla\phi=-\frac{\mu}{\kappa}\mathbf{u} \tag{3.2.1}$$

where $\mathbf{u}$ is the velocity, $\nabla\phi$ is the pressure gradient, μ is the viscosity, and κ is the permeability. On the microscopic level, flow is governed by the equillibrium Navier-Stokes equations

$$\mathbf{u}\cdot\nabla\mathbf{u}=-\frac{1}{\rho}\nabla\phi+\nu\nabla^2\mathbf{u} \tag{3.2.2}$$

where ρ is the density, ν is the kinematic viscosity, and $\rho\nu=\mu$. One can calculate the drag on a sphere using Eq. (3.2.2) in the low Reynolds number limit

$$\nabla\phi=\mu\nabla^2\mathbf{u}, \tag{3.2.3}$$

but this treatment is restricted to very low particle volume fractions. As a reasonable interpolation between Darcy's law and the Navier-Stokes equations, Brinkman proposed

$$\nabla\phi=\mu'\nabla^2\mathbf{u}-\frac{\mu}{\kappa}\mathbf{u} \tag{3.2.4}$$

where μ' is a "renormalised viscosity", not necessarily equal to μ. From this, one can calculate the drag force on a single sphere, with some confidence that the result will be better for smaller values of the porosity. The self-consistency requirement, that drag on a single sphere multiplied by the number density be equal to the mesoscopic drag per unit volume, will yield a formula for κ. An unfortunate feature of Brinkman's calculation is that the effective permeability disappears for a porosity of 1/3. Neale and Nader (1974) addressed this problem by assuming the test sphere to be surrounded by a spherical shell of pure fluid, with the porous medium extending outward from the shell. Wilkinson (1985), on the other hand, addressed the problem by building the medium iteratively, adding at each stage an infinitessimal volume fraction of grains, and treating the previously existing material as a homogeneous host medium.

One can also model the medium at microscopic scales by random networks. This

approach is complementary to the fixed-bed approach, since a random network is a better representation of a consolidated porous medium than is a fixed bed of spheres. Fatt (1956) modelled porous media as random networks both of tubes and of resistors, using analytical techniques for the tube model and experimental techniques (actual networks of resistors) for the resistor model. The two situations examined by Fatt are mathematically quite similar. Koplik (1981) used an effective medium approximation to study regular networks of random resistors. He used numerical methods to compute the effective-medium and directly-averaged conductances, then compared the two using a mixture of analytical and numerical methods.

Saffman (1959) assumed that a consolidated medium on microscopic scales could be regarded as an assembly of randomly oriented straight pores, and that the path of a tracer particle consisted of a sequence of statistically independent steps whose direction and duration would vary randomly. He first applied this scheme to a calculation of effective permeability: knowing the dependence of velocity in a capillary tube on the pressure drop across it, he averaged over pressure fluctuations and tube orientations. His result showed mean velocity directly proportional to mean pressure gradient, as Darcy's law would predict, but left the constant of proportionality undetermined. For the tracer problem, assuming that the microscopic Peclet number P is large, and in the limit of long times, he found the effective longitudinal dispersivity proportional to $P\ln P$, and effective lateral dispersivity proportional to P. If the effective dispersivity were due solely to twisting of streamlines, we would expect both lateral and longitudinal effective dispersivities to be proportional to P; the enhanced longitudinal dispersivity was due to zero velocity of the fluid at the capillary walls. In Saffman's calculations the fluctuations are uncorrelated, so that there is no equation of continuity. De Arcangelis et al. (1986) improved the model by imposing boundary conditions on the flow in each tube and at the nodes. They then recovered the Peclet number dependence of Saffman's results using numerical methods. Koplik et al. (1988) applied the improved random tube

model to a poorly connected porous medium. They used both analytical and numerical techniques to obtain exact moments for the distribution of tracer transit times. Koch and Brady (1985) regarded the medium as a dilute bed of fixed spheres. Using perturbation theory and analytical methods, they obtained effective dispersion constants for a wide range of Peclet numbers, and for porosities close to 1; in the limit of high P, they also recovered the Peclet number dependence of Saffman's results.

3.3 Perturbation theory

The most common way of obtaining an effective averaged description of fluid problems at macroscopic scales is through a perturbation expansion. After expanding in powers of the fluctuations, which are supposed to be small in some sense, one averages over the fluctuations. This averaging takes place over fluctuations of all length scales at each level in the expansion. Although there is a multitude of ways to formulate a perturbation theory for fluid flow problems, corresponding to what gets expanded and how, two in particular have been of some importance.

The first formulation was applied by Bakr et al. (1978) and by Gutjahr et al. (1978) to the simpler permeability problem. Their work was motivated by the fact that previous attempts to find effective permeabilities for porous media had neglected the structure of the medium. A representative example of such an attempt would be that of Warren and Price (1961), who used Monte Carlo simulations to compute the effective permeability. They chose the permeability of each block of material according to a log-normal distribution, but the permeability at adjacent sites was uncorrelated. Bakr and co-workers improved on previous treatments by explicitly characterising the permeability distribution in terms of its covariance. Their calculation began with the local transport equation, combining Darcy's law and the incompressibility condition. They expressed each quantity in the equation (the permeability

and the pressure) as a mean plus a fluctuating part. Then, after taking the mean of the local equation, they subtracted the mean equation from the local equation and dropped terms of higher order than one in the fluctuations. This left them with an easily solvable equation for the pressure fluctuation in terms of the permeability fluctuation, which was assumed known. With all fluctuating quantities known in terms of the permeability fluctuation, computing averages is an easy matter. Gelhar et al. (1979) applied a similar treatment to perfectly stratified porous media. His approach was similar to Taylor's discussion of dispersion in tubes (Taylor (1953)), in that the mean concentration was assumed to be independent of transverse position, so that the quantity of interest was the effective longitudinal dispersivity. Gelhar and Axness (1983) applied this treatment to a non-stratified porous medium: by neglecting fluctuations in dispersivity, they were able to obtain effective dispersivities both parallel to and transverse to bulk flow. This technique is quite useful as far as it goes, but it only goes to first order in perturbation theory, and it cannot be extended to higher orders.

A more general technique was employed by King (1987), and by Drummond and Horgan (1987). Instead of the more commonly investigated differential equation in real space, King considered an integral equation in Fourier space. The iterative solution to this integral equation is at the same time an expansion of the Green function for the equation, in powers of the fluctuations. King assumed that permeability has a log-normal distribution, although he was obliged to approximate this by a Gaussian distribution to get a clean calculation, and he calculated only first-order terms. Drummond and Horgan investigated a wider range of distributions, and utilised self-consistent perturbation theory to extend King's technique to higher orders. Although both explicitly dealt with the permeability problem, their techniques are easily extended to treat the passive tracer problem as well (see Appendix).

Although the perturbation approach has proven to be highly successful, it has its limitations. One such is that the calculations necessary become very difficult at relatively low

orders in the expansion, and still more difficult at higher orders. In Fourier space, each nth order term involves integrations, over n different d-dimensional momenta, of n velocity correlation functions multiplied by $2n-1$ Green functions. Such calculations can be done, but it is open to question whether or not the results obtained would be worth the effort put into obtaining them. A second limitation of the perturbation approach is that it can properly be applied only to systems with weak fluctuations. Consider as an example the CDE of Eq. (1.2.5), and suppose the velocity $\mathbf{u}(\mathbf{r})$ to be the sum of a constant term $\mathbf{u}_0$, and a fluctuation $\mathbf{u}_1(\mathbf{r})$ of mean zero. Suppose further that the correlation of the velocity fluctuations is given in Fourier space by

$$<u_{1i}(\mathbf{k})u_{1j}(\mathbf{k}')>=Fg(kL)\left[\delta_{ij}-\frac{k_ik_j}{k^2}\right](2\pi)^d\delta(\mathbf{k}+\mathbf{k}') \tag{3.3.1}$$

Here, L is a length characteristic of the velocity fluctuations; $g(kL)$ is some function, equal to 1 for kL=0, that approaches 0 as kL becomes large, and F is a constant which measures the strength of the fluctuations. (Aronovitz and Nelson (1984) use this velocity correlation, with $g(kL)$=1, in their study of anomalous diffusion.) It might naively appear that the expansion parameter is F, but the expansion parameter should be dimensionless, and F has dimensions of velocity squared times volume. Measuring time in units of L^2/D, distance in units of L, and the velocity fluctuations in units of $(F/L^3)^{1/2}$, one can see that the true expansion parameter is $(F/L^3)(L^2/D^2)$. If this latter quantity is too large, the series will not converge, and the perturbation approach cannot be used.

3.4 Renormalisation group

The renormalisation group method appropriate for fluid problems was developed by Ma and Mazenko (1975) to investigate the critical dynamics of ferromagnets. Their approach differed from the earlier approach exemplified by Wilson and Kogut (1974), in that Wilson and Kogut applied RG methods to static critical phenomena, while Ma and Mazenko extended

RG methods to dynamic critical phenomena. The basic idea is quite simple. One begins by assuming that the high momentum (short wavelength) fluctuations do not affect the dynamics of the problem. Effectively, this coarse-grains space, ignoring all fluctuations with wavelengths below a certain minimum. Next, one averages over fluctuations with characteristic length scales just greater than the graining of space. Finally, one rescales space to preserve the original graining, and other quantities to preserve as far as possible the original form of the equation of motion. The result resembles the original equation, but with renormalised parameters. This procedure will usually produce new interactions as well as renormalised parameters, but such new interactions can often be shown to be irrelevant to the large-distance, long-time behaviour. This process of averaging and rescaling can be iterated until one has averaged over all fluctuations.

The dynamic approach was used by Forster, Nelson, and Stephen (1977) to study the large-distance, long-time behaviour of velocity correlations generated by the incompressible Navier-Stokes equations with random forcing. This was an early application of RG techniques to non-critical problems. They went on to consider dispersion of a passive scalar by the fluctuating velocity obtained from the Navier-Stokes portion of their work. Since the velocity therefore fluctuated both in space and in time, their problem was more closely related to dispersion in turbulent flow, than to dispersion in flow through porous media. By obtaining their velocity in this way, they limited their discussion to cases for which the mean velocity was zero. This limitation, on the other hand, allowed them to assume that the renormalised dispersivity would be isotropic. Aronovitz and Nelson (1984) applied similar techniques to study anomalous diffusion in the tracer problem. They assumed a velocity with a non-zero mean $\mathbf{u}_0$, but were interested primarily in the limit $u_0 \to 0$, as it is in this limit that the divergences appear, which they need RG techniques to sort out. An interesting peculiarity of their correlation function for the transverse velocity fluctuations (3.3.1) is that the fluctuations are

incompressible only on average: $\langle \mathbf{k}\cdot\mathbf{u}_1(\mathbf{k})\mathbf{u}_1(\mathbf{k}')\rangle=0$, as can be seen from (3.3.1); but $\mathbf{k}\cdot\mathbf{u}_1(\mathbf{k})=0$ is not necessarily so. One must use a correlation function such as (3.3.1) if the problem has no preferred direction, which would be the case for $u_0=0$. In this model, the fluctuations are independent of the mean velocity, so that the former remain when the latter is equal to zero; but the authors are unclear as to when one might find a flow field fixed in space and zero on average in a porous medium.

Renormalisation group methods are most useful when fluctuations over all length scales are important, which is to say, the correlation length of the fluctuations must diverge. These are situations for which anomalous behaviour is expected, since if all length scales are important, the tracer will never sample a statistically representative selection of the fluctuating values. It follows that we would not expect RG methods to be useful for the CDE in unbounded space with isotropic velocity fluctuations and a non-zero mean velocity. D_0/u_0 is the length scale below which convection is less important than diffusion in moving a tracer particle around the medium. As long as u_0 is non-zero, we are guaranteed some length scales over which convection dominates. This is important because convection is the physical mechanism by which the tracer fully samples the medium. Mathematically, a non-zero u_0 cuts off the low momentum integral divergences. If diffusion is the physical mechanism by which the tracer moves about, the fluctuations will not be fully sampled, as was demonstrated by Aronovitz and Nelson (1984). The Matheron-de Marsily (1980) problem of the CDE in a stratified unbounded medium with flow parallel to the layering does show induced long-time correlations for the velocity fluctuations, and so may seem well suited to this technique. In fact, RG methods will work here, but they will not be especially useful, as the appropriate superdiffusive power law can be obtained without them. Furthermore, RG methods will not be useful for the first passage time version of this problem, since the induced long-time velocity correlations are cut off by the tracer particle leaving the region of interest.

Chapter 4

Path-integral variational method

4.1 Path integrals

Let us suppose for a moment that both the velocity and the dispersion tensor of Eq. (1.2.4) are constant, $\mathbf{u}(\mathbf{r})\rightarrow\mathbf{u}_0$ and $\mathbf{D}(\mathbf{r})\rightarrow\mathbf{D}_0$. Then the Green function $G_0(\mathbf{r}-\mathbf{r}_0,t-t_0)$ for the resulting equation is defined by

$$\left[\frac{\partial}{\partial t}+\mathbf{u}_0\cdot\nabla-\nabla\cdot\mathbf{D}_0\cdot\nabla\right]G_0(\mathbf{r}-\mathbf{r}_0,t-t_0)=\delta(\mathbf{r}-\mathbf{r}_0)\delta(t-t_0) \tag{4.1.1}$$

and is no more than the probability that a tracer particle starting at $(\mathbf{r}_0,t_0)$ will end up at $(\mathbf{r},t)$. This probability is in turn the sum over all possible paths of the probability that the tracer particle will take a particular path from $(\mathbf{r}_0,t_0)$ to $(\mathbf{r},t)$. Equation (4.1.1) has the following path-integral solution (Wiener (1923), Feynman (1948), Feynman and Hibbs (1965), Drummond (1982)):

$$G_0(\mathbf{r}_N-\mathbf{r}_0,t_N-t_0)=\int_{\mathbf{r}(t_0)=\mathbf{r}_0}^{\mathbf{r}(t_N)=\mathbf{r}_N}D\mathbf{r}\exp\left\{-\frac{1}{4}\int_{t_0}^{t_N}d\tau\left[\frac{d\mathbf{r}}{d\tau}-\mathbf{u}_0\right]\cdot\frac{1}{\mathbf{D}_0}\cdot\left[\frac{d\mathbf{r}}{d\tau}-\mathbf{u}_0\right]\right\} \tag{4.1.2}$$

It is useful to see how (4.1.2) is obtained. Suppose we wish to know the probability that a tracer particle will follow a given path $\mathbf{r}(t)$ from $(\mathbf{r}_0,t_0)$ to $(\mathbf{r}_N,t_N)$. We divide the time inter-

val into N equal segments, of length $\Delta t \equiv (t_N - t_0)/N$, and approximate the path by $N+1$ points $(\mathbf{r}_k \equiv \mathbf{r}(t_k), t_k \equiv t_0 + k\Delta t)$, where $0 \le k \le N$. The probability $\rho(k-1,k)$ of going from $(\mathbf{r}_{k-1}, t_{k-1})$ to $(\mathbf{r}_k, t_k)$ can be obtained from (4.1.1):

$$\rho(k-1,k) = \frac{1}{[4\pi\Delta t]^{3/2}[det\mathbf{D}_0]^{1/2}} \times$$
$$\times \exp\left\{-\frac{\Delta t}{4}\left[\frac{\mathbf{r}_k - \mathbf{r}_{k-1}}{\Delta t} - \mathbf{u}_0\right] \cdot \frac{1}{\mathbf{D}_0} \cdot \left[\frac{\mathbf{r}_k - \mathbf{r}_{k-1}}{\Delta t} - \mathbf{u}_0\right]\right\} \tag{4.1.3}$$

and the probability for taking the entire path is $\prod_{k=1}^{N} \rho(k-1,k)$. To get the Green function, we integrate this over all intermediate positions:

$$G_0(\mathbf{r}_N - \mathbf{r}_0, t_N - t_0) = \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_{N-1} \frac{1}{(4\pi\Delta t)^{3N/2}[det\mathbf{D}_0]^{N/2}} \times$$
$$\times \exp\left\{-\frac{\Delta t}{4}\sum_{k=1}^{N}\left[\frac{\mathbf{r}_k - \mathbf{r}_{k-1}}{\Delta t} - \mathbf{u}_0\right] \cdot \frac{1}{\mathbf{D}_0} \cdot \left[\frac{\mathbf{r}_k - \mathbf{r}_{k-1}}{\Delta t} - \mathbf{u}_0\right]\right\} \tag{4.1.4}$$

This is the proper way to interpret (4.1.2). We can show that the Green function of Eq. (4.1.4) obeys (4.1.1) to first order in Δt, assuming only that the irregularity is relatively well behaved (cf. Feynman (1948)). For simplicity let us set $\mathbf{r}_0 \equiv 0$ and $t_0 \equiv 0$. Then $G_0(\mathbf{r}_{N+1}, t_{N+1})$ can clearly be written as

$$G_0(\mathbf{r}_{N+1}, t_{N+1}) = \int d\mathbf{r}_N \frac{1}{(4\pi\Delta t)^{3/2}(det\mathbf{D}_0)^{1/2}} \times$$
$$\times \exp\left\{-\frac{\Delta t}{4}\left[\frac{\mathbf{r}_{N+1} - \mathbf{r}_N}{\Delta t} - \mathbf{u}_0\right] \cdot \frac{1}{\mathbf{D}_0} \cdot \left[\frac{\mathbf{r}_{N+1} - \mathbf{r}_N}{\Delta t} - \mathbf{u}_0\right]\right\} G_0(\mathbf{r}_N, t_N) \tag{4.1.5}$$

Now we set $\mathbf{r}_{N+1} \equiv \mathbf{r}$, $\mathbf{r}_{N+1} - \mathbf{r}_N \equiv \mathbf{y}$, $t_N \equiv t$. With these, (4.1.5) can be rewritten

$$G_0(\mathbf{r}, t+\Delta t) = \int d\mathbf{y} \frac{1}{(4\pi\Delta t)^{3/2}(det\mathbf{D}_0)^{1/2}} \times$$
$$\times \exp\left\{-\frac{\Delta t}{4}\left[\frac{\mathbf{y}}{\Delta t} - \mathbf{u}_0\right] \cdot \frac{1}{\mathbf{D}_0} \cdot \left[\frac{\mathbf{y}}{\Delta t} - \mathbf{u}_0\right]\right\} G(\mathbf{r} - \mathbf{y}, t) \tag{4.1.6}$$

If the irregularity of the motion is relatively well behaved, then $\mathbf{y}$ will be small, and $G_0(\mathbf{r}-\mathbf{y}, t)$ can be expanded in a Taylor series around $\mathbf{y}=0$. Likewise $G_0(\mathbf{r}, t+\Delta t)$ can be expanded in a Taylor series around $\Delta t = 0$. Performing all necessary computations, (4.1.6) becomes

$$G_0(\mathbf{r},t)+\Delta t\frac{\partial}{\partial t}G_0(\mathbf{r},t)+O((\Delta t)^2)$$
$$=G_0(\mathbf{r},t)-\Delta t\mathbf{u}_0\cdot\nabla G_0(\mathbf{r},t)+\Delta t\nabla\cdot\mathbf{D}_0\cdot\nabla G_0(\mathbf{r},t)+O((\Delta t)^2) \tag{4.1.7}$$

from which it follows that the Green function of Eq. (4.1.4) obeys Eq. (4.1.1) to first order in Δt.

Things become a bit more complicated if we wish to allow for space-dependent velocities and dispersion tensors. The Green function for Eq. (1.2.4), $G(\mathbf{r},\mathbf{r}_0,t-t_0)$ is defined by

$$\left[\frac{\partial}{\partial t}+\mathbf{u}(\mathbf{r})\cdot\nabla-\nabla\cdot\mathbf{D}(\mathbf{r})\cdot\nabla\right]G(\mathbf{r},\mathbf{r}_0,t-t_0)=\delta(\mathbf{r}-\mathbf{r}_0)\delta(t-t_0) \tag{4.1.8}$$

We cannot simply go by analogy, and suppose the solution to be

$$G(\mathbf{r}_N,\mathbf{r}_0,t_N-t_0)=\int_{\mathbf{r}(t_0)=\mathbf{r}_0}^{\mathbf{r}(t_N)=\mathbf{r}_N}D\mathbf{r}\exp\left\{-\frac{1}{4}\int_{t_0}^{t_N}d\tau\left[\frac{d\mathbf{r}}{d\tau}-\mathbf{u}(\mathbf{r})\right]\cdot\frac{1}{\mathbf{D}(\mathbf{r})}\cdot\left[\frac{d\mathbf{r}}{d\tau}-\mathbf{u}(\mathbf{r})\right]\right\} \tag{4.1.9}$$

because using the method just above, (4.1.9) can be shown to obey

$$\frac{\partial}{\partial t}G(\mathbf{r},\mathbf{r}_0,t-t_0)+\mathbf{u}(\mathbf{r})\cdot\nabla G(\mathbf{r},\mathbf{r}_0,t-t_0)=D_i(\mathbf{r})\frac{\partial^2}{\partial {r_i}^2}G(\mathbf{r},\mathbf{r}_0,t-t_0) \tag{4.1.10}$$

to first order in Δt. (We assume that $\mathbf{D}(\mathbf{r})$ is a diagonal matrix.) But

$$\frac{\partial}{\partial r_i}\left[D_i(\mathbf{r})\frac{\partial G}{\partial r_i}\right]=\left[\frac{\partial}{\partial r_i}D_i(\mathbf{r})\right]\frac{\partial G}{\partial r_i}+D_i(\mathbf{r})\frac{\partial^2 G}{\partial {r_i}^2}\quad(no\ sum) \tag{4.1.11}$$

suggests that

$$G(\mathbf{r}_N,\mathbf{r}_0,t_N-t_0)=\int_{\mathbf{r}(t_0)=\mathbf{r}_0}^{\mathbf{r}(t_N)=\mathbf{r}_N}D\mathbf{r}\times$$
$$\times\exp\left\{-\frac{1}{4}\int_{t_0}^{t_N}d\tau\left[\frac{d\mathbf{r}}{d\tau}-\mathbf{u}(\mathbf{r})+\mathbf{v}(\mathbf{r})\right]\cdot\frac{1}{\mathbf{D}(\mathbf{r})}\cdot\left[\frac{d\mathbf{r}}{d\tau}-\mathbf{u}(\mathbf{r})+\mathbf{v}(\mathbf{r})\right]\right\}, \tag{4.1.12}$$

where

$$v_i(\mathbf{r})\equiv\frac{\partial}{\partial r_i}D_i(\mathbf{r})\quad(no\ sum), \tag{4.1.13}$$

will obey (4.1.8). We can show this to be so, using the method outlined above. The proper way to interpret (4.1.12) would then be

$$G(\mathbf{r}_N,\mathbf{r}_0,t_N-t_0)=\int d\mathbf{r}_1\cdots\int d\mathbf{r}_{N-1}\times$$
$$\times\frac{1}{(4\pi\Delta t)^{3/2}[det\mathbf{D}(\mathbf{r}_1)]^{1/2}}\cdots\frac{1}{(4\pi\Delta t)^{3/2}[det\mathbf{D}(\mathbf{r}_N)]^{1/2}}\times$$
$$\times\exp\left\{-\frac{\Delta t}{4}\sum_{k=1}^{N}\left[\frac{\mathbf{r}_k-\mathbf{r}_{k-1}}{\Delta t}-\mathbf{u}(\mathbf{r}_k)+\mathbf{v}(\mathbf{r}_k)\right]\cdot\frac{1}{\mathbf{D}(\mathbf{r}_k)}\cdot\left[\frac{\mathbf{r}_k-\mathbf{r}_{k-1}}{\Delta t}-\mathbf{u}(\mathbf{r}_k)+\mathbf{v}(\mathbf{r}_k)\right]\right\} \qquad (4.1.14)$$

We use $(\mathbf{r}_k-\mathbf{r}_{k-1})/\Delta t$ in Eq. (4.1.14) for the velocity of the particle as it moves from $\mathbf{r}_{k-1}$ to $\mathbf{r}_k$; although this is the natural and obvious choice to make, it is not the only possible choice. Other choices differ from ours by terms of order Δt, and change the observations which follow. For cases of varying $\mathbf{D}(\mathbf{r})$ and $\mathbf{u}(\mathbf{r})$, our selection of $\mathbf{D}(\mathbf{r}_k)$ and $\mathbf{u}(\mathbf{r}_k)$ for their values respectively as the particle moves from $\mathbf{r}_{k-1}$ to $\mathbf{r}_k$ is most convenient. With a minor change in the drift velocity, we obtain a path-integral expression which obeys the proper equation of motion. Other selections for $\mathbf{D}(\mathbf{r})$, such as $\mathbf{D}(\mathbf{r}_{k-1})$, $\mathbf{D}(\frac{1}{2}[\mathbf{r}_{k-1}+\mathbf{r}_k])$, or $\frac{1}{2}[\mathbf{D}(\mathbf{r}_k)+\mathbf{D}(\mathbf{r}_{k-1})]$, define path-integral expressions which do not obey the proper equation of motion, and which cannot be made to do so by a simple redefinition of the drift velocity. A similar observation can be made about other selections for $\mathbf{u}(\mathbf{r})$.

It is difficult to average over the parameter fluctuations as they appear in Eq. (4.1.14). However, since

$$\rho(k-1,k)=\frac{1}{(4\pi\Delta t)^{3/2}[det\mathbf{D}(\mathbf{r}_k)]^{1/2}}\times$$
$$\times\exp\left\{-\frac{\Delta t}{4}\left[\frac{\mathbf{r}_k-\mathbf{r}_{k-1}}{\Delta t}-\mathbf{u}(\mathbf{r}_k)+\mathbf{v}(\mathbf{r}_k)\right]\cdot\frac{1}{\mathbf{D}(\mathbf{r}_k)}\cdot\left[\frac{\mathbf{r}_k-\mathbf{r}_{k-1}}{\Delta t}-\mathbf{u}(\mathbf{r}_k)+\mathbf{v}(\mathbf{r}_k)\right]\right\} \qquad (4.1.15)$$

can be rewritten

$$\rho(k-1,k)=\int\frac{d\mathbf{p}_{k-1}}{(2\pi)^3}\times$$
$$\times\exp\left\{-\Delta t\left[\mathbf{p}_{k-1}\cdot\mathbf{D}(\mathbf{r}_k)\cdot\mathbf{p}_{k-1}-i\mathbf{p}_{k-1}\cdot\left[\frac{\mathbf{r}_k-\mathbf{r}_{k-1}}{\Delta t}-\mathbf{u}(\mathbf{r}_k)+\mathbf{v}(\mathbf{r}_k)\right]\right]\right\} \qquad (4.1.16)$$

the Green function is equally well represented by

$$G(\mathbf{r}_N,\mathbf{r}_0,t_N-t_0)=\int d\mathbf{r}_1\cdots\int d\mathbf{r}_{N-1}\int\frac{d\mathbf{p}_0}{(2\pi)^3}\cdots\int\frac{d\mathbf{p}_{N-1}}{(2\pi)^3}\times$$
$$\times\exp\left\{-\Delta t\sum_{k=1}^{N}\left[\mathbf{p}_{k-1}\cdot\mathbf{D}(\mathbf{r}_k)\cdot\mathbf{p}_{k-1}-i\mathbf{p}_{k-1}\cdot\left[\frac{\mathbf{r}_k-\mathbf{r}_{k-1}}{\Delta t}-\mathbf{u}(\mathbf{r}_k)+\mathbf{v}(\mathbf{r}_k)\right]\right]\right\} \tag{4.1.17}$$

which is easier to work with. This is sometimes called the momentum representation of (4.1.14). The more elegant version of (4.1.17) is

$$G(\mathbf{r}_N,\mathbf{r}_0,t_N-t_0)=\int_{\mathbf{r}(t_0)=\mathbf{r}_0}^{\mathbf{r}(t_N)=\mathbf{r}_N}D\mathbf{r}\int D\mathbf{p}\times$$
$$\times\exp\left\{-\int_{t_0}^{t_N}d\tau\left[\mathbf{p}(\tau)\cdot\mathbf{D}(\mathbf{r})\cdot\mathbf{p}(\tau)-i\mathbf{p}(\tau)\cdot\left[\frac{d\mathbf{r}}{d\tau}-\mathbf{u}(\mathbf{r})+\mathbf{v}(\mathbf{r})\right]\right]\right\} \tag{4.1.18}$$

4.2 Path-integral problem formulation

We first give the tracer problem a path-integral formulation. We will assume that the dispersion tensor is a constant $\mathbf{D}_0$ while the velocity is allowed to fluctuate. One good reason for doing this, is that convection dominates diffusion in the limit of long times, since convective displacement is proportional to t, while diffusive root-mean-square displacement is proportional to $t^{1/2}$. Another good reason (perhaps a variant of the first) arises from the fact that the velocity fluctuations are multiplied by ∇ in the equation of motion, while dispersion fluctuations are multiplied by ∇^2. When averaging over two velocity fluctuations, one expects a term in the averaged equation of motion proportional to ∇^2, which changes the second moment of the distribution. But averaging over a velocity fluctuation and a dispersion fluctuation, one expects a term proportional to ∇^3; and, averaging over two dispersion fluctuations, one expects a term proportional to ∇^4. Thus we expect that dispersion fluctuations will not influence the effective dispersion, but only the higher moments of the distribution.

The velocity is assumed to vary as $\mathbf{u}(\mathbf{r})=\mathbf{u}_0+\mathbf{u}_1(\mathbf{r})$, with $\mathbf{u}_1(\mathbf{r})$ a Gaussian random vari-

able of mean zero, exactly as one would get by dropping the higher order fluctuating terms in (2.2.8) and (2.2.9). We average the $G(\mathbf{r}_N,\mathbf{r}_0,t_N-t_0)$ of (4.1.18) over fluctuations in velocity to obtain

$$\begin{aligned}
<G(\mathbf{r}_N,\mathbf{r}_0,t_N-t_0)> &= \int D\mathbf{r}\int D\mathbf{p}\int D\mathbf{u}_1 \exp\left\{-\frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\,\mathbf{u}_1(\mathbf{r})\cdot\mathbf{A}^{-1}(\mathbf{r}-\mathbf{r}')\cdot\mathbf{u}_1(\mathbf{r}')\right\}\times \\
&\times\exp\left\{-\int d\tau\left[\mathbf{p}(\tau)\cdot\mathbf{D}_0\cdot\mathbf{p}(\tau)-i\mathbf{p}(\tau)\cdot\left[\frac{d\mathbf{r}}{d\tau}-\mathbf{u}_0-\mathbf{u}_1(\mathbf{r})\right]\right]\right\} \\
&= \int D\mathbf{r}\int D\mathbf{p}\exp\left\{-\int d\tau\left[\mathbf{p}(\tau)\cdot\mathbf{D}_0\cdot\mathbf{p}(\tau)-i\mathbf{p}(\tau)\cdot\left[\frac{d\mathbf{r}}{d\tau}-\mathbf{u}_0\right]\right]\right. \\
&\left.-\frac{1}{2}\int d\tau d\tau'\,\mathbf{p}(\tau)\cdot\mathbf{A}[\mathbf{r}(\tau)-\mathbf{r}(\tau')]\cdot\mathbf{p}(\tau')\right\} \qquad (4.2.1)
\end{aligned}$$

where

$$\mathbf{A}(\mathbf{r})=\int\frac{d\mathbf{q}}{(2\pi)^d}e^{i\mathbf{q}\cdot\mathbf{r}}\rho(q^2)[\mathbf{u}_0\cdot(\mathbf{I}-\hat{\mathbf{q}}\hat{\mathbf{q}})][(\mathbf{I}-\hat{\mathbf{q}}\hat{\mathbf{q}})\cdot\mathbf{u}_0] \qquad (4.2.2)$$

To give the permeability problem a path-integral formulation, we use a trick previously employed by Drummond and Horgan (1987). This problem is governed by Eq. (1.2.3), for which we can define a Green function,

$$\nabla\cdot\kappa(\mathbf{r})\nabla G(\mathbf{r},\mathbf{r}_0)=-\delta(\mathbf{r}-\mathbf{r}_0) \qquad (4.2.3)$$

But there is a diffusion problem associated with (1.2.3):

$$\left[\frac{\partial}{\partial t}-\nabla\cdot\kappa(\mathbf{r})\nabla\right]\phi(\mathbf{r},t)=0 \qquad (4.2.4)$$

for which we can also define a Green function,

$$\left[\frac{\partial}{\partial t}-\nabla\cdot\kappa(\mathbf{r})\nabla\right]G(\mathbf{r},\mathbf{r}_0,t-t_0)=\delta(\mathbf{r}-\mathbf{r}_0)\delta(t-t_0) \qquad (4.2.5)$$

These two problems are closely connected. For example, if

$$\lim_{t\to\infty}\frac{\partial\phi(\mathbf{r},t)}{\partial t}\to 0,$$

then a solution of (4.2.4) which obeys a given set of boundary conditions in space will relax to

a solution of (1.2.3) with the same boundary conditions in the limit of large t; in addition, if

$$\lim_{t\to 0} G(\mathbf{r},\mathbf{r}_0,t)\to\delta(\mathbf{r}-\mathbf{r}_0),$$
$$\lim_{t\to\infty} G(\mathbf{r},\mathbf{r}_0,t)\to 0,$$

then

$$G(\mathbf{r},\mathbf{r}_0)=\int_0^\infty dt G(\mathbf{r},\mathbf{r}_0,t). \tag{4.2.6}$$

If we average over fluctuations, we expect that (4.2.3) will look like

$$\kappa_{eff}\nabla^2\langle G(\mathbf{r},\mathbf{r}_0)\rangle=-\delta(\mathbf{r}-\mathbf{r}_0), \tag{4.2.7}$$

and (4.2.5) will look like

$$\left[\frac{\partial}{\partial t}-\kappa_{eff}\nabla^2\right]\langle G(\mathbf{r},\mathbf{r}_0,t-t_0)\rangle=\delta(\mathbf{r}-\mathbf{r}_0)\delta(t-t_0). \tag{4.2.8}$$

Equation (4.2.6) leads us to expect that the effective parameters in (4.2.7) and (4.2.8) are the same. Because of the similarity of the permeability problem and its associated diffusion problem, we assume that our already-obtained path-integral formulation of the latter will serve as a suitable formulation of the former. Equation (4.2.5) can be written

$$\left[\frac{\partial}{\partial t}-[\nabla\kappa(\mathbf{r})]\cdot\nabla-\kappa(\mathbf{r})\nabla^2\right]G(\mathbf{r},\mathbf{r}_0,t-t_0)=\delta(\mathbf{r}-\mathbf{r}_0)\delta(t-t_0), \tag{4.2.9}$$

indicating that its path-integral version is

$$G(\mathbf{r}_N,\mathbf{r}_0,t_N-t_0)=\int_{\mathbf{r}(t_0)=\mathbf{r}_0}^{\mathbf{r}(t_N)=\mathbf{r}_N} D\mathbf{r}\int D\mathbf{p}\exp\left\{-\int_{t_0}^{t_N} d\tau\left[\kappa(\mathbf{r})p^2(\tau)-i\mathbf{p}(\tau)\cdot\left[\frac{d\mathbf{r}}{d\tau}+\nabla\kappa(\mathbf{r})\right]\right]\right\} \tag{4.2.10}$$

In order to obtain more tractable equations, and results directly comparable to those of previous investigators, we will use a Gaussian distribution to approximate the actual log-normal distribution of $\kappa(\mathbf{r})$. This approximation is reasonable if the variance of the distribution is small compared to the mean. Averaging (4.2.10) over fluctuations in permeability will thus give

$$<G(\mathbf{r}_N,\mathbf{r}_0,t_N-t_0)>=\int D\kappa_1\int D\mathbf{r}\int D\mathbf{p}\exp\left\{-\int\frac{d\mathbf{r}d\mathbf{r}'\rho^{-1}(\mathbf{r}-\mathbf{r}')\kappa_1(\mathbf{r})\kappa_1(\mathbf{r}')}{2\kappa_0{}^2}\right.$$
$$\left.-\int d\tau\left[\kappa(\mathbf{r})p^2(\tau)-i\mathbf{p}(\tau)\cdot\left[\frac{d\mathbf{r}}{d\tau}+\nabla\kappa_1(\mathbf{r})\right]\right]\right\}$$
$$=\int D\mathbf{r}\int D\mathbf{p}\exp\left\{-\int d\tau\left[\kappa_0 p^2(\tau)-i\mathbf{p}(\tau)\cdot\frac{d\mathbf{r}}{d\tau}\right]\right.$$
$$\left.+\frac{1}{2}\int d\tau d\tau'\kappa_0{}^2[p^2(\tau)-i\mathbf{p}(\tau)\cdot\nabla][p^2(\tau')-i\mathbf{p}(\tau')\cdot\nabla']\rho(\mathbf{r}-\mathbf{r}')\right\}. \tag{4.2.11}$$

The first passage problem is governed by Eq. (1.2.5), for which we can define a Green function

$$\left[\frac{\partial}{\partial t}+\mathbf{u}(\mathbf{r})\cdot\nabla-D\nabla^2\right]G(\mathbf{r},\mathbf{r}_0,t-t_0)=\delta(\mathbf{r}-\mathbf{r}_0)\delta(t-t_0), \tag{4.2.12}$$

We take the layering to be parallel to $\hat{\mathbf{x}}$. We will assume that the mean flow is zero (center of mass frame), that the region of interest is bounded by absorbing walls (sinks) oriented normal to the flow, and that the tracer is released half-way between the two walls. The boundary conditions on $c(\mathbf{r},t)$ thus become $c(\mathbf{r},t)=0$ at $x=\pm L$, and as $y\to\pm\infty$, which correspond to the same conditions on $G(\mathbf{r},\mathbf{r}_0,t-t_0)$. While the tracer has a finite distance it can travel parallel to the flow, it also has an indefinitely large distance it can travel normal to the flow, and an indefinitely large number of layers it can visit. The usual experimental apparatus is not actually of infinite thickness, but it can be made effectively so if the characteristic time necessary to leave the system by moving parallel to the flow is much less than the characteristic time necessary to leave the system by diffusing normal to the flow. Making explicit the bounds on the integration in (1.2.6), the exit time distribution becomes

$$p(\mathbf{r}_0,t-t_0)=-\frac{\partial}{\partial t}\int_{-L}^{+L}dx\int_{-\infty}^{+\infty}dyG(\mathbf{r},\mathbf{r}_0,t-t_0). \tag{4.2.13}$$

The mean first passage time $T(\mathbf{r})$ is defined as

$$T(\mathbf{r})\equiv\int_0^{+\infty}dt\ t\ p(\mathbf{r},t). \tag{4.2.14}$$

One can obtain for $T(\mathbf{r})$ from the CDE (Gardiner (1983))

$$D\nabla^2 T(\mathbf{r})+\mathbf{u}(\mathbf{r})\cdot\nabla T(\mathbf{r})+1=0. \tag{4.2.15}$$

Usually, Eq. (4.2.15) would be preferred to Eq. (1.2.5), for the obvious reasons of fewer variables and fewer derivatives. None the less, we will not make use of Eq. (4.2.15). For the averaged system, the simplest naive argument gives $<T>\sim L^{4/3}$: since we know that $<x^2(t)>\sim t^{3/2}$, we might guess $L^2\sim<T>^{3/2}$, which implies $<T>\sim L^{4/3}$. (This sort of handwaving argument is of course not always correct.) A more refined argument based on crossover scaling due to Redner (1994) gives $<T>\sim(L\ln L)^{4/3}$. But our unperturbed system is governed by pure diffusion in the x direction, so that $T_0\sim L^2$. It is difficult to see how one might perturb about $T_0\sim L^2$, and reach $<T>\sim L^{4/3}$ for large L, as the unperturbed quantity would dominate the expected averaged quantity in the parameter range of interest. Furthermore, from a perturbation expansion, one can readily see that the first order correction scales as L^3. This indicates that perturbative methods are best limited to cases for which L is small and the fluctuations are weak. We therefore desire a non-perturbative calculation, but we do not know of a non-perturbative technique which can be applied immediately to Eq. (4.2.15). The Rayleigh-Ritz technique familiar from standard quantum mechanics may be a suitable starting place for developing such a method, but some differences, as between what is calculated in quantum mechanics (a complex probability density) and what is calculated here (a real first passage time), make the application problematic. On the other hand, such a technique does exist for Eq. (1.2.5).

To obtain a path-integral version of the first passage problem, we need the solution to Eq. (4.2.12) in the special case that the velocity is a non-zero constant $u_0\hat{\mathbf{x}}$:

$$\left[\frac{\partial}{\partial t}+u_0\frac{\partial}{\partial x}-D\nabla^2\right]G_0(\mathbf{r},\mathbf{r}_0,t-t_0)=\delta(\mathbf{r}-\mathbf{r}_0)\delta(t-t_0) \tag{4.2.16}$$

Transport in the y direction is independent of transport in the x direction, and the former is

simple unbounded Brownian transport, which is to say

$$G_0(\mathbf{r},\mathbf{r}_0,t)=G_{0x}(x,x_0,t)G_{0y}(y,y_0,t) \tag{4.2.17}$$

$$G_{0y}(y,y_0,t)=\frac{1}{(4\pi Dt)^{1/2}}\exp\left\{-\frac{(y-y_0)^2}{4Dt}\right\} \tag{4.2.18}$$

$G_{0x}(x,x_0,t)$ can be obtained using images, as is familiar from elementary electrostatics. The idea of images in electrostatics is that, given a bounded region of space with a charge inside, the boundary conditions governing the electrostatic potential can be mimicked by placing "image charges" of appropriate magnitude at certain points outside the region of interest. The result is an electrostatic potential which obeys (1) Poisson's equation within the region and (2) the boundary conditions, and which therefore must be the solution. The idea is similar here. We assume that a particle is released at x_0 such that $-L\le x_0\le L$. If the boundaries were at $\pm\infty$, then the Green function at time t would be

$$G_{0x}^{(0)}(x,x_0,t)=\frac{1}{(4\pi Dt)^{1/2}}\exp\left\{-\frac{(x-x_0-u_0t)^2}{4Dt}\right\} \tag{4.2.19}$$

To satisfy the boundary condition at $x=L$, we place an image $G_{0x}^{(1)}(x,x_0,t)$ at $x=L+(L-x_0)$:

$$G_{0x}^{(1)}(x,x_0,t)=\frac{A_1}{(4\pi Dt)^{1/2}}\exp\left\{-\frac{(x-2L+x_0-u_0t)^2}{4Dt}\right\} \tag{4.2.20}$$

Note that the particle and its image are the same distance from the boundary in question. The magnitude A_1 is chosen so that $G_{0x}^{(0)}(L,x_0,t)+G_{0x}^{(1)}(L,x_0,t)=0$, which reduces to

$$A_1=-\exp\left\{\frac{u_0}{D}(L-x_0)\right\} \tag{4.2.21}$$

To satisfy the boundary condition at $x=-L$, we place an image $G_{0x}^{(-1)}(x,x_0,t)$ at $x=-L-(x_0+L)$:

$$G_{0x}^{(-1)}(x,x_0,t)=-\frac{A_{-1}}{(4\pi Dt)^{1/2}}\exp\left\{-\frac{(x+2L+x_0-u_0t)^2}{4Dt}\right\} \tag{4.2.22}$$

Note again that the particle and its image are the same distance from the boundary in question. The magnitude A_{-1} is chosen so that $G_{0x}^{(0)}(-L,x_0,t)+G_{0x}^{(-1)}(-L,x_0,t)=0$, which reduces to

$$A_{-1}=-\exp\left\{\frac{u_0}{D}(-L-x_0)\right\} \tag{4.2.23}$$

We next require a second image on the right to satisfy the boundary condition at $x=L$ for the first image on the left, and a second image on the left to satisfy the boundary condition at $x=-L$ for the first image on the right. The process leads, in a straightforward manner, to an infinite number of images, which can be collected together as

$$G_{0x}(x,x_0,t)=\frac{1}{(4\pi Dt)^{1/2}}\sum_{n=-\infty}^{+\infty}(-)^n\exp\left\{\frac{u_0}{D}\left[nL+\frac{(-1+(-)^n)x_0}{2}\right]\right.$$
$$\left.-\frac{1}{4Dt}\left[x-2nL-(-)^n x_0-u_0 t\right]^2\right\} \tag{4.2.24}$$

Returning to the more involved notation, we have as our solution of (4.2.16)

$$G_0(\mathbf{r}_N,t_N;\mathbf{r}_0,t_0)=\frac{1}{4\pi D(t_N-t_0)}\exp\left\{-\frac{(y_N-y_0)^2}{4D(t_N-t_0)}\right\}\times$$
$$\times\sum_{n=-\infty}^{+\infty}(-)^n\exp\left\{\frac{u_0}{D}\left[nL+\frac{(-1+(-)^n)x_0}{2}\right]\right.$$
$$\left.-\frac{1}{4D(t_N-t_0)}\left[x_N-2nL-(-)^n x_0-u_0(t_N-t_0)\right]^2\right\} \tag{4.2.25}$$

This can be rewritten using the integral identity

$$\frac{1}{(2\pi M)^{1/2}}\exp\left\{-\frac{z^2}{2M}\right\}=\int_{-\infty}^{+\infty}\frac{dp}{2\pi}\exp\left\{-\frac{1}{2}Mp^2+ipz\right\} \tag{4.2.26}$$

so that

$$G_0(\mathbf{r}_N,t_N;\mathbf{r}_0,t_0)=\frac{1}{[4\pi D(t_N-t_0)]^{1/2}}\exp\left\{-\frac{(y_N-y_0)^2}{4D(t_N-t_0)}\right\}\int_{-\infty}^{+\infty}\frac{dp}{2\pi}\times$$
$$\times\sum_{n=-\infty}^{+\infty}(-)^n\exp\left\{\frac{u_0}{D}\left[nL+\frac{(-1+(-)^n)x_0}{2}\right]\right.$$
$$\left.-D(t_N-t_0)p^2+ip\left[x_N-2nL-(-)^n x_0-u_0(t_N-t_0)\right]\right\} \tag{4.2.27}$$

To obtain the concentration with fluctuating parameters, we divide the time interval into N equal segments of length $\Delta t=\frac{t_N-t_0}{N}$. Then any given path from $\mathbf{r}_0$ to $\mathbf{r}_N$ can be parametrised

as a series of $N+1$ points $\mathbf{r}_k \equiv \mathbf{r}(k\Delta t + t_0)$, $0 \le k \le N$. The probability of going from $\mathbf{r}_k$ to $\mathbf{r}_{k+1}$ can be found from Eq. (4.2.27) by replacing $N \to k+1$, $0 \to k$, $p \to p_k$, $n \to n_k$, and $u_0 \to u(y_{k+1})$. We choose $u(y_{k+1})$ so that the path integral expression we eventually obtain obeys Eq. (4.2.12) (cf. Sect. 4.1). The probability for taking the entire path is the product of the probabilities of taking each link in the path, and the total probability of going from $(\mathbf{r}_0, t_0)$ to $(\mathbf{r}_N, t_N)$ is obtained by integrating this last quantity over all possible paths. The result is

$$G(\mathbf{r}_N,t_N;\mathbf{r}_0,t_0)=\prod_{j=1}^{N-1}\int dx_j dy_j \prod_{k=0}^{N-1}\int \frac{dp_k}{2\pi} \prod_{l=0}^{N-1}\sum_{n_l=-\infty}^{+\infty}(-)^{n_l}\frac{1}{(4\pi D\Delta t)^{N/2}}\times$$
$$\times\exp\left\{-\sum_{m=0}^{N-1}\frac{(y_{m+1}-y_m)^2}{4D\Delta t}+\sum_{m=0}^{N-1}\left[\frac{u(y_{m+1})}{D}\left[n_m L+\frac{(-1+(-)^{n_m})x_m}{2}\right]\right.\right.$$
$$\left.\left.-D\Delta t p_m{}^2+ip_m\left[x_{m+1}-2n_m L-(-)^{n_m}x_m-u(y_{m+1})\Delta t\right]\right]\right\} \qquad (4.2.28)$$

We use the momentum representation because the function in the exponent is linear in the velocity, which makes averaging over velocity fluctuations much easier. Averaging over fluctuations in velocity gives

$$\langle G(\mathbf{r}_N,t_N;\mathbf{r}_0,t_0)\rangle=\int Du\exp\left\{-\frac{1}{2}\int dy dy' \rho^{-1}(|y-y'|)u(y)u(y')\right\}G(\mathbf{r}_N,t_N;\mathbf{r}_0,t_0)$$
$$=\prod_{j=1}^{N-1}\int dx_j dy_j \prod_{k=0}^{N-1}\int\frac{dp_k}{2\pi}\prod_{l=0}^{N-1}\sum_{n_l=-\infty}^{+\infty}(-)^{n_l}\frac{1}{(4\pi\Delta t)^{N/2}}\exp\left\{-\sum_{m=0}^{N-1}\frac{(y_{m+1}-y_m)^2}{4D\Delta t}\right.$$
$$\left.+\sum_{m=0}^{N-1}\left[-D\Delta t p_m{}^2+ip_m\left[x_{m+1}-2n_m L-(-)^{n_m}x_m\right]\right]+\frac{1}{2}\sum_{m=0}^{N-1}\sum_{q=0}^{N-1}\sigma^2\delta(y_{m+1}-y_{q+1})\times\right.$$
$$\left.\times\left[\frac{n_m L}{D}+\frac{(-1+(-)^{n_m})x_m}{2D}-ip_m\Delta t\right]\left[\frac{n_q L}{D}+\frac{(-1+(-)^{n_q})x_q}{2D}-ip_q\Delta t\right]\right\} \qquad (4.2.29)$$

Although this expression contains factors of $(-)^n$ and i, it is none the less real and positive, since it is a probability. Given our assumptions about the velocity fluctuations, Eq. (4.2.29) is an exact expression.

4.3 Variational method

This procedure was developed by Feynman (1955, 1972) as a path-integral version of the

variational method of quantum mechanics. We start with the path integral for the average Green function $<G>$, which we write

$$<G>\equiv e^{-W}\equiv\int D\mathbf{x}e^{-S'} \tag{4.3.1}$$

where S' is a sort of action. If we have another action S_A' which is simple and in some sense an approximation of S', Eq. (4.3.1) can be rewritten

$$e^{-W}=e^{-W_A}\left[\frac{\int D\mathbf{x}e^{-(S'-S_A')}e^{-S_A'}}{\int D\mathbf{x}e^{-S_A'}}\right]\equiv e^{-W_A}<e^{-(S'-S_A')}>_A' \tag{4.3.2}$$

where

$$e^{-W_A}\equiv\int D\mathbf{x}e^{-S_A'}. \tag{4.3.3}$$

The term of (4.3.2) in brackets can be thought of as the average of $e^{-(S'-S_A')}$, the weight for each path being $e^{-S_A'}$. Now, for any set of real quantities $\{f\}$, we have

$$<e^{-f}>\geq e^{-<f>}, \tag{4.3.4}$$

where the brackets denote a weighted mean. If S' and S_A' are both real, this inequality can be applied to (4.3.2), allowing us to write

$$e^{-W}=e^{-W_A}<e^{-(S'-S_A')}>_A'\geq e^{-W_A}e^{-<S'-S_A'>_A'}, \tag{4.3.5}$$

$$W\leq W_A+<S'-S_A'>_A'\equiv W_{eff} \tag{4.3.6}$$

The values of any free parameters in W_A are chosen to make W_{eff} a least upper bound for W.

The average Green function in (4.2.1) and (4.2.11) are written in the momentum representation, in which they are complex; thus, we cannot apply (4.3.4) directly to them. But that representation was used for computational convenience, and was not intrinsic to the problem. Equation (4.1.2) is written entirely in terms of real quantities; averaging over Gaussian fluctuations would not alter that fact, and the treatment leading up to (4.3.6) could be directly applied to the result. Having properly obtained (4.3.6), we can write a momentum-space version of it by defining

$$e^{-S'}=\int D\mathbf{p}e^{-S} \tag{4.3.7}$$

$$e^{-S_A'}=\int D\mathbf{p}e^{-S_A}, \tag{4.3.8}$$

and

$$<F>_A\equiv\frac{\int D\mathbf{x}\int D\mathbf{p}Fe^{-S_A}}{\int D\mathbf{x}\int D\mathbf{p}e^{-S_A}} \tag{4.3.9}$$

It follows from (4.3.7) and (4.3.8) that

$$(S'-S_A')e^{-S_A'}=\int D\mathbf{p}(S-S_A)e^{-S_A} \tag{4.3.10}$$

to first order in $(S-S_A)$, and so (4.3.6) becomes

$$W\leq W_A+<S-S_A>_A\equiv W_{eff}. \tag{4.3.11}$$

The values of any free parameters in W_A are chosen to obtain the minimum upper bound at the distribution's point of maximum probability, as this is where the most representative tracer particles would end up.

It might be illuminating to pause at this point and reconsider what we have done. Our task is to approximate e^{-W}. The closer S_A' is to S' in (4.3.2), the better we can expect the bound in (4.3.3) to be. But it would be a mistake to argue further, in too-close analogy with the standard quantum-mechanical case, that e^{-W_A} by itself is the approximate Green function we seek. Consider an expansion of (4.3.2), by which we obtain a formal expression for e^{-W} in terms of the integrations we can do:

$$e^{-W}=e^{-W_A}\left[1-<S'-S_A'>_A'+{}^1\!/_2<(S'-S_A')^2>_A'-\cdots\right] \tag{4.3.12}$$

Note that e^{-W_A} is only the zero-order term of this expansion and that a better approximation is given by including the first-order term and an estimate of the second-order term, as has been done in (4.3.5). In effect, e^{-W_A} is a guess in our attempt to approximate e^{-W}, and $e^{-W_{eff}}$ is a refinement of that guess.

Chapter 5

Calculations

5.1 Calculation of effective permeability

With finite-range correlations in the permeability fluctuations, at large enough length scales we expect the porous medium to look like a homogeneous isotropic continuum, and Darcy's law with a global scalar permeability, Eq. (4.2.7), should apply. Because of the close connection between (4.2.7) and (4.2.8), a good choice for this problem's test action would therefore be

$$S_A=\int_{t_0}^{t_f} d\tau \left[\kappa p^2(\tau)-i\mathbf{p}(\tau)\cdot\frac{d\mathbf{r}}{d\tau}\right]. \tag{5.1.1}$$

It follows from (4.2.11), (4.3.11), and (5.1.1) that we need to calculate

$$W_{eff}=W_A+e^{W_A}\int D\mathbf{r}\int D\mathbf{p}\exp\left[-\int d\tau\left[\kappa p^2(\tau)-i\mathbf{p}(\tau)\cdot\frac{d\mathbf{r}}{d\tau}\right]\right]\left\{(\kappa_0-\kappa)\int d\tau p^2(\tau)\right.$$
$$\left.-\tfrac{1}{2}\int d\tau d\tau' \kappa_0^2[p^2(\tau)-i\mathbf{p}(\tau)\cdot\nabla][p^2(\tau')-i\mathbf{p}(\tau')\cdot\nabla']\rho(\mathbf{r}-\mathbf{r}')\right\}, \tag{5.1.2}$$

where, according to (4.3.3) and (4.3.8),

$$W_A=\frac{3}{2}\ln(4\pi\kappa t)+\frac{\mathbf{r}^2}{4\kappa t}, \tag{5.1.3}$$

with $\mathbf{r}\equiv\mathbf{r}_f-\mathbf{r}_0$ and $t\equiv t_f-t_0$. The resulting integrals can be expanded in the limit of long times,

keeping terms of order $\mathbf{r}^2/t$ but dropping those of order $\mathbf{r}^2/t^2$, so that

$$W_{eff}=W_A+\left[\kappa_0-\kappa-\frac{\rho(0)\kappa_0^2}{3\kappa}\right]\frac{\partial W_A}{\partial \kappa}, \tag{5.1.4}$$

where

$$\rho(0)\equiv\int\frac{d\mathbf{q}}{(2\pi)^3}\rho(q^2). \tag{5.1.5}$$

This can also be written

$$W_{eff}=\frac{3}{2}\ln(4\pi\kappa_1 t)+\frac{\mathbf{r}^2}{4\kappa_2 t}, \tag{5.1.6}$$

with suitably defined κ_1 and κ_2. Since $e^{-W_{eff}}$ is not in general a diffusive Green function, it does not immediately yield an effective diffusion constant κ_{eff}. However, we have assumed that the best value of κ_{eff} is obtained at the distribution's point of maximum probability, $\mathbf{r}=0$. This is equivalent to taking $\kappa_{eff}=\kappa_1$. The optimisation procedure reduces to

$$\frac{\partial \kappa_1}{\partial \kappa}=0, \tag{5.1.7}$$

which implies

$$\kappa^2-\kappa_0\kappa+\frac{2\rho(0)\kappa_0^2}{3}=0. \tag{5.1.8}$$

For $\rho(0)>3/8$, this equation has no roots, and the method fails. (This should not surprise us. In approximating a log-normal distribution by a Gaussian distribution, we allow some sites in the medium to have permeability values less than zero. As $\rho(0)$ increases from zero, the fraction of sites with negative permeabilities also increases from zero, to around 5% for $\rho(0)=3/8$. We cannot reasonably believe the theory will work when a significant fraction of sites is assumed to have permeability values that are physically absurd.) While there is a double root and thus an unambiguous solution for $\rho(0)=3/8$, there are two roots for $0\le\rho(0)<3/8$:

$$\kappa_\pm=\frac{\kappa_0}{2}\left[1\pm\left[1-\frac{8\rho(0)}{3}\right]^{1/2}\right]. \tag{5.1.9}$$

We select κ_+ because $\ln\kappa_1(\kappa_+)<\ln\kappa_1(\kappa_-)$ for $0\le\rho(0)<3/8$: while both κ_+ and κ_- are local minima, κ_+ is the global minimum. In the limit of small $\rho(0)$, $\kappa_1(\kappa=\kappa_+)$ can be expanded to give

$$\kappa_1(\kappa=\kappa_+)=\kappa_0\left[1-\frac{\rho(0)}{3}-\frac{\rho(0)^2}{6}+\cdots\right]. \tag{5.1.10}$$

To first order in $\rho(0)$, this is the same as the perturbative result obtained by King (1987).

5.2 Calculation of effective dispersion

If the velocity fluctuations have correlations of finite range, the averaged tracer problem will be governed at large enough length and time scales by an effective CDE. We expect that the effective velocity will be equal to the mean velocity, since $\mathbf{u}(\mathbf{r})$ is assumed to consist of a mean plus a Gaussian fluctuation, and the fluctuations should cancel out on average. We further expect that the effective dispersion tensor will be diagonal, with components parallel and normal to bulk flow, because on average the medium looks like a homogeneous isotropic continuum, and for such a medium the only preferred direction is that of bulk flow. A reasonable choice for the test action would therefore be

$$S_A=\int_{t_0}^{t_f}d\tau\left[\mathbf{p}(\tau)\cdot\mathbf{D}\cdot\mathbf{p}(\tau)-i\mathbf{p}(\tau)\cdot\left[\frac{d\mathbf{r}}{d\tau}-\mathbf{u}_0\right]\right], \tag{5.2.1}$$

where

$$\mathbf{D}=D_{long}\hat{\mathbf{u}}_0\hat{\mathbf{u}}_0+D_{lat}(\mathbf{I}-\hat{\mathbf{u}}_0\hat{\mathbf{u}}_0). \tag{5.2.2}$$

Using this S_A, (4.2.1), and (4.3.11), we find that we need to calculate

$$W_{eff}=W_A+e^{W_A}\int D\mathbf{r}\int D\mathbf{p}\left\{\int d\tau\mathbf{p}(\tau)\cdot(\mathbf{D}_0-\mathbf{D})\cdot\mathbf{p}(\tau)+\frac{1}{2}\int d\tau d\tau'\,\mathbf{p}(\tau)\cdot\mathbf{A}(\mathbf{r}-\mathbf{r}')\cdot\mathbf{p}(\tau')\right\}\times$$
$$\times\exp\left\{-\int d\tau\left[\mathbf{p}(\tau)\cdot\mathbf{D}\cdot\mathbf{p}(\tau)-i\mathbf{p}(\tau)\cdot\left[\frac{d\mathbf{r}}{d\tau}-\mathbf{u}_0\right]\right]\right\}, \tag{5.2.3}$$

where, from (4.3.3) and (4.3.8)

$$W_A=\frac{3}{2}\ln(4\pi t)+\frac{1}{2}\ln(\det\mathbf{D})+\frac{t}{4}\left[\frac{\mathbf{r}}{t}-\mathbf{u}_0\right]\cdot\frac{1}{\mathbf{D}}\cdot\left[\frac{\mathbf{r}}{t}-\mathbf{u}_0\right]. \tag{5.2.4}$$

We substitute into the resulting integrals $\mathbf{r}=\mathbf{u}_0 t+\mathbf{y}$, and expand in the limit of long times, keeping terms of order $\mathbf{y}^2/t$ but dropping those of order $\mathbf{y}^2/t^2$. Defining for convenience

$$\hat{\mathbf{q}}\cdot\hat{\mathbf{u}}_0=\mu,$$
$$\mathbf{D}_0=D_{0long}\hat{\mathbf{u}}_0\hat{\mathbf{u}}_0+D_{0lat}(\mathbf{I}-\hat{\mathbf{u}}_0\hat{\mathbf{u}}_0),$$

the result is

$$W_{eff}=W_A+\left[D_{0long}-D_{long}+\int\frac{d\mathbf{q}}{(2\pi)^3}\rho(q^2)\frac{(1-\mu^2)^2u_0^2}{\mathbf{q}\cdot\mathbf{D}\cdot\mathbf{q}-i\mathbf{u}_0\cdot\mathbf{q}}\right]\frac{\partial W_A}{\partial D_{long}}$$
$$+\left[D_{0lat}-D_{lat}+\frac{1}{2}\int\frac{d\mathbf{q}}{(2\pi)^3}\rho(q^2)\frac{\mu^2(1-\mu^2)u_0^2}{\mathbf{q}\cdot\mathbf{D}\cdot\mathbf{q}-i\mathbf{u}_0\cdot\mathbf{q}}\right]\frac{\partial W_A}{\partial D_{lat}}. \tag{5.2.5}$$

This can also be written

$$W_{eff}=\frac{3}{2}\ln(4\pi t)+\frac{1}{2}\ln(det\mathbf{D}_1)+\frac{1}{4t}\mathbf{y}\cdot\frac{1}{\mathbf{D}_2}\cdot\mathbf{y}, \tag{5.2.6}$$

with suitably defined $\mathbf{D}_1$ and $\mathbf{D}_2$. In this case, we cannot pick $\mathbf{D}_1$ to be the effective dispersion tensor $\mathbf{D}_{eff}$, because (5.2.6) tells us its determinant only, and not its individual components. We are thus obliged to take $\mathbf{D}_2$ as the effective dispersion tensor. This $\mathbf{D}_2$ can be thought of as the dispersion tensor of a diffusive Green function e^{-W_2} which bounds $e^{-W_{eff}}$, and therefore e^{-W}, from below. We choose $\mathbf{D}$ to make e^{-W_2} a maximum lower bound at the distribution's point of maximum probability $\mathbf{y}=0$, or, in other words, we fix $\mathbf{D}$ by minimising $\frac{1}{2}\ln(det\mathbf{D}_2)$ with respect to variations in D_{long} and D_{lat}. This can be done numerically.

We will take for our correlation function a simple cutoff in Fourier space:

$$\rho(q^2)=\rho_0, q<\Lambda$$
$$\rho(q^2)=0, q>\Lambda \tag{5.2.7}$$

Although this oscillates in coordinate space, the oscillations are exponentially damped to zero. It is easier to do the calculations for this correlation function than for an alternative such as $\rho_0\Lambda^4/(q^2+\Lambda^2)^2$, and there is no significant change in the final results. Having chosen $\rho(q^2)$,

the integrals of (5.2.5) can be expressed in terms of three quantities. The first, $\nu(0)$, is a measure of the anisotropy of $\mathbf{D}_0$,

$$\nu^2(0)+1=\frac{D_{0long}}{D_{0lat}}. \tag{5.2.8}$$

The second is the mesoscopic Peclet number P,

$$P\equiv\frac{u_0 L_{meso}}{D_{0lat}}. \tag{5.2.9}$$

This measures the competition between convection and dispersion over length scales L_{meso} characteristic of the mesoscopic disorder. The third, $\rho(0)$, is a measure of the fluctuation strength, and is defined in (5.1.5).

Most cases of interest will be such that $\mathbf{D}_0$ is roughly proportional to the first power of the microscopic Peclet number

$$P_{micro}=\frac{u_0 L_{micro}}{D_{mol}},$$

where L_{micro} is a length characteristic of the microscopic disorder and D_{mol} is the molecular diffusion constant of the tracer in the fluid. In such flow regimes, $\nu^2(0)+1$ will be around 20 (Dagan (1987)) or 30 (Perkins and Johnson (1963)); we will take 26, i.e., $\nu(0)=5$, as a representative value. The mesoscopic Peclet number will be approximately proportional to the ratio of the length scales involved:

$$P\rightarrow\frac{L_{meso}}{L_{micro}}. \tag{5.2.10}$$

We expect P to be fairly large, but it will also prove interesting to examine effective dispersion for $P\rightarrow 0$. Note that u_0 does not disappear. Since we measure dispersion constants in terms of D_{0lat}, the effective dispersion constants will have the same dependence on u_0 as does D_{0lat}. In other cases of interest, the convective dispersion tensor is small and varies directly with the second power of the microscopic Peclet number. For such cases, $\nu(0)$ will be roughly

zero, and the mesoscopic Peclet number will be

$$P=\frac{u_0 L_{meso}}{D_{mol}}=P_{micro}\left[\frac{L_{meso}}{L_{micro}}\right], \tag{5.2.11}$$

which could be small or large.

The last parameter, $\rho(0)$, is the mean square deviation of the natural-log, log-normal permeability distribution. Some representative figures can be obtained from Law (1944), whose numbers are equivalent to $0.2\leq\rho(0)\leq1.3$; from Dykstra and Parsons (1950), whose numbers are equivalent to $0.1\leq\rho(0)\leq2.3$; and from Arya et al. (1988), whose numbers are equivalent to $0.8\leq\rho(0)\leq2.6$. Since we have assumed $\rho(0)$ to be small compared to 1, so that we can use a Gaussian probability distribution, and so that we can get the velocity fluctuations in the tracer problem from Darcy's law, we see that the values of $\rho(0)$ for which we expect our method to work reasonably well are at best on the lower end of the values found in the field. This does not mean that the method will fail absolutely for values of $\rho(0)$ of order 1, as it does in the permeability problem. The velocity fluctuation model of (2.2.8) and (2.2.9) is interesting of itself, without regard to its derivation from Darcy's law, for reasons mentioned in Sect. 2.2. That $\rho(0)$ is of order 1 means only that a significant fraction of sites will have negative velocities. This may be unusual, but it is not physically impossible in a highly disordered medium.

If $\rho(0)$ and P are very small in comparison to 1, $\frac{1}{2}\ln(det\mathbf{D}_2)$ appears to have only one minimum with respect to variations in D_{long} and D_{lat}. The corresponding solution $\mathbf{D}_2$ approaches $\mathbf{D}_0$ as $\rho(0)$ and P approach 0. For somewhat larger values of $\rho(0)$ or P, a second local minimum will appear. This second minimum may become the global minimum for large enough values of $\rho(0)$ and P. In such a case, the method no longer gives the optimal bound for parameter values greater than the "critical value" at which the two minima are equal. We expect that the effective dispersion tensor will be a continuous function of its parameters, and take the first minimum as our solution in any case.

Figures 1 through 4 show the components of the effective dispersion tensor, measured in units of D_{0lat}, for some representative values of the problem's parameters. For each set of graphs, $\nu(0)$ and $\rho(0)$ are fixed, and P is allowed to vary. In the graphs of function value, the line marked "optimum variation" is the value of $\frac{1}{2}\ln(det\mathbf{D}_1)$ minimised with respect to variations in D_{long} and D_{lat}. This is called optimum from a consideration of (5.2.6): since we expect the best information to be found at the distribution's peak, the minimised $\frac{1}{2}\ln(det\mathbf{D}_1)$ is the best estimate of $\frac{1}{2}\ln(det\mathbf{D}_{eff})$. The line marked "variation" is the minimised value of $\frac{1}{2}\ln(det\mathbf{D}_2)$, the value of $\frac{1}{2}\ln(det\mathbf{D}_{eff})$ which we are obliged to use in order to have D_{eff} itself. Comparison of the two will indicate how closely the information in the distribution's peak agrees with that in the distribution's wings. The lines marked "perturbation" were obtained by expanding the Green function in powers of the velocity fluctuations, then averaging and keeping terms of first order in $\rho(0)$.

The variational results have several interesting features. As $P\rightarrow 0$, $\mathbf{D}_{eff}$ is proportional to P^2 in all cases, in agreement with perturbation theory and experiment. For values of P less than 5 or 10, the perturbative results for effective dispersion are slightly greater than the variational results. (Analogously, the first-order perturbative estimate of permeability was greater than the variational estimate of that quantity.) This means that $\frac{1}{2}\ln(det\mathbf{D}_{eff})$ is greater for perturbation theory than for the variational method, making the variational result a better upper bound for W. On the other hand, given that our choice for $\rho(q^2)$ is merely a well-informed guess, the numerical results obtained by the two methods do not differ significantly. For large P, $\mathbf{D}_{eff}$ is proprotional to P in three of the four cases, with minor deviations for $\rho(0)$=0.1. This result agrees with experiment, but disagrees with perturbation theory, which predicts that effective lateral dispersion is independent of P for large P. (This prediction is noted by Dagan (1987) as well.) The disagreement arises from the fact that perturbation theory is not valid in this domain. In general, perturbation theory can be expected to work only if the difference

between an effective quantity and its initial value is small. Also, in a problem with several parameters, one cannot expand in powers of one of them, without regard to the others. For the tracer problem, the difference between $\mathbf{D}_{eff}$ and $\mathbf{D}_0$ is a function not only of $\rho(0)$, but also of P. One is not free to expand in powers of $\rho(0)$ alone, since no matter how small one chooses $\rho(0)$, the difference between $\mathbf{D}_{eff}$ and $\mathbf{D}_0$ can be made large by the selection of a sufficiently large P. It is for this reason that our model of the velocity fluctuations,which was derived from a perturbation expansion of Darcy's law, gives rise to an effective dispersion which cannot be treated by perturbative methods.

5.3 Calculation of mean first passage time

For the first passage problem, $e^{-W} \equiv \int dy_N \langle G(\mathbf{r}_N,t_N;\mathbf{r}_0,t_0)\rangle$, with $\langle G(\mathbf{r}_N,t_N;\mathbf{r}_0,t_0)\rangle$ given by Eq. (4.2.29). We integrate over y_N because we are interested in when the particle leaves the interval, but not where. The choice of S_A depends on two important considerations, one being whether or not we can do the integrals, and the other being how well the resulting e^{-W_A} fits our expectation of the tracer particle's average behaviour. Now, the stratified system has been thoroughly investigated in free space (Fisher (1966), Matheron and de Marsily (1980), Bouchaud et al. (1990), Zumofen et al. (1990)): the first two moments of x are given by $\langle x(t)\rangle=0$ and $\langle x^2(t)\rangle \sim t^{\alpha}$, with $\alpha=3/2$, and the shape of the distribution itself is known for certain limiting cases. If $x/t^{\alpha/2}$ is small, then

$$\langle e^{-W}\rangle \sim \exp\left[-\beta_1\left[\frac{x}{t^{\alpha/2}}\right]^2\right], \tag{5.3.1a}$$

and if $x/t^{\alpha/2}$ is large, then

$$\langle e^{-W}\rangle \sim \exp\left[-\beta_2\left[\frac{x}{t^{\alpha/2}}\right]^{4/3}\right], \tag{5.3.1b}$$

where β_1 and β_2 are constants. Since we require a calculation that can be done analytically, we choose S_A so that e^{-W_A} is a Gaussian distribution. Although this does not agree with the

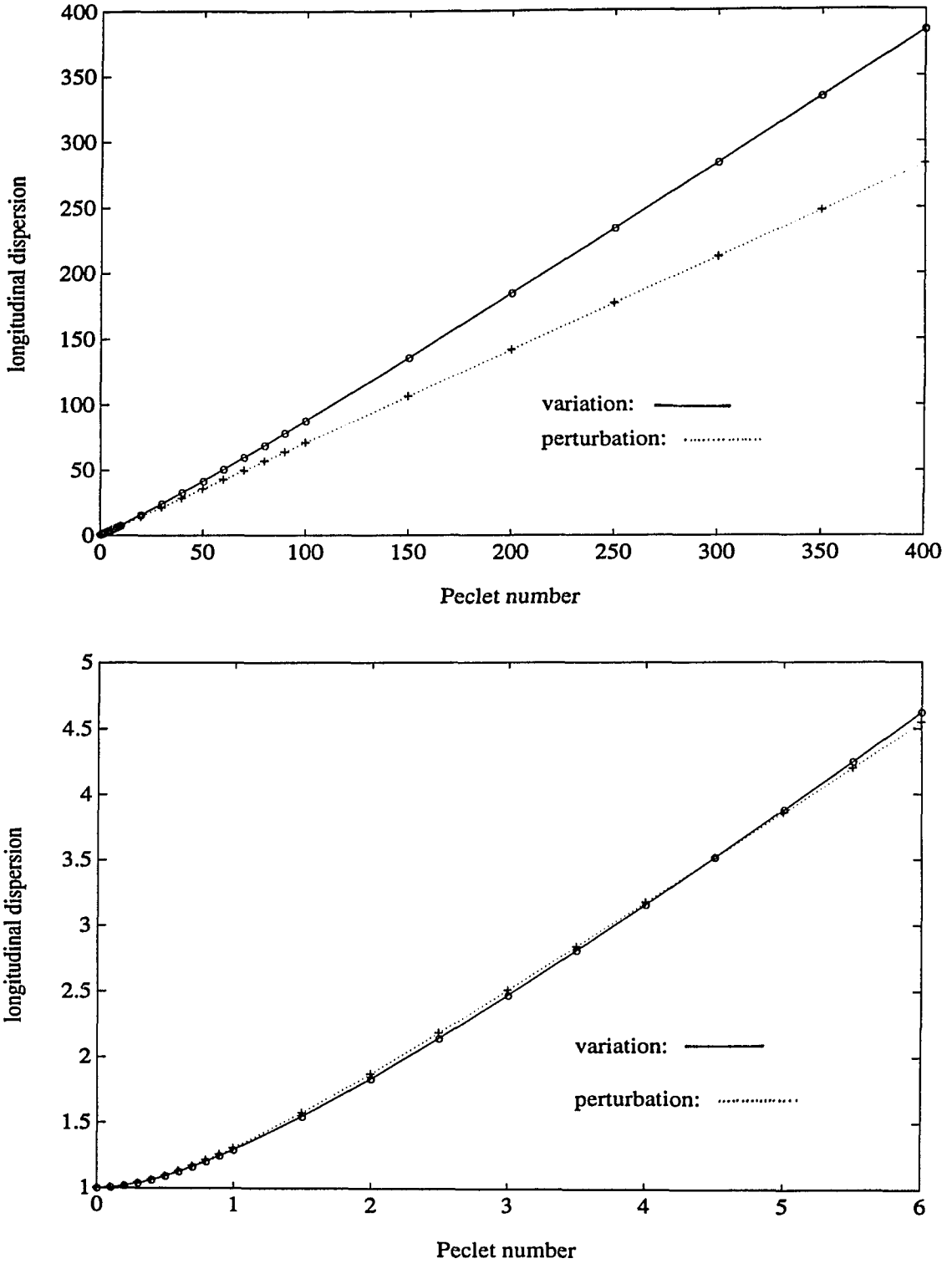

Figure 1 (a) Effective longitudinal dispersion constant vs. Peclet number: $\nu(0)=0$, $\rho(0)=0.3$

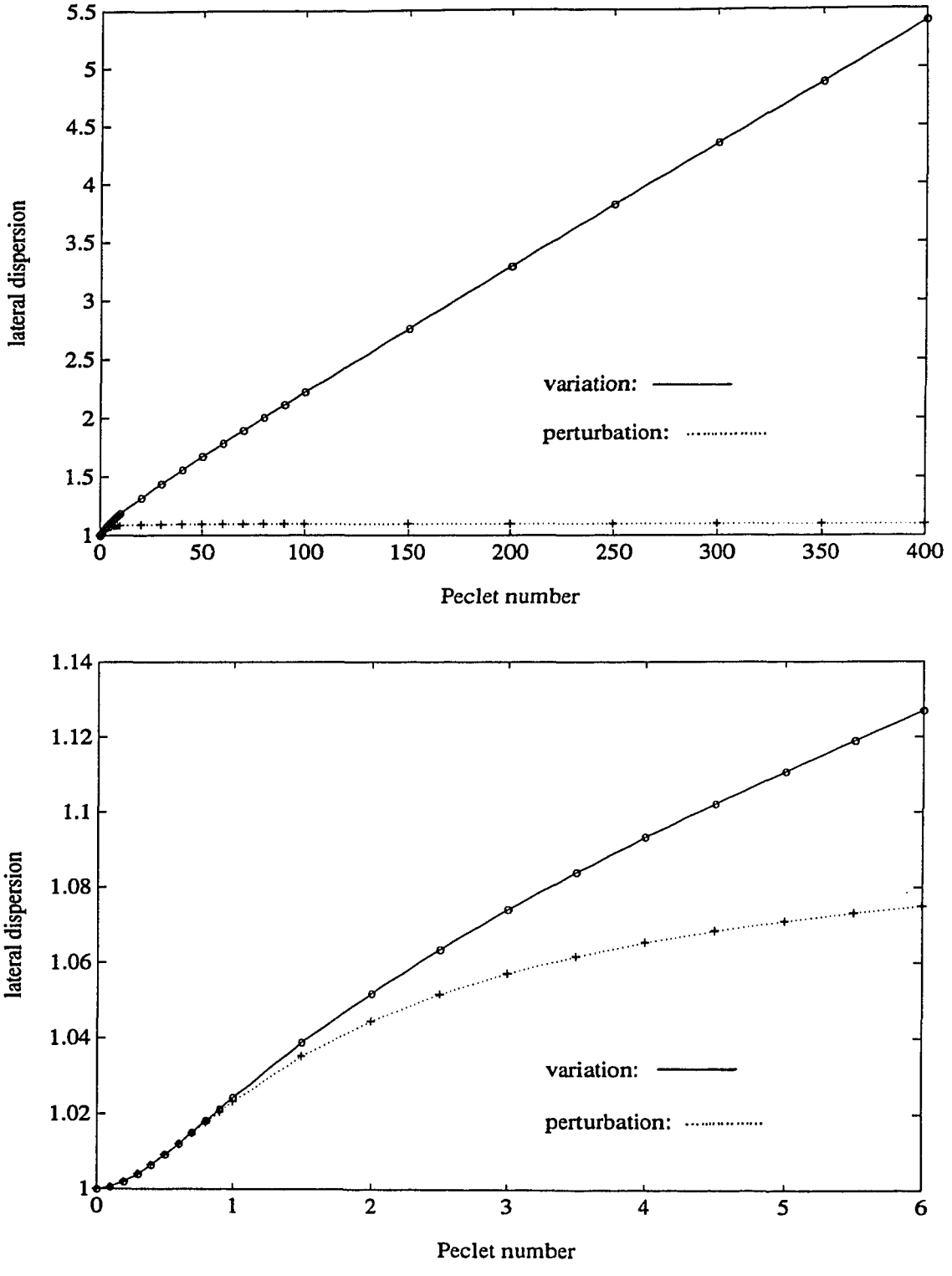

Figure 1 (b) Effective lateral dispersion constant vs. Peclet number: $\nu(0)=0$, $\rho(0)=0.3$

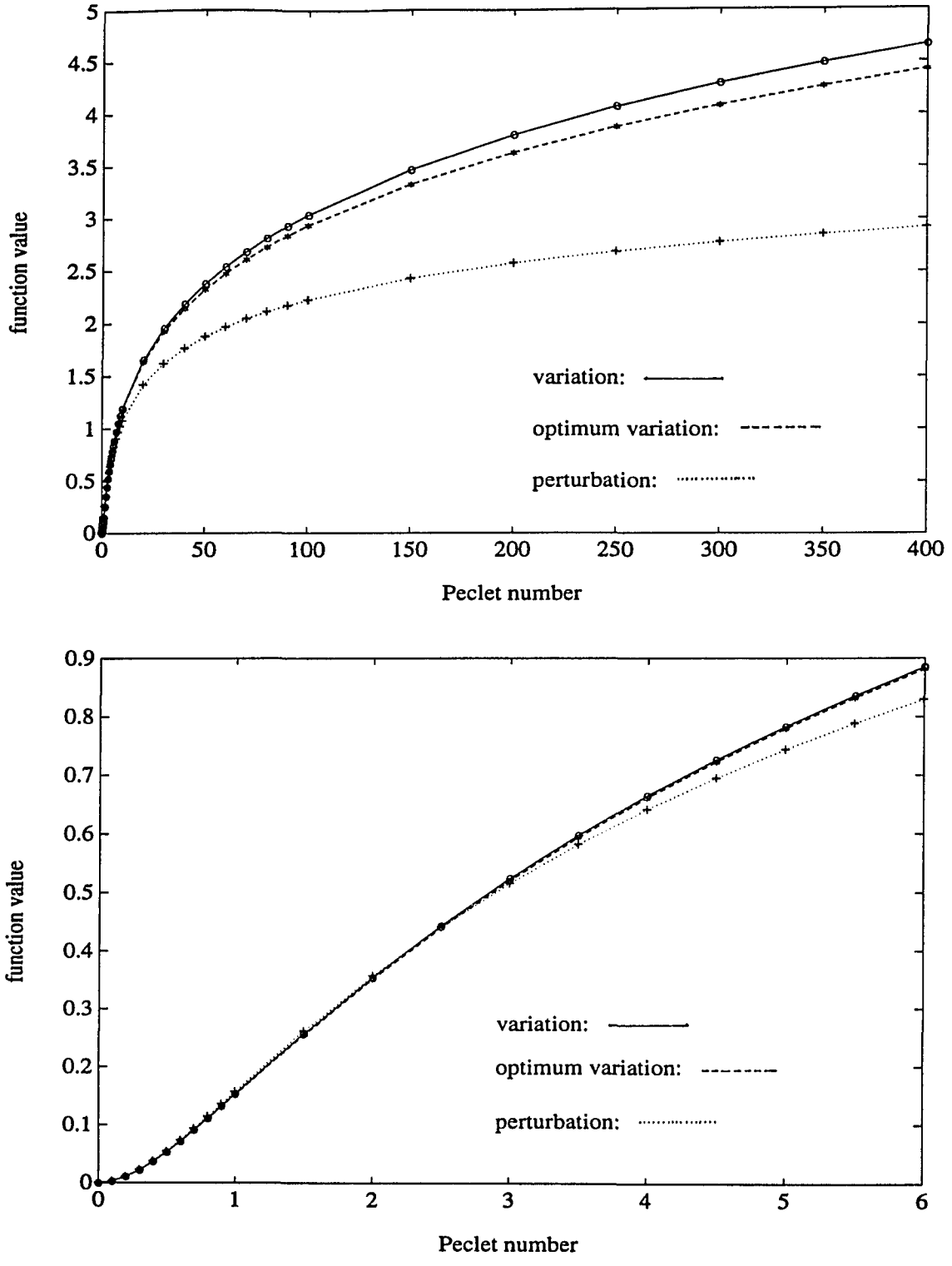

Figure 1 (c) $\frac{1}{2}\ln(\det \mathbf{D}_{eff})$ vs. Peclet number: $\nu(0)=0$, $\rho(0)=0.3$

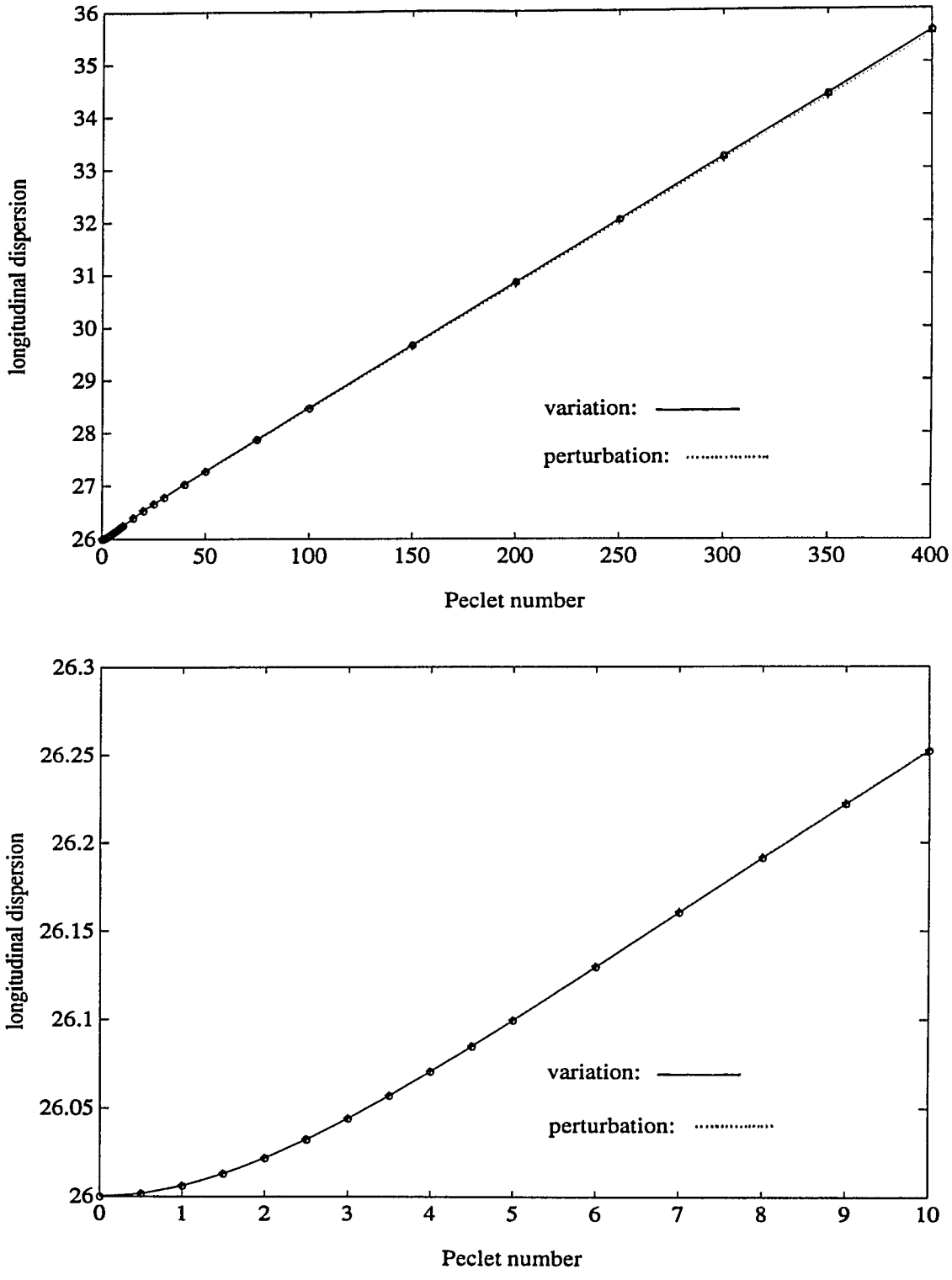

Figure 2 (a) Effective longitudinal dispersion constant vs. Peclet number: $\nu(0)=5$, $\rho(0)=0.01$

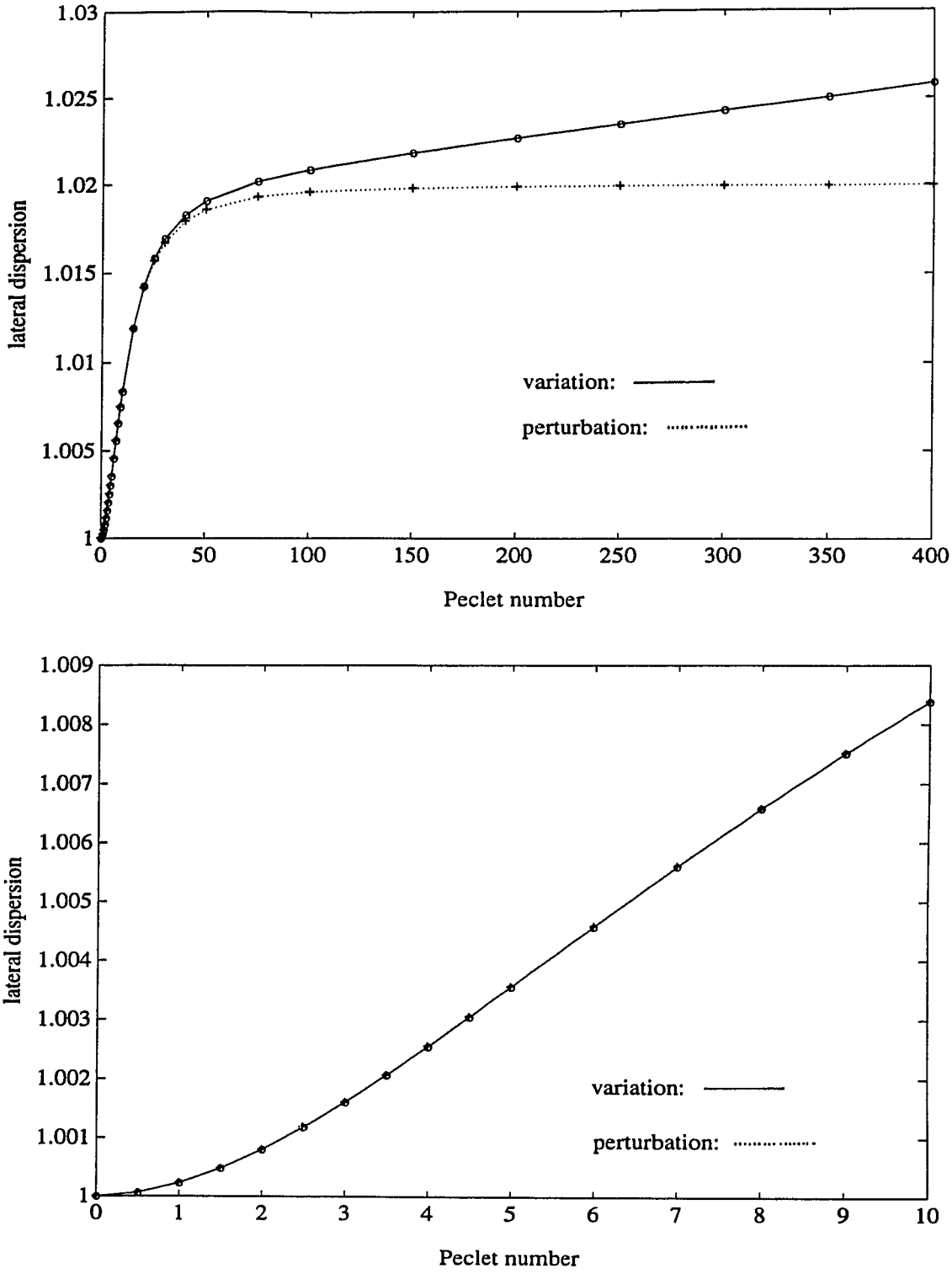

Figure 2 (b) Effective lateral dispersion constant vs. Peclet number: $\nu(0)=5$, $\rho(0)=0.01$

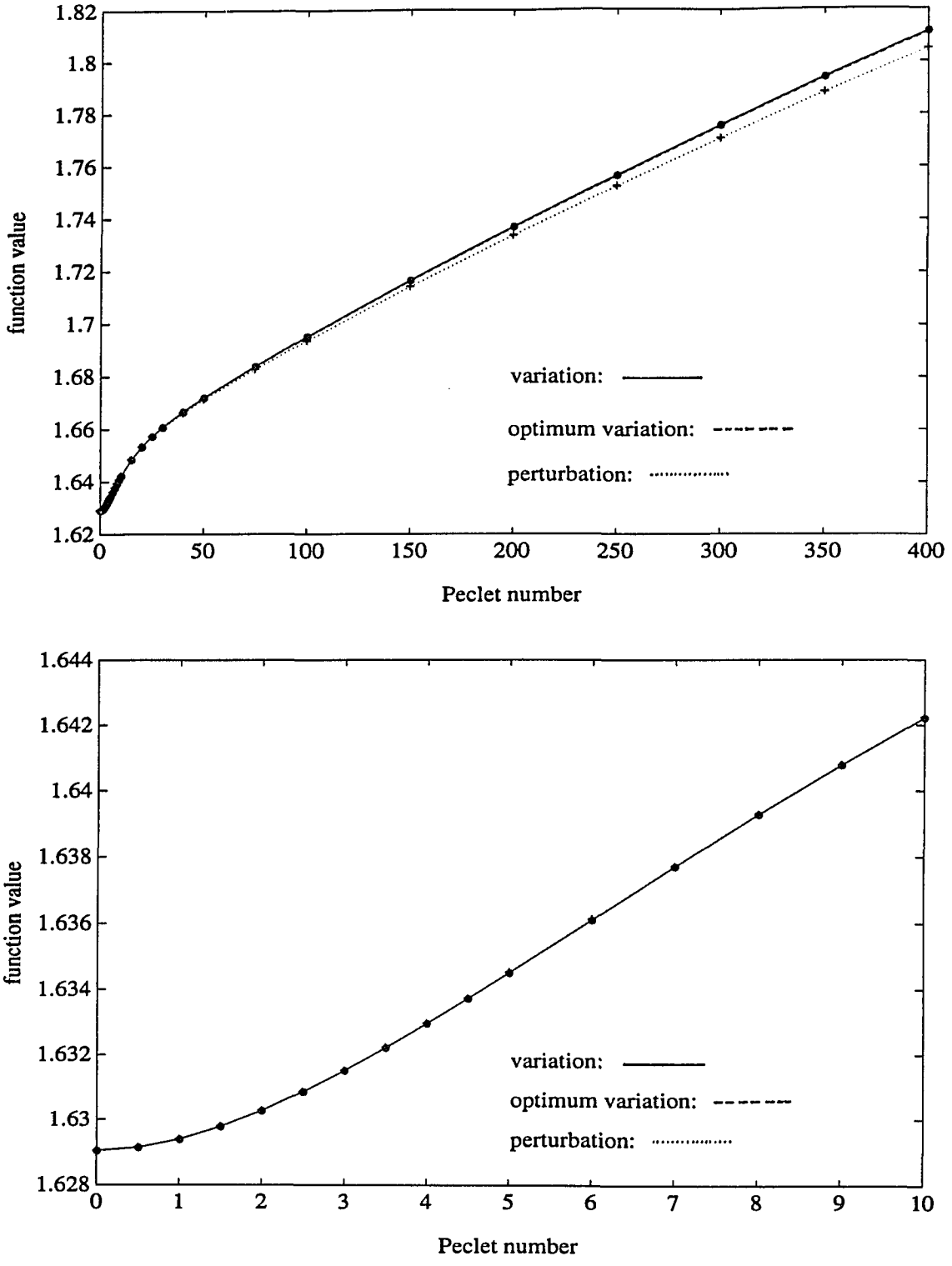

Figure 2 (c) $\frac{1}{2}\ln(\det \mathbf{D}_{eff})$ vs. Peclet number: $\nu(0)=5$, $\rho(0)=0.01$

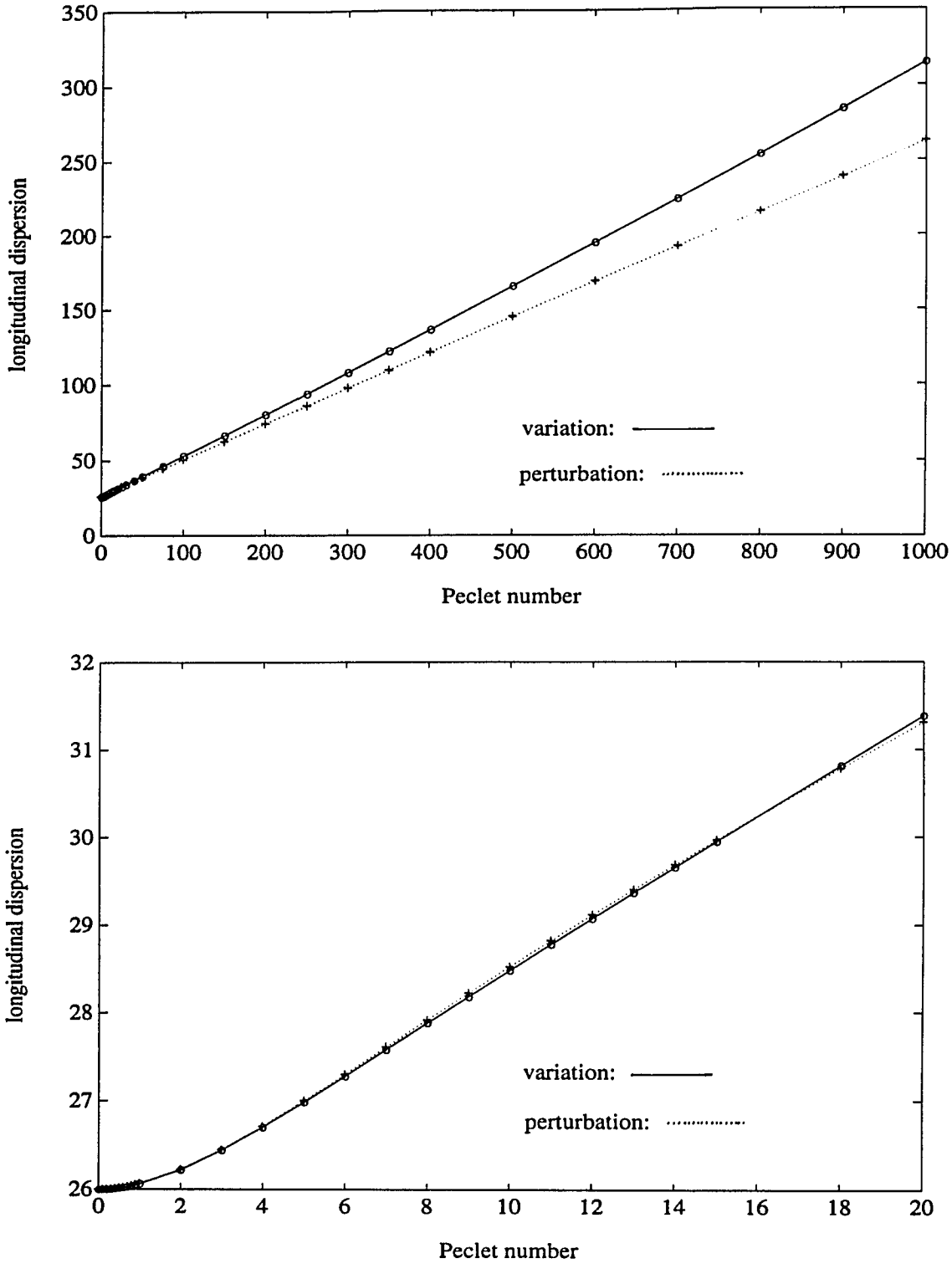

Figure 3 (a) Effective longitudinal dispersion constant vs. Peclet number: $\nu(0)=5$, $\rho(0)=0.1$

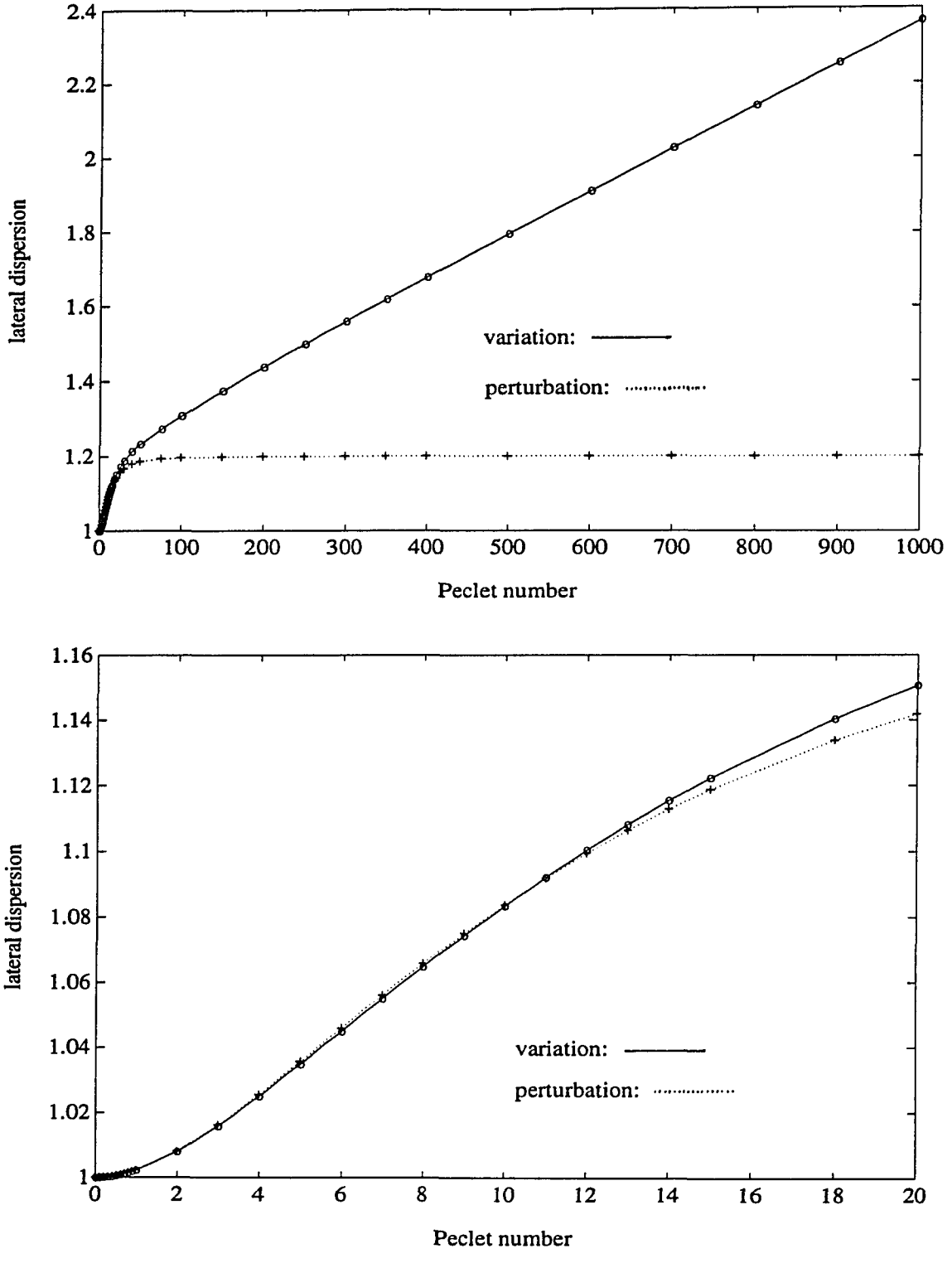

Figure 3 (b) Effective lateral dispersion constant vs. Peclet number: $\nu(0)=5$, $\rho(0)=0.1$

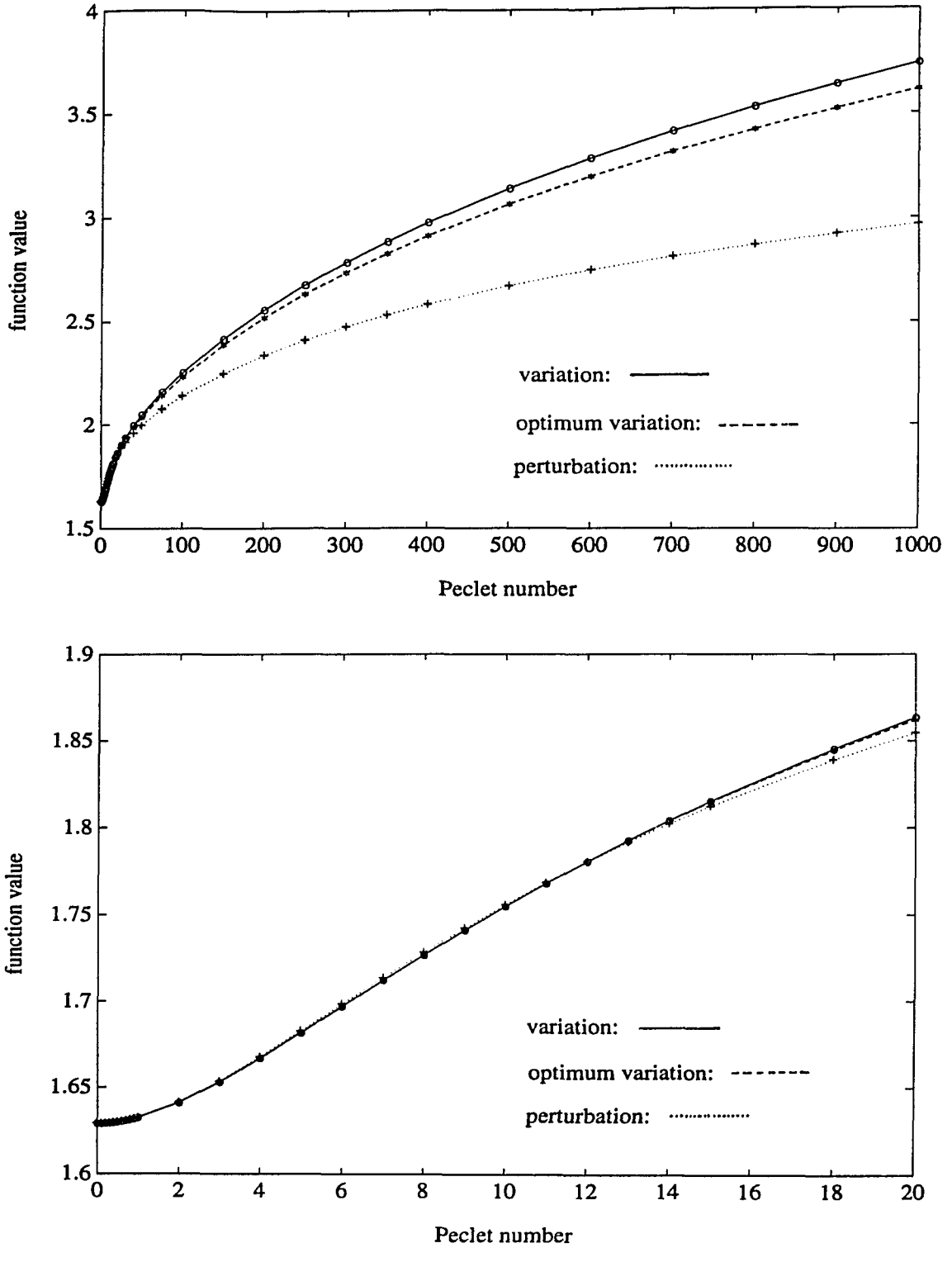

Figure 3 (c) $\frac{1}{2}\ln(\det \mathbf{D}_{eff})$ vs. Peclet number: $\nu(0)=5$, $\rho(0)=0.1$

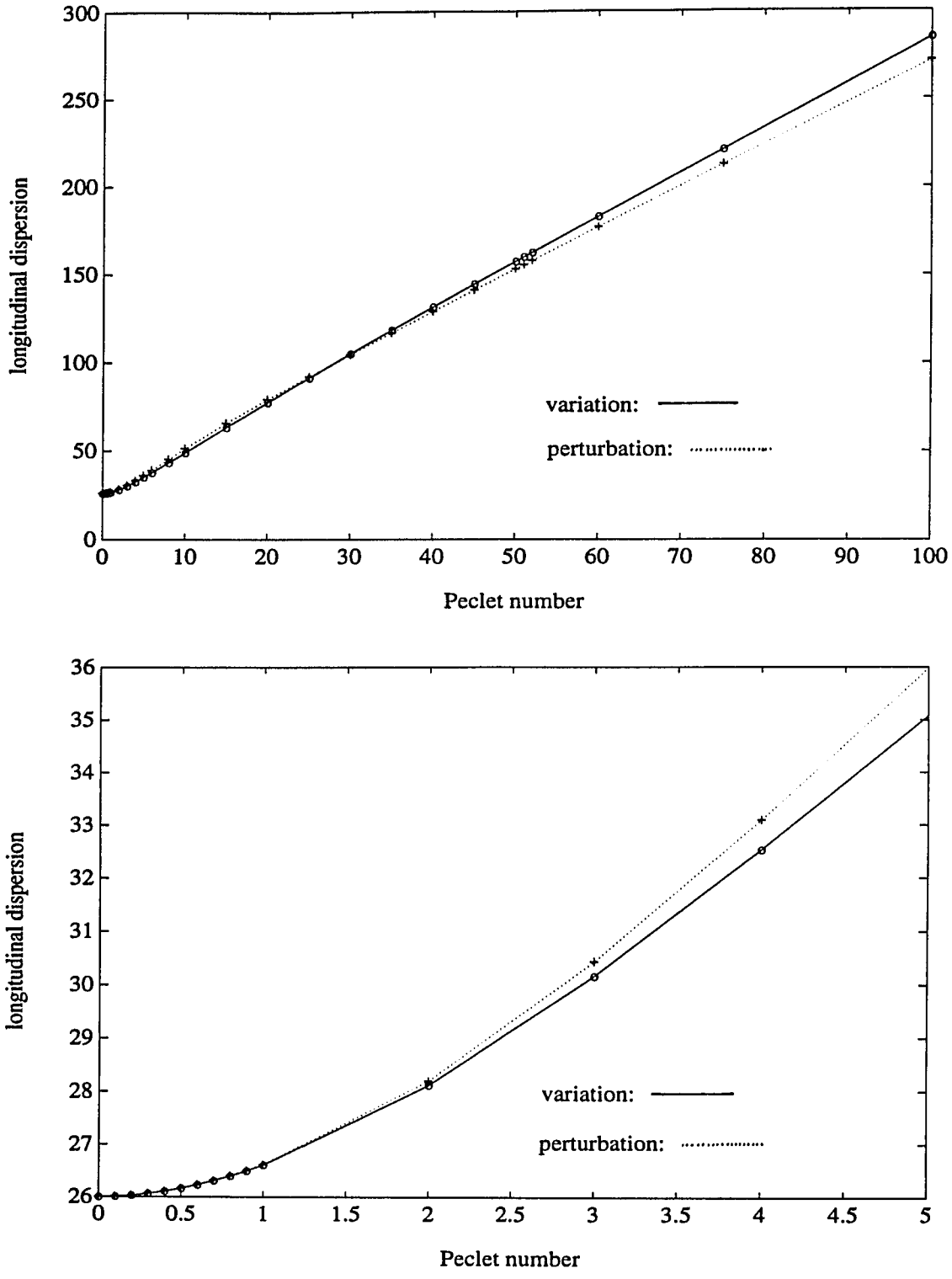

Figure 4 (a) Effective longitudinal dispersion constant vs. Peclet number: $\nu(0)=5$, $\rho(0)=1.0$

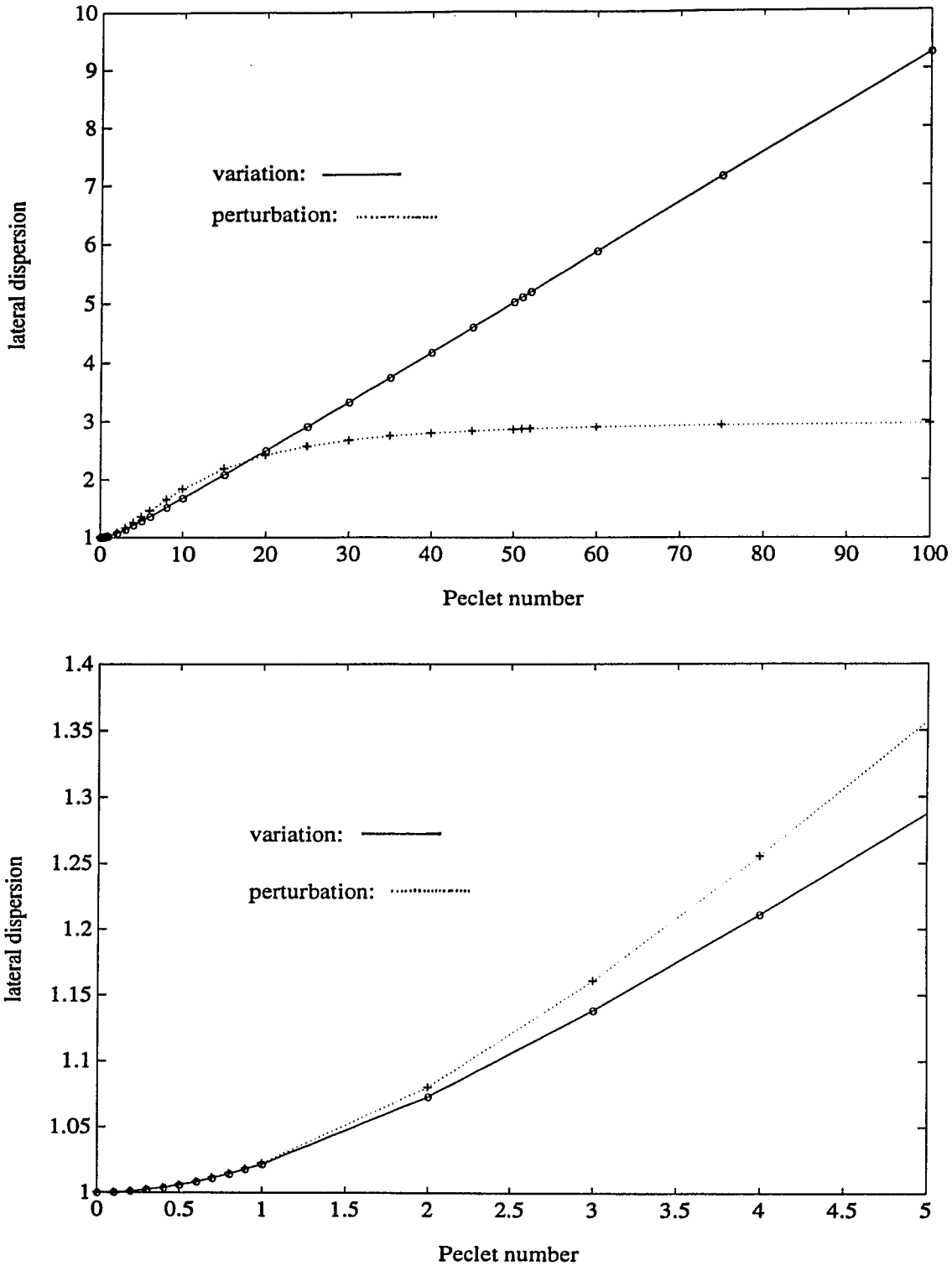

Figure 4 (b) Effective lateral dispersion constant vs. Peclet number: $\nu(0)=5$, $\rho(0)=1.0$

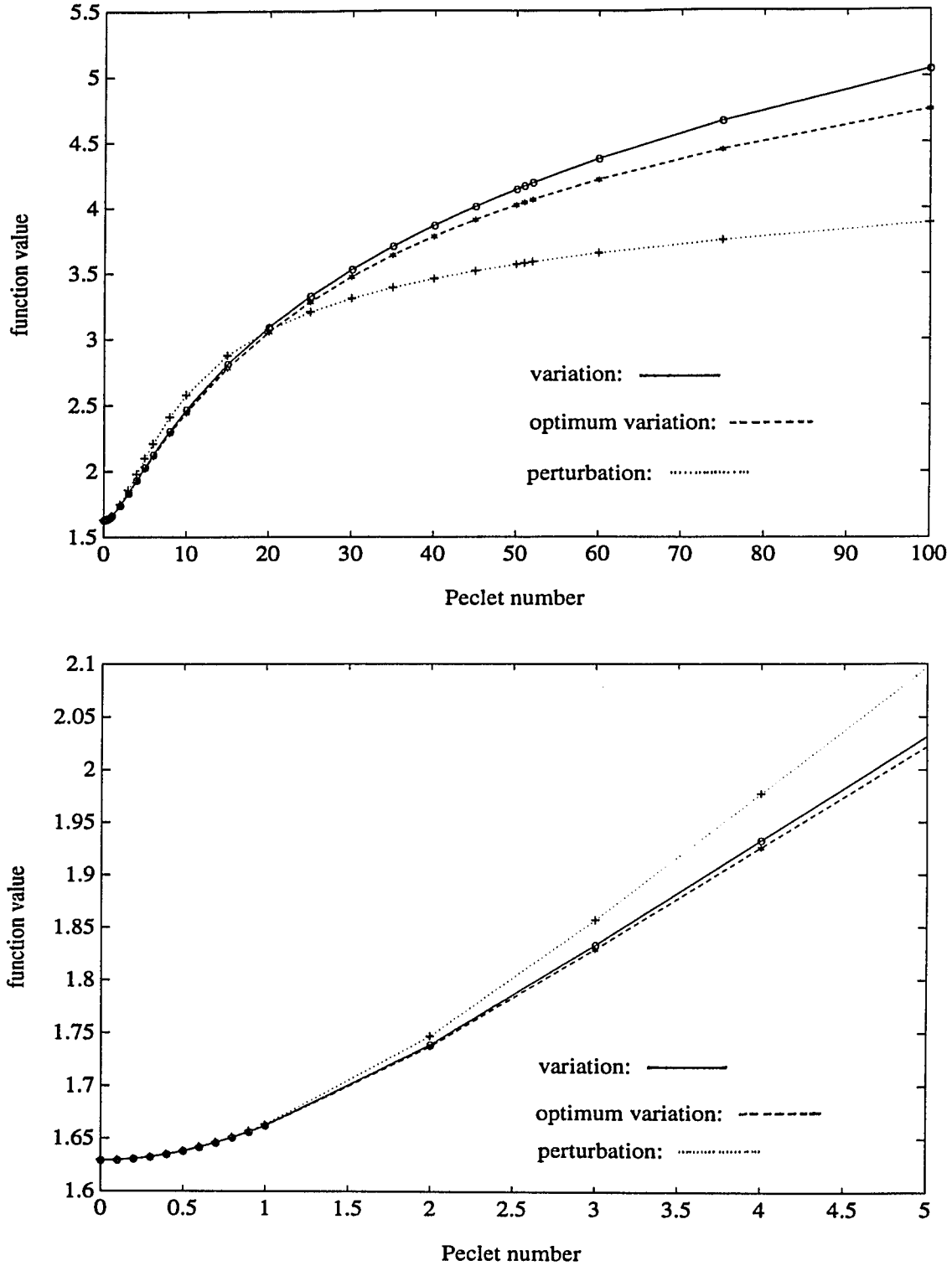

Figure 4 (c) $\frac{1}{2}\ln(\det \mathbf{D}_{eff})$ vs. Peclet number: $\nu(0)=5$, $\rho(0)=1.0$

limiting case of Eq. (5.3.1b), it does agree with the limiting case of Eq. (5.3.1a), so our choice is not only necessary in practice, but reasonable as well. We can easily incorporate our knowledge of the first two moments of x in S_A. Although α is known for the free space problem, we can leave it unspecified in S_A, assuming only that $\alpha \geq 1$. This will allow us to frame the first passage time calculation a little more generally. We note that

$$G'(x,t;x_0,t_0)=\frac{1}{[4\pi E(t^\alpha-t_0{}^\alpha)]^{1/2}}\exp\left\{-\frac{(x-x_0)^2}{4E(t^\alpha-t_0{}^\alpha)}\right\} \tag{5.3.2}$$

satisfies

$$\left[\frac{\partial}{\partial t}-\alpha E t^{\alpha-1}\frac{\partial^2}{\partial x^2}\right]G'(x,t;x_0,t_0)=\delta(x-x_0)\delta(t-t_0) \tag{5.3.3}$$

and that

$$\begin{aligned}G'(x_{N+1},t_{N+1};x_0,t_0)=&\int dx_N \frac{1}{[4\pi E(t_{N+1}{}^\alpha-t_N{}^\alpha)]^{1/2}}\times\\ \times&\exp\left\{-\frac{(x_{N+1}-x_N)^2}{4E(t_{N+1}{}^\alpha-t_N{}^\alpha)}\right\}G'(x_N,t_N;x_0,t_0)\end{aligned} \tag{5.3.4}$$

for free space. Therefore, imposing the boundary conditions of the first passage time problem at $x=\pm L$, and working from analogy with the e^{-W} of Eq. (4.2.29), we will take

$$\begin{aligned}e^{-W_A}=&\int dy_N \prod_{j=1}^{N-1}\int dx_j dy_j \prod_{k=0}^{N-1}\int\frac{dp_k}{2\pi}\prod_{l=0}^{N-1}\sum_{n_l=-\infty}^{+\infty}(-)^{n_l}\frac{1}{(4\pi D\Delta t)^{N/2}}\exp\left\{-\sum_{m=0}^{N-1}\frac{(y_{m+1}-y_m)^2}{4D\Delta t}\right\}\times\\ \times&\exp\left\{\sum_{m=0}^{N-1}\left[-E(t_{m+1}{}^\alpha-t_m{}^\alpha)p_m{}^2+ip_m(x_{m+1}-2n_mL-(-)^{n_m}x_m)\right]\right\}.\end{aligned} \tag{5.3.5}$$

At this point E and α are undetermined variational parameters. From these definitions, we can see that

$$\begin{aligned}S-S_A=&\sum_{m=0}^{N-1}p_m{}^2\left[D\Delta t-E(t_{m+1}{}^\alpha-t_m{}^\alpha)\right]-\frac{1}{2}\sum_{m=0}^{N-1}\sum_{q=0}^{N-1}\sigma^2\delta(y_{m+1}-y_{q+1})\times\\ \times&\left[\frac{n_mL}{D}+\frac{(-1+(-)^{n_m})x_m}{2D}-ip_m\Delta t\right]\left[\frac{n_qL}{D}+\frac{(-1+(-)^{n_q})x_q}{2D}-ip_q\Delta t\right].\end{aligned} \tag{5.3.6}$$

After some work, we obtain

$$e^{-W_A}=\frac{1}{[4\pi E(t_N{}^{\alpha}-t_0{}^{\alpha})]^{1/2}}\sum_{n=-\infty}^{+\infty}(-)^n\exp\left\{-\frac{(x_N-2nL-(-)^n x_0)^2}{4E(t_N{}^{\alpha}-t_0{}^{\alpha})}\right\} \tag{5.3.7}$$

and

$$e^{-W_A}<S-S_A>=\frac{[D(t_N-t_0)-E(t_N{}^{\alpha}-t_0{}^{\alpha})+4\sigma^2(t_N{}^{3/2}-t_0{}^{3/2})/3(4\pi D)^{1/2}]}{2E(t_N{}^{\alpha}-t_0{}^{\alpha})[4\pi E(t_N{}^{\alpha}-t_0{}^{\alpha})]^{1/2}}\times$$
$$\times\sum_{n=-\infty}^{+\infty}(-)^n\exp\left\{-\frac{(x_N-2nL-(-)^n x_0)^2}{4E(t_N{}^{\alpha}-t_0{}^{\alpha})}\right\}\left\{1-\frac{(x_N-2nL-(-)^n x_0)^2}{2E(t_N{}^{\alpha}-t_0{}^{\alpha})}\right\}. \tag{5.3.8}$$

We have in $W_{eff}=W_A+<S-S_A>$ an upper bound for W. We expect the bound to be most reliable at the distribution's point of maximum probability, $x_N=x_0$, as this is where the most representative tracer particles still in the interval would be. Since we have assumed that the particle starts exactly between the two absorbing walls, $x_0=0$. We take $t_0=0$ with no loss of generality, and set $t_N=t$. The appropriate quantities become

$$e^{-W_A}\to\frac{1}{(4\pi Et^{\alpha})^{1/2}}\sum_{n=-\infty}^{+\infty}(-)^n\exp\left\{-\frac{n^2L^2}{Et^{\alpha}}\right\} \tag{5.3.9}$$

and

$$e^{-W_A}<S-S_A>\to\left[Dt-Et^{\alpha}+\frac{4\sigma^2t^{3/2}}{3(4\pi D)^{1/2}}\right]\frac{1}{2Et^{\alpha}(4\pi Et^{\alpha})^{1/2}}\times$$
$$\times\sum_{n=-\infty}^{+\infty}(-)^n\exp\left\{-\frac{n^2L^2}{Et^{\alpha}}\right\}\left\{1-\frac{2n^2L^2}{Et^{\alpha}}\right\}. \tag{5.3.10}$$

The values of the free parameters are fixed by setting $\frac{\partial}{\partial E}W_{eff}=0$, which reduces to

$$Et^{\alpha}=Dt+\frac{4\sigma^2t^{3/2}}{3(4\pi D)^{1/2}}. \tag{5.3.11}$$

In other words, the optimum value of $e^{-W_A}<S-S_A>$ is zero. In the long-time limit, $Et^{\alpha}\to\frac{4\sigma^2t^{3/2}}{3(4\pi D)^{1/2}}$, so $E\to\frac{4\sigma^2}{3(4\pi D)^{1/2}}$ and $\alpha\to3/2$. It is interesting to note here that a first order perturbation expansion in powers of the fluctuations corresponds to $Et^{\alpha}=Dt$ in Eqs. (5.3.10) and (5.3.11). Thus the first order perturbative result is itself a lower bound, and not generally the optimal one (Feynman (1955)).

Setting as before $x_0=0$, $t_0=0$, $x_N=x$, and $t_N=t$, and integrating over the final vertical position, the variational bound for the average concentration becomes

$$<G'(x,t)>=\frac{1}{(4\pi Et^{3/2})^{1/2}}\sum_{n=-\infty}^{+\infty}(-)^n\exp\left\{-\frac{(x-2nL)^2}{4Et^{3/2}}\right\} \tag{5.3.12}$$

with E given above. We can obtain the exit time distribution via $p(t)=-\frac{\partial}{\partial t}\int_{-L}^{+L}dx<G'(x,t)>$ (cf. Eq. (1.2.6)), but this would involve a very difficult summation of error functions. We instead rewrite $p(t)$ using the equation of motion for $<G'(x,t)>$, Eq. (5.3.3):

$$p(t)=\int_{-L}^{+L}dx\left[-\frac{\partial}{\partial t}<G'(x,t)>\right]=\int_{-L}^{+L}dx\left[-\alpha Et^{\alpha-1}\frac{\partial^2}{\partial x^2}<G'(x,t)>\right]. \tag{5.3.13}$$

Note that the exit time distribution is essentially the total current out of the region of interest. We find from (5.3.12) and (5.3.13) that

$$p(t)=\frac{3L}{2t}\frac{1}{(4\pi Et^{3/2})^{1/2}}\sum_{n=-\infty}^{+\infty}(-)^n(1-2n)\exp\left\{-\frac{L^2(1-2n)^2}{4Et^{3/2}}\right\}. \tag{5.3.14}$$

We can compute the sum

$$\sum_{n=-\infty}^{+\infty}(-)^n(1-2n)\exp\left\{-\frac{L^2(1-2n)^2}{4Et^{3/2}}\right\} \tag{5.3.15}$$

by approximating it as an integral, then, either by completing the square or by the method of steepest descent. The sum becomes

$$\left[\frac{\pi Et^{3/2}}{L^2}\right]^{3/2}\exp\left\{-\frac{\pi^2Et^{3/2}}{4L^2}\right\}. \tag{5.3.16}$$

This result depends on the assumption that $\frac{\pi^2Et^{3/2}}{8L^2}\gg 1$, for if $\frac{8L^2}{\pi^2Et^{3/2}}\gg 1$, we expect the sum would be dominated by its largest term, $n=0$. In this approximation,

$$p(t)\to\frac{\sigma^2t^{1/2}\pi^{1/2}}{D^{1/2}L^2}\exp\left\{-\frac{\sigma^2t^{3/2}\pi^{3/2}}{6L^2D^{1/2}}.\right\} \tag{5.3.17}$$

This is not a simple exponential, as occurs in the case of two layers (Lee and Koplik (1995)).

The mean first passage time

$$<T>=\int_0^{+\infty} dt\, t\, p(t) \rightarrow \frac{6^{5/3} D^{1/3} L^{4/3}}{\sigma^{4/3}\pi^2} \int_0^{+\infty} dt\, t^{3/2} \exp\left\{-t^{3/2}\right\} \tag{5.3.18}$$

is proportional to $L^{4/3}$, as predicted by the naive argument of Sec. 4.2. The variational estimate of $<T>$ in (5.3.18) is actually a lower bound for the exact quantity. Since $W \leq W_{eff}$, we have $e^{-W} \geq e^{-W_{eff}}$, from which it follows that $\int_{-L}^{+L} dx e^{-W} \geq \int_{-L}^{+L} dx e^{-W_{eff}}$. In other words, we have a lower bound for the probability that a tracer particle is still within the interval. Since

$$<T>=\int_0^{\infty} dt\, t(-)\frac{\partial}{\partial t}\int_{-L}^{+L} dx e^{-W} = \int_0^{\infty} dt \int_{-L}^{+L} dx e^{-W}, \tag{5.3.19}$$

our estimate of $<T>$ is a lower bound for its exact value. In the limit of large L, our result of $<T> \sim L^{4/3}$ is therefore consistent with Redner's result $<T> \sim (L \ln L)^{4/3}$ (Redner (1994)).

Chapter 6

Summary

We have applied Feynman's variational method, based on path integrals, to problems arising from flow of a single fluid through a porous medium. Results obtained by the variational method are compared to results obtained by first-order perturbation theory, which is the technique usually applied to such problems. For the permeability problem, and the tracer problem at small P, the variational results are consistent with first-order perturbative results. For the tracer problem at large P, the variational method predicts the expected linear dependence of the effective dispersion tensor on P, which perturbation theory does not. This indicates that, for the problems considered here and others like them, a first-order perturbation expansion can be of limited utility. We expect that the variational method could be used to study a wider range of problems for which perturbation theory is inadequate, since development of the method assumes only that the problem at hand can be put into the path-integral formulation, and that the problem involves averaging over fluctuations. Our results for the permeability problem were restricted in range to $\rho(0) \leq 3/8$, due to the fact that we used a Gaussian, rather than a log-normal probability distribution function for the permeability fluctuations. This substitution was necessary in order to get a clean computational result, and not in order to develop the method itself. It points to the method's chief drawback, which is that the

fluctuations that can be handled with reasonable ease are limited to those with Gaussian distributions. However, it also obscures the method's chief advantage, which is that it works for any Gaussian distribution, and not merely one for which the variance is small compared to the mean, or one for which the fluctuations are weakly correlated. This advantage suggests other problems for which the method may prove useful, e.g., anomalous (non-Brownian) dispersion, which can arise in flow through a porous medium if the velocity fluctuations are strongly correlated (Koch and Brady (1988)).

We have also used Feynman's variational method to approximate the Green function corresponding to convective-diffusive transport through a layered medium with layering parallel to x and absorbing boundaries at $x=\pm L$. From this Green function, we have obtained a variational estimate of the exit time distribution and the mean first passage time for a test particle starting at $x=0$. Our method provides a lower bound for the mean first passage time; in the limit of large L, our result $<T>\sim L^{4/3}$ is therefore consistent with Redner's result $<T>\sim(L\ln L)^{4/3}$ (Redner (1994)). We expect our exit time distribution will give increasingly unsatisfactory results for higher moments of the first passage time, since our variational bound for the average Green function is Gaussian, while the known tail of the average Green function (Eq. (5.3.16)) has broader wings than a Gaussian, and the wings of a distribution more strongly influence its higher moments.

A very interesting aspect of our variational result for the Green function of the first passage problem is that one would get the same result by a direct application of King's partial-summation perturbation approach (King (1987)). As our calculation is somewhat more involved than King's, one could reasonably wonder if the extra trouble is necessary. Perhaps it is not strictly necessary, but it does give us an alternative way of thinking about what we do to get the result. King's method amounts to the summation of a particularly convenient subset of terms of the full perturbation expansion. Feynman's variational method, on the other hand,

attempts to find the Gaussian distribution which is a best lower bound to the actual Green function. These two methods give the same result for this problem because motion transverse to the layering is not affected by convection, leaving all the interesting enhanced dispersion to take place in one dimension. The story would be different if convection were not parallel to the layering; the interplay between convection and diffusion would no longer induce long-term correlations in time for fluctuations in the direction of flow, and the overall effective behaviour would be normal diffusion with enhanced coefficients both parallel and transverse to the flow (Matheron and de Marsily (1980)). Of course, strictly speaking, the perturbation method is supposed to be limited to situations for which the perturbed state and the averaged state are close in some sense to the unperturbed state. For this problem, then, the perturbation expansion would be expected to fail at large t, even as this is the parameter range of interest.

Appendix

Perturbation theory

In this appendix we apply to the CDE the perturbative method that King (1987) applied to the permeability problem. The Green function for the CDE $G(\mathbf{r},\mathbf{r}_0,t-t_0)$ is defined by Eq. (4.1.8), where the dispersion tensor $\mathbf{D}(\mathbf{r})\equiv\mathbf{D}_0$ is constant, and the incompressible velocity $\mathbf{u}(\mathbf{r})\equiv\mathbf{u}_0+\mathbf{u}_1(\mathbf{r})$ fluctuates. The unperturbed Green function $G_0(\mathbf{r}-\mathbf{r}_0,t-t_0)$, defined by Eq. (4.1.1), is the zero-order approximation to $G(\mathbf{r},\mathbf{r}_0,t-t_0)$. We set the left-hand sides of Eqs. (4.1.1) and (4.1.8) equal to one another, and consider the Fourier transform of the resulting equation:

$$G(\mathbf{k},\mathbf{k}_0,\omega)=G_0(\mathbf{k},\omega)(2\pi)^3\delta(\mathbf{k}+\mathbf{k}_0)-G_0(\mathbf{k},\omega)\int\frac{d\mathbf{q}}{(2\pi)^3}i\mathbf{k}\cdot\mathbf{u}_1(\mathbf{q})G(\mathbf{k}-\mathbf{q},\mathbf{k}_0,\omega), \qquad \text{(A1)}$$

where

$$f(\mathbf{r})\equiv\int\frac{d\mathbf{k}}{(2\pi)^3}e^{i\mathbf{k}\cdot\mathbf{r}}f(\mathbf{k}) \qquad \text{(A2)}$$

and

$$g(t)\equiv\int\frac{d\omega}{2\pi}e^{-i\omega t}g(\omega). \qquad \text{(A3)}$$

Equation (A1) can be solved by iteration. The zero-order approximation is

$$G(\mathbf{k},\mathbf{k}_0,\omega)=G_0(\mathbf{k},\omega)(2\pi)^3\delta(\mathbf{k}+\mathbf{k}_0);$$

this is fed back into (A1) under the integration to get the first-order approximation, the first-order approximation is fed back into (A1) under the integration to get the second-order approximation, and so on. We obtain a series solution of (A1):

$$G(\mathbf{k},\mathbf{k}_0,\omega)=G_0(\mathbf{k},\omega)(2\pi)^3\delta(\mathbf{k}+\mathbf{k}_0)-G_0(\mathbf{k},\omega)i\mathbf{k}\cdot\mathbf{u}_1(\mathbf{k}+\mathbf{k}_0)G_0(-\mathbf{k}_0,\omega)$$
$$-G_0(\mathbf{k},\omega)\int\frac{d\mathbf{q}}{(2\pi)^3}\mathbf{k}\cdot\mathbf{u}_1(\mathbf{q})G_0(\mathbf{k}-\mathbf{q},\omega)(-\mathbf{k}_0)\cdot\mathbf{u}_1(\mathbf{k}-\mathbf{q}+\mathbf{k}_0)G_0(-\mathbf{k}_0,\omega)+\cdots. \tag{A4}$$

The Fourier-space correlation function for the velocity fluctuations is given by (2.2.9). The average of $G(\mathbf{k},\mathbf{k}_0,\omega)$ will be proportional to $(2\pi)^3\delta(\mathbf{k}+\mathbf{k}_0)$, so we define

$$<G(\mathbf{k},\mathbf{k}_0,\omega)>\equiv<G(\mathbf{k},\omega)>(2\pi)^3\delta(\mathbf{k}+\mathbf{k}_0). \tag{A5}$$

Finally, taking the average of (A4), we get

$$<G(\mathbf{k},\omega)>=G_0(\mathbf{k},\omega)$$
$$-G_0^2(\mathbf{k},\omega)\int\frac{d\mathbf{q}}{(2\pi)^3}\rho(q^2)G_0(\mathbf{k}-\mathbf{q})\mathbf{k}\cdot(\mathbf{I}-\hat{\mathbf{q}}\hat{\mathbf{q}})\cdot\mathbf{u}_0\mathbf{u}_0\cdot(\mathbf{I}-\hat{\mathbf{q}}\hat{\mathbf{q}})\cdot\mathbf{k}+\cdots. \tag{A6}$$

The information concerning $<G(\mathbf{k},\omega)>$ can be more easily understood if it is differently arranged. From Eqs. (4.1.1), (A2), and (A3),

$$G_0(\mathbf{k},\omega)=\frac{1}{\mathbf{k}\cdot\mathbf{D}_0\cdot\mathbf{k}+i\mathbf{u}_0\cdot\mathbf{k}-i\omega}. \tag{A7}$$

This suggests that $<G(\mathbf{k},\omega)>$ would be less convenient to examine than its inverse, which can be obtained by algebraic inversion of (A6):

$$<G(\mathbf{k},\omega)>^{-1}=\mathbf{k}\cdot\mathbf{D}_0\cdot\mathbf{k}+i\mathbf{u}_0\cdot\mathbf{k}-i\omega+$$
$$+\int\frac{d\mathbf{q}}{(2\pi)^3}\rho(q^2)G_0(\mathbf{k}-\mathbf{q},\omega)\mathbf{k}\cdot(\mathbf{I}-\hat{\mathbf{q}}\hat{\mathbf{q}})\cdot\mathbf{u}_0\mathbf{u}_0\cdot(\mathbf{I}-\hat{\mathbf{q}}\hat{\mathbf{q}})\cdot\mathbf{k}+\cdots. \tag{A8}$$

Notice that the integral in (A8) is of the form $\mathbf{k}\cdot\mathbf{F}(\mathbf{k},\omega)\cdot\mathbf{k}$; in fact, the contribution of any higher-order term is also of this form. Thus we define an effective dispersion tensor $\mathbf{D}_{eff}(\mathbf{k},\omega)$:

$$<G(\mathbf{k},\omega)>^{-1}\equiv\mathbf{k}\cdot\mathbf{D}_{eff}(\mathbf{k},\omega)\cdot\mathbf{k}+i\mathbf{u}_0\cdot\mathbf{k}-i\omega, \tag{A9}$$

where (A9) should be considered in conjunction with (A8). We wish to find the large-distance and long-time properties, and so consider $\mathbf{D}_{eff}(\mathbf{0},0)$.

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