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Excerpt
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1 Aperitifs

Non-equilibrium statistical physics describes the time evolution of many-particle systems. The individual particles are elemental interacting entities which, in some situations, can change in the process of interaction. In the most interesting cases, interactions between particles are strong and hence a deterministic description of even a few-particle system is beyond the reach of any exact theoretical approach. On the other hand, many-particle systems often admit an analytical statistical description when their number becomes large. In that sense they are *simpler* than few-particle systems. This feature has several different names – the law of large numbers, ergodicity, etc. – and it is one of the reasons for the spectacular successes of statistical physics and probability theory.

Non-equilibrium statistical physics is also quite different from other branches of physics, such as the “fundamental” fields of electrodynamics, gravity, and high-energy physics that involve a reductionist description of few-particle systems, as well as applied fields, such as hydrodynamics and elasticity, that are primarily concerned with the consequences of fundamental governing equations. Some of the key and distinguishing features of non-equilibrium statistical physics include the following:

- there are no basic equations (like Maxwell equations in electrodynamics or Navier–Stokes equations in hydrodynamics) from which the rest follows;
- it is intermediate between fundamental and applied physics;
- common underlying techniques and concepts exist in spite of the wide diversity of the field;
- it naturally leads to the creation of methods that are useful in applications outside of physics (for example the Monte Carlo method and simulated annealing).

Our guiding philosophy is that, in the absence of underlying principles or governing equations, non-equilibrium statistical physics should be oriented toward studying concrete interacting particle systems rather than developing a theoretical formalism.

1.1 Diffusion

Let’s start by looking briefly at the random walk to illustrate a few key ideas and to introduce several useful analysis tools that can be applied to more general problems.

For the symmetric diffusion on a line, the probability density

$$\text{Prob}\,[\text{particle} \in (x, x+dx)] \equiv P(x,t)\,dx \tag{1.1}$$

satisfies the diffusion equation

$$\frac{\partial P}{\partial t} = D\frac{\partial^2 P}{\partial x^2}. \tag{1.2}$$

As we discuss soon, this equation describes the continuum limit of an unbiased random walk. The diffusion equation must be supplemented by an initial condition that we take to be $P(x,0) = \delta(x)$, corresponding to a walk that starts at the origin.

Dimensional analysis

Let's pretend that we don't know how to solve (1.2) and try to understand the behavior of the walker without explicit solution. What is the mean displacement $\langle x\rangle$? There is no bias, so clearly

$$\langle x\rangle \equiv \int_{-\infty}^{\infty} x\, P(x,t)\, dx = 0.$$

The next moment, the mean-square displacement,

$$\langle x^2\rangle \equiv \int_{-\infty}^{\infty} x^2\, P(x,t)\, dx$$

is non-trivial. Obviously, it should depend on the diffusion coefficient D and time t. We now apply dimensional analysis to determine these dependences. If L denotes the unit of length and T denotes the time unit, then from (1.2) the dimensions of $\langle x^2\rangle$, D, and t are

$$[\langle x^2\rangle] = L^2, \qquad [D] = L^2/T, \qquad [t] = T.$$

The only quantities with units of length squared that can be formed from these parameters are the mean-square displacement itself and the product Dt. Hence

$$\langle x^2\rangle = C \times Dt. \tag{1.3}$$

Equation (1.3) is one of the central results in non-equilibrium statistical physics, and we derived it using just dimensional analysis! To determine the numerical constant $C = 2$ in (1.3) one must work a bit harder (e.g. by solving (1.2), or by multiplying Eq. (1.2) by x^2 and integrating over the spatial coordinate to give $d\langle x^2\rangle/dt = 2D$).

This seemingly trivial reasoning works for much more complex problems, such as estimating the age of the universe from its density or the energy of an atomic blast from the time dependence of the blast wave radius. Because of its simplicity and power, dimensional analysis should be used as the first resort for investigating real problems.

Scaling

Let's now apply dimensional analysis to the probability density $P(x,t|\,D)$; here D is explicitly displayed to remind us that the density does depend on the diffusion coefficient.

Since $[P] = L^{-1}$, the quantity $\sqrt{Dt}\, P(x,t|\, D)$ is dimensionless, so it must depend on dimensionless quantities only. From variables x, t, D we can form a single dimensionless quantity $x/\sqrt{Dt}$. Therefore the most general dependence of the density on the basic variables that is allowed by dimensional analysis is

$$P(x,t) = \frac{1}{\sqrt{Dt}}\, \mathcal{P}(\xi), \qquad \xi = \frac{x}{\sqrt{Dt}}. \tag{1.4}$$

The density depends on a single *scaling variable* rather than on two basic variables x and t. This remarkable feature greatly simplifies analysis of the typical partial differential equations that describe non-equilibrium systems. Equation (1.4) is often referred to as the *scaling ansatz*. Finding the right scaling ansatz for a physical problem often represents a large step toward a solution. For the diffusion equation (1.2), substituting in the ansatz (1.4) reduces this partial differential equation to the ordinary differential equation

$$2\mathcal{P}'' + \xi\mathcal{P}' + \mathcal{P} = 0.$$

Integrating twice and invoking both symmetry ($\mathcal{P}'(0) = 0$) and normalization, we obtain $\mathcal{P} = (4\pi)^{-1/2}\, e^{-\xi^2/4}$, and finally the Gaussian probability distribution

$$P(x,t) = \frac{1}{\sqrt{4\pi\, Dt}}\, \exp\left[-\frac{x^2}{4Dt}\right]. \tag{1.5}$$

In this example, the scaling form was rigorously derived from dimensional reasoning alone. In more complicated situations, arguments in favor of scaling are less rigorous, and scaling is usually achieved only in some asymptotic limit. The above example where scaling applies for all t is an exception; for the diffusion equation with an initial condition on a finite domain rather than a point support, scaling holds only in the limit $x, t \to \infty$, with the scaling variable ξ kept finite. Nevertheless, we shall see that, whenever it is applicable, scaling immediately advances the understanding of a problem.

Renormalization

The strategy of the renormalization group method is to understand the behavior on large "scales" – here meaning long times – by iterating the properties of random walks on smaller time scales. For the diffusion equation, we start with the identity

$$P(x,2t) = \int_{-\infty}^{\infty} P(y,t)\, P(x-y,t)\, dy, \tag{1.6}$$

which expresses the probability that the walk is at position x at time $2t$ in terms of the propagation from time 0 to t and from time t to $2t$. Mathematically, the probability distribution after time $2t$ is given by the convolution of the probability distribution to propagate from $(0,0)$ to (y,t) and then from (y,t) to $(x,2t)$. Equation (1.6) is known as a Chapman–Kolmogorov equation and it reflects the memory-less Markov nature of the random walk; more precisely, the Markov nature implies that propagation from (y,t) to $(x,2t)$ is the same as from $(0,0)$ to $(x-y,t)$. (Equation (1.6) is also the basis for the path integral treatment of diffusion processes but we will not delve into this subject here.)

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The convolution form of Eq. (1.6) calls out for applying the Fourier transform,

$$P(k,t) = \int_{-\infty}^{\infty} e^{ikx}\, P(x,t)\, dx, \tag{1.7}$$

that recasts (1.6) into the algebraic relation $P(k,2t) = [P(k,t)]^2$. The scaling form (1.4) shows that $P(k,t) = \mathcal{P}(\kappa)$ with $\kappa = k\sqrt{Dt}$, so the renormalization group equation is

$$\mathcal{P}(\sqrt{2}\,\kappa) = [\mathcal{P}(\kappa)]^2.$$

Taking logarithms and defining $z \equiv \kappa^2$, $Q(z) \equiv \ln \mathcal{P}(\kappa)$, we arrive at $Q(2z) = 2Q(z)$, whose solution is $Q(z) = -Cz$, or $P(k,t) = e^{-2k^2 Dt}$. (The constant $C = 2$ may be found, e.g. by expanding (1.7) for small k, $P(k,t) = 1 - k^2\langle x^2\rangle$, and recalling that $\langle x^2\rangle = 2Dt$.) Performing the inverse Fourier transform we recover (1.5). Thus the Gaussian probability distribution represents an exact solution to a renormalization group equation. This derivation shows that the renormalization group is ultimately related to scaling.

Master equation approach

The *master equation* provides a comprehensive way to describe the evolution of many non-equilibrium systems. Such systems may be described statistically by the probability that its state variables have specified values. The rate at which these state variables change in time is accounted for by the master equation. Let us illustrate this equation with the simple example of a symmetric random walk on a one-dimensional lattice. The walk is described by the probability $P_n(t)$ that the walk is at site n at time t. This probability evolves as

$$\frac{\partial P_n}{\partial t} = P_{n-1} + P_{n+1} - 2P_n. \tag{1.8}$$

The first two terms on the right account for the increase in P_n because of a hop from $n-1$ to n or because of a hop from $n+1$ to n, respectively. Similarly, the last term accounts for the decrease of P_n because of hopping from n to $n \pm 1$.

As we will discuss throughout this book, random walks underlie many aspects of non-equilibrium statistical physics. Chapter 2 will be devoted to understanding random walks and related diffusion processes. We will also present, in Chapters 2 and 10, physically motivated generalizations, including: (i) global bias in the hopping rates, (ii) long-range hopping, and (iii) hopping rates that are random functions of position. The insights gained from studying random walks will provide essential background for dealing with the governing equations that describe the evolution of non-equilibrium processes in interacting many-body systems.

1.2 Single-species annihilation/coalescence

In non-equilibrium statistical physics, we study systems that contain a macroscopic number of interacting particles. To understand collective behaviors it is useful to ignore complications resulting from finiteness, i.e. to focus on situations when the number of particles is infinite. Perhaps the simplest interacting infinite-particle systems of this kind are *single-species annihilation*, where particles diffuse freely and annihilate instantaneously upon contact, and *single-species coalescence*, where the reactants merge upon contact. These processes have played an important role in the development of non-equilibrium statistical physics and they provide excellent illustrations of techniques that can be applied to other infinite-particle systems.

These two processes are symbolically represented by the respective reaction schemes

$$A + A \longrightarrow \emptyset, \tag{1.9a}$$

$$A + A \longrightarrow A. \tag{1.9b}$$

The density $\rho(t)$ of A particles for both reactions obviously decays with time. The question is: how?

Hydrodynamic description

In the hydrodynamic approach, one assumes that the reactants are perfectly mixed at all times. This means that the density at every site is the same and that every particle has the same probability to react at the next instant. In this well-mixed limit, and also assuming the continuum limit, the particle density ρ in the coalescence reaction decays with time according to the *rate equation*

$$\frac{d\rho}{dt} = -K\rho^2. \tag{1.10}$$

Indeed, since two particles have to be at the same location for a reaction to occur, the right-hand side is proportional to the density squared. Here K is the reaction rate that describes the propensity for two diffusing particles to interact; the computation of this rate requires a detailed microscopic treatment (see Section 2.7). For the annihilation reaction, we can use essentially the same governing equation, namely $d\rho/dt = -2K\rho^2$, with now a prefactor of 2 to account for two particles being eliminated in each collision.

Equations of the form (1.10) are typical of a hydrodynamic description; the solution to this equation is

$$\rho(t) = \frac{\rho_0}{1 + K\rho_0 t} \sim (Kt)^{-1}, \tag{1.11}$$

where ρ_0 is the initial density. However, the true asymptotic behavior is more interesting and depends on the spatial dimension d:

$$\rho(t) \sim \begin{cases} t^{-1/2}, & d = 1, \\ t^{-1} \ln t, & d = 2, \\ t^{-1}, & d > 2. \end{cases} \tag{1.12}$$

The change at $d_c = 2$ illustrates the important notion of the critical dimension: above d_c, the rate equation description leads to asymptotically correct behavior; below d_c, this approach is wrong; at d_c, this approach is almost correct – it typically is in error by a logarithmic correction term.

To obtain a complete theory of the reaction, one might try to write formally exact equations for correlation functions. That is, if the two-argument function $\rho(\mathbf{r}, t)$ is the microscopic density, the true dynamical equation for $\rho(t) \equiv \langle\rho(\mathbf{r}, t)\rangle$ involves the second-order correlation functions (or correlators) $\langle\rho(\mathbf{r}, t)\rho(\mathbf{r}', t)\rangle$ since two particles need to be in proximity for a reaction to occur. Similarly, the equation for the second-order correlation functions involves third-order correlators, etc. These equations are hierarchical and the only way to proceed is to impose some sort of closure scheme in which higher-order correlators are factorized in terms of lower-order correlators. In particular, the hydrodynamic equation (1.10) is recovered if we assume that second-order correlators factorize; that is, $\langle\rho(\mathbf{r}, t)\rho(\mathbf{r}', t)\rangle = \langle\rho(\mathbf{r}, t)\rangle\langle\rho(\mathbf{r}', t)\rangle = \rho(t)^2$. Thus Eq. (1.10) is the factorized version of the Boltzmann equation for the annihilation process (1.9a). Attempts to describe this reaction scheme more faithfully by higher-order correlators have not been fruitful. Thus the revered kinetic theory approach is essentially useless for the innocent-looking annihilation process $A + A \to \emptyset$! Because of this failure of approaches that are based on traditional calculations, alternative methods are needed.

Dimensional analysis

Let's determine the dependence of the rate K on fundamental parameters of the reaction, i.e. on the diffusion coefficient D of the reactants and radius R of each particle. From Eq. (1.10), the dimension of the reaction rate is $[K] = L^d/T$, and hence the only possible dependence is

$$K = DR^{d-2}. \tag{1.13}$$

Here we omit a numerical factor of the order of one that cannot be determined within the realm of dimensional analysis; in the future, we shall often ignore such factors without explicit warning. Note that the reaction rate is not proportional to the cross-sectional area, R^{d-1}, but rather to R^{d-2}; this feature stems from the vagaries of diffusive motion; see also Section 2.7.

Using (1.13) in (1.10) and solving this equation yields

$$\rho(t) \sim \frac{1}{R^{d-2}Dt}. \tag{1.14}$$

We anticipate that the density ought to decay more quickly when the radius of the particles is increased. According to (1.14), this anticipation is true only when $d > 2$. Thus the rate equation could be correct in this regime. For $d = 2$, the decay is independent of the size of particles – already a surprise. For $d < 2$, we obtain the obviously wrong result that the density decays more slowly if particles are larger.

The density is actually *independent* of R for $d < 2$. This feature is self-evident for $d = 1$ because all that matters is the spacing between particles. If we now seek, on dimensional grounds, the density in the R-independent form $\rho = \rho(D, t)$, we find that the only possibility is $\rho \sim (Dt)^{-d/2}$, in agreement with the prediction of (1.12) in one dimension. In the context of the reaction rate, this slow decay is equivalent to a reaction rate that decreases with time. We will return to this point in the next chapter.

Heuristic arguments

Dimensional analysis often gives correct dependences but does not really explain why these behaviors are correct. For the annihilation process (1.9a), we can understand the one-dimensional asymptotic, $\rho \sim (Dt)^{-1/2}$, in a physical way by using a basic feature (1.3) of random walks: in a time interval t, each particle explores the region $\ell \sim \sqrt{Dt}$. Therefore the typical separation between surviving particles is of the order of ℓ, from which $\rho \sim \ell^{-1} \sim (Dt)^{-1/2}$ follows.

Guided by this understanding, let's try to understand (1.12) in all spatial dimensions. It is helpful to consider a slightly modified situation in which particles undergo random walks on a lattice in d dimensions (the lattice spacing plays the role of the particle radius). What is the average number of *distinct* sites $\mathcal{N}$ visited by a random walker after N steps? This question has a well-known and beautiful answer:

$$\mathcal{N} \sim \begin{cases} N^{1/2}, & d = 1, \\ N/\ln N, & d = 2, \\ N, & d > 2. \end{cases} \tag{1.15}$$

With a little contemplation, one should be convinced that the density in single-species annihilation scales as the inverse of the average number of sites visited by a random walker; if there is more than one particle in the visited region, it should have been annihilated previously. Thus (1.15) is equivalent to (1.12).

Exact solution in one dimension

Diffusion-controlled annihilation admits an exact solution in one dimension. This is an exceptional feature – most interacting infinite-particle systems cannot be solved, even in one dimension. Moreover, even in solvable cases, we can usually compute only a limited number of quantities. For one-dimensional annihilation, for example, while the density is known exactly, the distribution of distances ℓ between adjacent particles $P(\ell, t)$ is unknown, even in the simpler scaling limit $\ell, t \to \infty$, with $\xi = \ell/\sqrt{Dt}$ finite, where $P(\ell, t)$ can be written as $(Dt)^{-1}\,\mathcal{P}(\xi)$, with $\mathcal{P}$ as yet unknown.[1]

Exact results for diffusion-controlled annihilation will be presented in Chapters 8 and 13, where we develop the necessary technical tools. For now, let's consider diffusion-controlled coalescence, $A + A \longrightarrow A$, that *is* readily soluble in one dimension because it can be reduced to a two-particle problem. To compute the density, it is convenient to define particle labels so that in each collision the left particle disappears and the right particle survives (Fig. 1.1). Then to compute the survival probability of a test particle we

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[1] The $(Dt)^{-1}$ prefactor ensures that the "conservation law" $\int_0^\infty \ell\, P(\ell, t)\, d\ell = 1$ can be written in the manifestly time-independent form $\int_0^\infty \xi\, \mathcal{P}(\xi)\, d\xi = 1$.

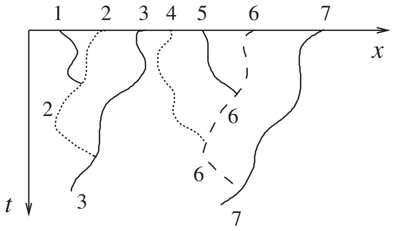

Fig. 1.1 **Space-time trajectories of diffusing particle in one dimension, showing the propagation of particle labels in diffusion-controlled coalescence, $A + A \to A$.**

may ignore all particles to the left. This reduction of the original two-sided problem to a one-sided problem considerably simplifies the analysis because only the closest particle to the right of the test particle is relevant. While the right neighbor can merge with other particles further to the right, these reactions never affect the fate of the test particle. Thus the system reduces to a soluble two-particle problem.

The distance between the test particle and its right neighbor undergoes diffusion with diffusivity $2D$ because the spacing diffuses at twice the rate of each particle. Consequently, the probability density $p(\ell, t)$ that the test particle is separated by distance ℓ from its right neighbor satisfies the diffusion equation subject to the absorbing boundary condition:

$$\frac{\partial p}{\partial t} = 2D\,\frac{\partial^2 p}{\partial \ell^2}\,, \qquad \text{with} \quad p(0,t) = 0. \tag{1.16}$$

The solution to (1.16) for an arbitrary initial condition $p(y, t=0)$ is

$$\begin{aligned} p(\ell,t) &= \frac{1}{\sqrt{8\pi Dt}} \int_0^\infty p(y,t=0)\,[e^{-(\ell-y)^2/8Dt} - e^{-(\ell+y)^2/8Dt}]\,dy \\ &= \frac{1}{\sqrt{2\pi Dt}} \exp\left(-\frac{\ell^2}{8Dt}\right) \int_0^\infty p(y,t=0)\, \exp\left(-\frac{y^2}{8Dt}\right) \sinh\left(\frac{\ell y}{4Dt}\right) dy. \end{aligned} \tag{1.17}$$

In the first line, the solution is expressed as the superposition of a Gaussian and an image anti-Gaussian that automatically satisfies the absorbing boundary condition. In the long-time limit, the integral on the second line tends to

$$\frac{\ell}{4Dt} \int_0^\infty y\, p(y, t=0)\, dy = \frac{\ell}{4Dt\rho_0},$$

where ρ_0 is the initial density. Therefore

$$p(\ell,t) \simeq \frac{\ell}{4Dt\rho_0\sqrt{2\pi Dt}} \exp\left(-\frac{\ell^2}{8Dt}\right),$$

leading to the asymptotic density decay

$$\rho(t) = \rho_0 \int_0^\infty p(\ell,t)\, d\ell \simeq (2\pi Dt)^{-1/2}, \tag{1.18}$$

which is independent of the initial density.

Since the interval length distribution $P(\ell,t)$ is equal to $\rho_0\, p(\ell,t)$, we see that for diffusion-controlled coalescence the scaled distribution reads

$$\mathcal{P}(\xi) = \frac{\xi}{4\sqrt{2\pi}}\,\exp\left(-\frac{\xi^2}{8}\right), \qquad \xi = \frac{\ell}{\sqrt{Dt}}.$$

1.3 Two-species annihilation

Consider two diffusing species A and B that are initially distributed at random with equal concentrations: $\rho_A(0) = \rho_B(0) = \rho_0$. When two particles of opposite species approach within the reaction radius, they immediately annihilate according to

$$A + B \longrightarrow \emptyset. \tag{1.19}$$

For this reaction, the density decreases as

$$\rho(t) \sim \begin{cases} t^{-d/4}, & d \le 4, \\ t^{-1}, & d > 4, \end{cases} \tag{1.20}$$

as $t \to \infty$, so the critical dimension is $d_c = 4$. This result shows that the hydrodynamic description is wrong even in the physically relevant case of three dimensions. A peculiar feature of Eq. (1.20) is the absence of logarithmic corrections for $d = d_c$. Typically, logarithmic corrections arise at the critical dimension and their absence for two-species annihilation is, as yet, unexplained.

In this example, neither a hydrodynamic description (that gives $\rho \sim t^{-1}$) nor dimensional analysis can explain the decay of the density. To understand why the naive approaches fail, consider a snapshot of a two-dimensional system at some time $t \gg 1$ (Fig. 1.2), where the system spontaneously organizes into a mosaic of alternating A and B domains. Because of this organization, annihilation can occur only along domain boundaries rather than throughout the system. This screening effect explains why the density is larger than in the hydrodynamic picture, where particles are taken to be well mixed.

A heuristic argument that is based on this domain picture allows us to determine the density decay in Eq. (1.20). In a spatial region of linear size ℓ, the initial number of A particles is

$$N_A = \rho_0 \ell^d \pm \sqrt{\rho_0 \ell^d}, \tag{1.21}$$

and similarly for B particles. Here the ± term signifies that the particle number in a finite region is a stochastic variable that typically fluctuates in a range of the order of $\sqrt{\rho_0 \ell^d}$ about the mean value $\rho_0 \ell^d$. Consequently, the typical value of the difference $N_A - N_B$ in a region of size ℓ is

$$N_A - N_B = \pm\sqrt{\rho_0 \ell^d}.$$

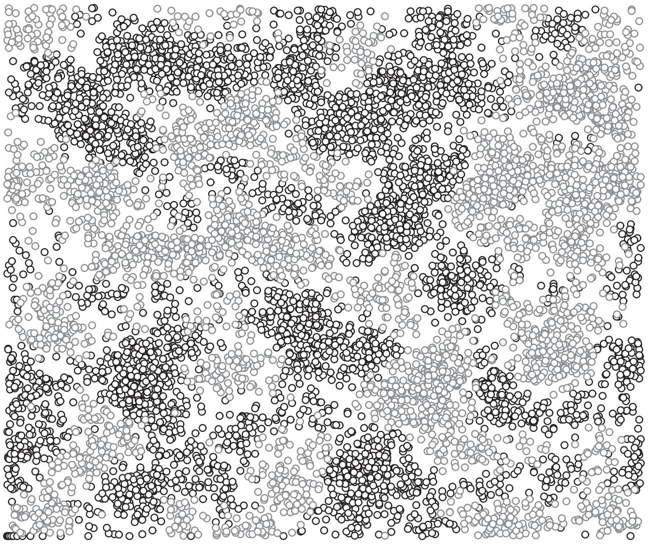

Fig. 1.2

Snapshot of the particle positions in two-species annihilation in two dimensions. The particle sizes are enlarged for visibility.

This number difference is not affected by annihilation events. Therefore after the minority species in a given region is eliminated, the local density becomes $\rho \sim \sqrt{\rho_0 \ell^d}/\ell^d$. Because of the diffusive spreading (1.3), the average domain size scales as $\ell \sim \sqrt{Dt}$, and hence

$$\rho(t) \sim \sqrt{\rho_0}\,(Dt)^{-d/4}. \tag{1.22}$$

In contrast to the single-species annihilation where the initial density is asymptotically irrelevant, the initial density affects the asymptotic behavior of two-species annihilation.

Finally, notice that the density decay cannot be obtained by dimensional analysis alone because now there are at least two independent length scales, the domain size $\sqrt{Dt}$ and the interparticle spacing. Additional physical input, here in the form of the domain picture, is needed to obtain the time dependence of the density.

1.4 Notes

There is considerable literature on the topics discussed in this introductory chapter. Random walks and diffusion are classic subjects for which essential background and additional references can be found in [1,2,3,4,5,6]. Dimensional analysis and the concept of scaling go back to Galileo [7]. A modern perspective and the historical roots of scaling are presented in [8]. A field where dimensional analysis and scaling are especially popular is hydrodynamics. An informative exposition appears in the book by Barenblatt [9] that discusses the connection between scaling, intermediate asymptotics, and the renormalization group. The latter connections are also emphasized in Goldenfeld's book [10]. Another very useful book that emphasizes the scaling approach for polymer physics is that of de Gennes [11]. The