Chapter 1

APERITIFS

Broadly speaking, non-equilibrium statistical physics describes the time-dependent 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 the deterministic description of even few-particle systems are beyond the reach of exact theoretical approaches. On the other hand, many-particle systems often admit an analytical statistical description when their number becomes large and 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 quite different from other branches of physics, such as the 'fundamental' fields of electrodynamics, gravity, and elementary-particle physics that involve a reductionist description of few-particle systems, and 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:

- no basic equations (like Maxwell equations in electrodynamics or Navier-Stokes equations in hydrodynamics) from which the rest follows;
- intermediate between fundamental applied physics;
- the existence of common underlying techniques and concepts in spite of the wide diversity of the field;
- non-equilibrium statistical physics naturally leads to the creation of methods that are quite useful in applications far removed from 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 explicit and illustrative examples rather than attempting to develop a theoretical formalism that is still incomplete.

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.

1.1 Diffusion

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? 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

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

The ratio $\langle x^2 \rangle / Dt$ is dimensionless and thus be constant, as a dimensionless quantity cannot depend on dimensional quantities. 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 $\frac{d}{dt}\langle x^2 \rangle = 2D$). We shall therefore use the power of dimensional analysis whenever possible.

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 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 simple dimensional reasoning. 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 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 where applicable, scaling provides a significant step toward the understanding of a problem.

Renormalization

The strategy of the renormalization group method is to understand the behavior on large 'scale'—here large time—iteratively in terms of the behavior on smaller scales. For the diffusion equation, we start with identity

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

that reflects the fact that the random walk is a Markov process. Namely, to reach x at time $2t$, the walk first reaches some intermediate point y at time t and then completes the journey to y in the remaining time 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.)

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

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

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

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

Taking logarithms and defining $z \equiv \kappa^2, Q(z) \equiv \ln \hat{\mathcal{P}}(\kappa)$, we arrive at $Q(2z) = 2Q(z)$, whose solution is $Q(z) = -Cz$, or $\hat{P}(k,t) = e^{-2k^2 Dt}$. (The constant $C = 2$ may be found, *e.g.*, by expanding (1.7) for small k, $\hat{P}(k,t) = 1 - k^2\langle x^2\rangle$, 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. Our derivation shows that the renormalization group is ultimately related to scaling.

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 development of non-equilibrium statistical physics and they provide excellent illustrations of techniques that can be applied to other infinite-particle systems.

The annihilation process is symbolically represented by the reaction scheme

$$A + A \longrightarrow \emptyset\,, \tag{1.8}$$

while the coalescence reaction is represented by

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

The density $n(t)$ of A particles for both reactions obviously decays with time; the question is: how?

Hydrodynamics

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 global particle density n for both annihilation and coalescence decays with time according to the *rate equation*

$$\frac{dn}{dt} = -Kn^2\,. \tag{1.10}$$

This equation reflects that fact that two particles are needed for a reaction to occur and the probability for two particle to be at the same location 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 chapter 4). The rate equation (1.10) is a typical hydrodynamic-like equation whose solution is

$$n(t) = \frac{n_0}{1 + Kn_0 t} \sim (Kt)^{-1}\,. \tag{1.11}$$

However, simulations show more interesting long-time behaviors that depends on the spatial dimension d:

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

The sudden change at $d_c = 2$ illustrates the important notion of the critical dimension: above d_c, the rate equation leads to asymptotically correct behavior; below d_c, the rate equation is wrong; at d_c, the rate equation 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 $\rho(\mathbf{r}, t)$ is the microscopic density, the true dynamical equation for $n(t) \equiv \langle\rho(\mathbf{r}, t)\rangle$ involves the second-order correlators $\langle\rho(\mathbf{r}, t)\rho(\mathbf{r}', t)\rangle$. Then an 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, $\langle\rho(\mathbf{r}, t)\rho(\mathbf{r}', t)\rangle = \langle\rho(\mathbf{r}, t)\rangle\langle\rho(\mathbf{r}', t)\rangle = n(t)^2$. Thus Eq. (1.10) is the factorized version of the Boltzmann equation for the annihilation process (1.8). Attempts to describe this reaction scheme more faithfully by higher-order correlators have not been fruitful. Thus the revered kinetic theory approach is helpless for the innocent-looking process (1.8)! Let's try some other approaches.

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), $[K] = L^d/T$, and the only possible dependence is [1]

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

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

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

We anticipate that the density ought to decay more quickly when the radius of the particles is increased. According to (1.14), this is true only when $d > 2$. Thus the rate equation could be correct in this regime. Surprisingly, however, 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. For $d = 2$, the decay is independent of the size of particles—already a bit of a surprising result. However, 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 fact is easy to see 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 $n(D, t)$, we find that the only possibility is $n \propto (Dt)^{-d/2}$ in agreement with 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.

[1] Here we omit a numerical factor of order one; in the future, we shall often ignore such factors without explicit warning.

Heuristic Arguments

Dimensional analysis often gives correct dependences but does not really explain why these behaviors are correct. For the annihilation process (1.8), we can understand the one-dimensional asymptotic, $n \sim (Dt)^{-1/2}$, in a physical way by using a basic feature (1.3) of random walks: in a time interval $(0, t)$, each particle explores the region $\ell \sim \sqrt{Dt}$, and therefore a typical separation between surviving particles is of order ℓ, from which $n \sim \ell^{-1} \sim (Dt)^{-1/2}$ follows.

Guided by this understanding, let's try to understand (1.12) for all dimensions. First, we slightly modify the process so that particles undergo diffusion on a lattice in d dimensions (lattice spacing plays the role of the radius). What is the average number of 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 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 that one particle in the visited region, it should have been annihilated previously. Thus (1.15) is essentially equivalent to (1.12).

Exact Solution in One Dimension

The diffusion-controlled annihilation process admits an exact solution in one dimension. This is an exceptional feature—most infinite-particle systems cannot be solved even in one dimension. Moreover, for these 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 scaling limit $\ell \to \infty$ and $t \to \infty$, with $\xi = \ell/\sqrt{Dt}$ being finite. Although numerical simulations strongly indicate that the interval length distribution approaches the scaling form, $P(\ell, t) \to (Dt)^{-1/2}\mathcal{P}(\xi)$, nobody yet knows how to compute the scaled length distribution $\mathcal{P}(\xi)$.

Exact results for the diffusion-controlled annihilation process will be presented later when we develop the necessary technical tools. However to illustrate a simple exact solution, 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. Then to compute the survival probability of a test particle we may ignore all particles to the left. Such a reduction of the original two-sided problem to a one-sided one is extremely helpful. Furthermore, only the closest particle to the right of the test particles is relevant—the right neighbor can merge with other particles further to the right; however, these reactions never affect the fate of the test particle. Thus the system reduces to a soluble two-particle problem.

The interparticle 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 $\rho(\ell, t)$ that the test particle is separated by distance ℓ from its right neighbor satisfies the diffusion equation subject to the absorbing boundary condition:

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

The solution (1.16) for an arbitrary initial condition $\rho_0(\ell)$ is

$$\begin{aligned} \rho(\ell, t) &= \frac{1}{\sqrt{8\pi Dt}} \int_0^\infty \rho_0(y) \left[e^{-(\ell-y)^2/8Dt} - e^{-(\ell+y)^2/8Dt} \right] dy \\ &= \frac{1}{\sqrt{2\pi Dt}} \exp\left(-\frac{\ell^2}{8Dt}\right) \int_0^\infty \rho_0(y) \exp\left(-\frac{y^2}{8Dt}\right) \sinh\left(\frac{\ell y}{4Dt}\right) dy\,. \end{aligned} \tag{1.17}$$

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 $\frac{\ell}{4Dt}\int_0^\infty dy\,\rho_0(y)\,y = \frac{\ell}{4Dtn_0}$. Therefore

$$\rho(\ell,t) \to \frac{\ell}{4Dtn_0\sqrt{2\pi Dt}}\,\exp\left(-\frac{\ell^2}{8Dt}\right),$$

so that the survival probability is

$$S(t) = \int_0^\infty \rho(\ell,t)\,d\ell \to n_0^{-1}(2\pi Dt)^{-1/2},$$

and the density $n(t) = n_0\,S(t)$ decays as

$$n(t) \to (2\pi Dt)^{-1/2} \quad \text{when} \quad t\to\infty\,. \tag{1.18}$$

To summarize, the interval length distribution $P(\ell,t)$ is just the probability density $\rho(\ell,t)$ conditioned on the survival of the test particle. Hence

$$P(\ell,t) \equiv \frac{\rho(\ell,t)}{S(t)} \to \frac{\ell}{4Dt}\,\exp\left(-\frac{\ell^2}{8Dt}\right).$$

The average interparticle spacing grows as $\sqrt{Dt}$ which equivalent to the particle density decaying as $1/\sqrt{Dt}$.

1.3 Two-Species Annihilation

Consider two diffusing species A and B which are initially distributed at random with equal concentrations: $n_A(0) = n_B(0) = n_0$. When two particles of opposite species approach within the reaction radius, they immediately annihilate:

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

For this reaction, the density decreases as

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

as $t\to\infty$, so the critical dimension is $d_c = 4$. This result shows that hydrodynamic description is wrong even in the most relevant three-dimensional case.

In this striking example, neither a hydrodynamic description (that gives $n \sim t^{-1}$) nor dimensional analysis can explain the decay of the density. Here, a simple heuristic argument helps us determine the density decay of Eq. (1.20). To understand why the naive approaches fail, consider a snapshot of a two-dimensional system at some time $t \gg 1$ (Fig. fig-aper-snapshot). We see that the system spontaneously organizes into a mosaic of alternating 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 much larger than in the hydrodynamic picture where particles are assumed to be well-mixed.

To turn this picture into a semi-quantitative estimate for the density, note that in a spatial region of linear size ℓ, the initial number of A particles is $N_A = n_0\ell^d \pm (n_0\ell)^{d/2}$ and similarly for B particles. Here the $\pm$ term signifies that the particle number in a finite region is a stochastic variable that typically fluctuates in a range of order $(n_0\ell)^{d/2}$ about the mean value $n_0\ell^d$. The typical value of the difference $N_A - N_B$ for this d-dimensional region

$$N_A - N_B = \pm(n_0\ell)^{d/2},$$

arises because of initial fluctuations and is not affected by annihilation events. Therefore after the minority species in a given region is eliminated, the local density becomes $n \sim (n_0\ell)^{d/2}/\ell^d$. Because of the diffusive spreading (1.3), the average domain size scales as $\ell \sim \sqrt{Dt}$, and thus $n \sim \sqrt{n_0}\,(Dt)^{-d/4}$. Finally, notice that the density decay cannot be obtained by dimensional analysis alone because now are there 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 $n(t)$.

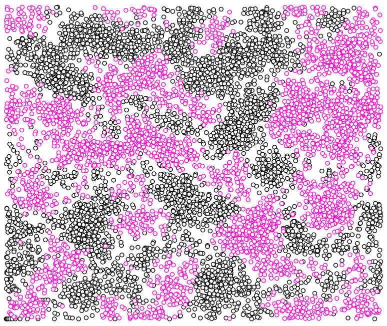

Figure 1.1: Snapshot of the particle positions in two-species annihilation in two dimensions.

Notes

There is a large literature on the topics discussed in this introductory chapter. Among the great many books on random walks we mention 3; 8 which contain numerous further references. Dimensional analysis and scaling are especially popular in hydrodynamics, see e.g. excellent reviews in 4 and the classical book by Barenblatt 1 which additionally emphasizes the connection of scaling, especially intermediate asymptotics, and the renormalization group. This latter connection has been further explored by many authors, particularly Goldenfeld and co-workers (see 6). Kinetics of single-species and two-species annihilation processes were understood in a pioneering works of Zeldovich, Ovchinnikov, Burlatskii, Toussaint, Wilczek, Bramson, Lebowitz, and many others; a review of this work is given in 5; 2. One-dimensional diffusion-controlled coalescence process is one of the very few examples which can justifiably be called "completely solvable"; numerous exact solutions of this model (and generalizations thereof) found by ben-Avraham, Doering, and others are presented in Ref. 2.