Some Fundamental Problems in Statistical Mechanics

Lectures held at the Tokyo Institute of Technology
July/August 1997

Urbaan M. Titulaer
Institute for Theoretical Physics
Johannes Kepler University
Linz, Austria

CONTENTS

1 General introduction ; levels of description in nonequilibrium statistical mechanics

The goal of statistical physics is understanding the behavior of matter on the basis of its microscopic structure and of the microscopic laws of nature (Newton's or Hamilton's equations of motion, Schrödinger's equation in quantum mechanics). Solving the microscopic equations of motion is in practice an impossible task. Even when quantum effects can be neglected : Newton's equations for the molecules in a container of gas are about 10^{23} coupled nonlinear equations, whose solutions depend very sensitively on the initial conditions

, which are never known accurately in practice. However, even if some supercomputer could calculate the positions and momenta of all molecules at all times, this would not solve our problem : we would be presented with huge amounts of data, in which the information that really interests us is completely obscured. One way to identify the relevant information for the macroscopic behavior of matter is to go back to the times before physicists knew about the microscopic nature of matter. In the nineteenth century, *phenomenological theories* , such as hydrodynamics or the theory of elasticity, were developed. The variables occurring in these theories, which we shall call *macrovariables*, such as densities, fluid velocities or temperatures, can be interpreted more or less directly in terms of the positions and velocities of the individual molecules. Our next hope might be to derive exact equations for the macrovariables from the microscopic equations of motion, and hope that they assume the form of the macroscopic equations, e.g. of hydrodynamics. There are at least two this reasons why this naive program cannot succeed :

1. The phenomenological equations are *closed* systems of equations : knowing the macrovariables at a given point in time allows one to predict their values for all later times. On the other hand, if one tries to calculate the development of the microscopic equivalent of a macrovariable, e.g. the number of molecules in a given volume in space , one needs more and more detailed information about the system : to keep track of the number of molecules in the given volume one has to know which molecules enter or leave it, and this depends on the way in which collisions between the molecules affect their velocities. In the end, we are carried back to the problem of solving all the original equations of motion for the individual molecules.

2. An even more direct proof , that the phenomenological equations are no simple consequence of the microscopic ones is the behavior under *time reversal*. If one takes any solution of the microscopic equations of motion over a time interval (0 ,T), denoted by $\{\mathbf{r}_i(t), \mathbf{v}_i(t)\}$, then there is a time-reversed solution $\{\mathbf{r}_i(T-t), -\mathbf{v}_i(T-t)\}$, which also obeys the equations of motion

> with initial and final states exchanged, but for a change in the sign of the velocities (at least for a Hamiltonian invariant under time reversal, i.e. in the absence of magnetic fields, rotating frames etc.). For a phenomenological equation this not the case : the hydrodynamic equations (with regular boundary conditions) have solutions in which an originally inhomogeneous density distribution becomes uniform, but none in which an originally almost homogeneous distribution develops sharp peaks.

This means that to derive the phenomenological equations from the microscopic ones, one needs additional assumptions ; since Boltzmann, Maxwell and Gibbs one knows these additional assumptions are of a statistical nature : the microscopic laws are not universally valid, but hold with a probability practically indistinguishable from unity.

One of the goals of statistical physics is therefore, to analyse, justify and, if possible, prove the statistical assumptions underlying the phenomenogical equations. In addition, one hopes to find a microscopic interpretation for, and if possible to calculate, the phenomenological parameters that occur in the hydrodynamic equations (heat conductivity, bulk and shear viscosity, diffusion coefficients). Part of this program, in particular in the field of equilibrium statistical mechanics, is in rather good shape. The statistical assumptions needed are treated in ergodic theory, and there is a well-established algorithm, the formalism of statistical ensembles, to derive equilibrium properties from the microscopic Hamiltonian .

In nonequilibrium statistical mechanics, the situation is less satisfactory. In most treatments one does not go in one single step from the microscopic to the macroscopic level ; instead one interposes one or more intermediate, so called mesoscopic levels of description. The most celebrated one is kinetic theory ; instead of specifying position and momentum of all molecules, one merely specifies how many molecules there are with positions and velocities of a given value (within given tolerance limits). The evolution in time of this so called distribution function is , at least for dilute gases, described by the Boltzmann equation. Its status is intermediate between the microscopic and the macroscopic equations : it is an irreversible equation, (as follows from the famous H-theorem) that can only be derived from the microscopic equations by a "leap of faith", an essentially uncontrolled statistical assumption, the famous "Stosszahlansatz".

In modern derivations, the Stosszahlansatz is replaced by assumptions that look less drastic, but are still hard to justify in a really convincing way. On the other hand, the variables occurring in the Boltzmann equation are, at least in principle, measurable : light scattering experiments can measure local densities , at least averaged over small regions, and the spectral profile of the scattered light gives information about the local velocity distribution. The parameters occurring in the Boltzmann equation, the collision cross sections, have an immediate interpretation in terms of the intermolecular potentials. Moreover, and this is the main advantage, once we accept the Boltzmann equation, we can derive the hydrodynamic equations by means of a systematic and well-defind algorithm. This algorithm not only "derives" the hydrodynamic equations, but it also expresses the phenomenological coefficients (viscosity, heat conductivity) in terms of the molecular potentials. Finally, the solution of kinetic equations, though not easy, is at least feasible with the help of modern computers or with well controlled approximation schemes.

The situation is recapitulated in the following figure :

Microscopic Equations
Variables : $p_i(t), q_i(t)$
Parameters : microscopic (potentials)
Reversible in time

œB!!!!!!!!!!!!!!!!!!!œ($Bintuitiveleap Mesoscopic$ *Equations*

Variables :$f(\mathbf{p}, \mathbf{q})$
Parameters : microscopically derivable
œB!!!!!!!!!!!!!œ($B(crosssections)$
Irreversible in time œB!!!!!!!!!!!!!!!!!!!œ($Bwell - definedalgorithms Macroscopic$

Equations
Variables : (e.g) $n(\mathbf{r}, t), T(\mathbf{r}, t)$
Parameters : phenomenological
Irreversible in time

In the course of these lectures I shall try and illustrate various aspects of the scheme sketched above, using the simplest available example where possible. The examples are atypical in one respect : they are often characterized by linear equations, whereas in the general case the equations are nonlinear. I shall try to point out where this difference is crucial, and where it is not.œB!!œ(B

2 Elements of ergodic theory ; introducing irreversibility

In this part of the lectures I shall introduce a few ideas from classical ergodic theory, i.e. from the general theory about the behavior of the solutions of Hamilton's equations of motion. I do not aim at mathematical rigor and I shall present results in a weaker form than necessary, as they relate to typical, rather than to individual solutions of the equations of motion. This allows us to use mainly mathematics familiar from quantum mechanics.

If one denotes the coordinates and momenta of all N particles $(p, \cdots, p_{3N} \,;\, q_1, \cdots, q_{3N})$ collectively by $\mathbf{X} \equiv (\mathbf{P}, \mathbf{Q})$, then Hamilton's equations of motion can be written as

$$\frac{d}{dt}\mathbf{X} = \mathbf{V}(\mathbf{X});\ \ \mathbf{V}(\mathbf{X}) = \left(\left\{-\frac{\partial H}{\partial q_i}\right\};\left\{\frac{\partial H}{\partial p_i}\right\}\right) \tag{1}$$

$\mathbf{V}(\mathbf{X})$ is a velocity field in phase space, which describes an incompressible flow :

$$\nabla \cdot \mathbf{V} = \sum_i \left[\frac{\partial}{\partial p_i}\left(-\frac{\partial H}{\partial q_i}\right) + \frac{\partial}{\partial q_i}\left(\frac{\partial H}{\partial p_i}\right)\right] = 0. \tag{2}$$

This means that the flow is volume preserving and the Jacobian of the time evolution, $|F_{ij}(t)| = |\partial X_i(t)/\partial X_j(0)|$ is unity. The time derivative of $F_{ij}(t)$ describes how two neighboring trajectories develop relative to one another :

$$\frac{d}{dt}\left(\mathbf{X} + d\mathbf{X}\right) = \mathbf{V}\left(\mathbf{X} + d\mathbf{X}\right) = \mathbf{V}(\mathbf{X}) + \mathbf{A}(\mathbf{X}) \cdot d\mathbf{X}, \tag{3}$$

with

$$A_{ij} = \frac{\partial V_i}{\partial X_j} = \frac{\partial}{\partial t}\left(\frac{\partial X_i(t)}{\partial X_j}\right) = \frac{\partial}{\partial t}F_{ij}(t)\bigg|_{t=0}.$$

The eigenvalues of A_{ij} are called the Lyapunov exponents of the system. Since the determinant of F_{ij} is unity, the trace of A_{ij}, and hence the sum of all Lyapunov exponents, must be zero. We have to distinguish three cases :

1. if an exponent is zero or purely imaginary, two trajectories $\mathrm{X}(t)$ whose distance vector at $t = 0$ lies along the corresponding eigenvector keep the same distance up to terms of order t^2

2. if an exponent has a postive real part, two trajectories separated along the corresponding eigenvector diverge at a rate $Re(\lambda)$, where λ is the relevant Lyapunov exponent

3. if the exponent has a negative real part, the two trajectories converge with the rate $Re(\lambda)$.

Numerical studies of systems in a few dimensions, such as the Hénon-Heiles system :

$$H = \frac{1}{2}\left(p_x^2 + p_y^2\right) + \frac{1}{2}\left(x^2 + y^2 + 2x^2y - \frac{2}{3}y^3\right)$$

show that the phase space in general has *regular* regions, where all Lyapunov exponents have vanishing real parts, and *chaotic* regions, where at least one Lyapunov exponent has a positive real part. Finally we notice, that there are at least two Lyapunov exponents that are zero. If $d\mathbf{X}$ is directed along $\mathbf{V}$, i.e. if we consider two points on the same trajectory, their distance stays constant (up to terms of order t^2). Similarly, it is easy to show that trajectories must stay on the energy surfaces $H(\mathbf{X}) = E$, hence the component of the separation of two trajectories along the gradient of H must also stay constant, at least to first order.

We now shift our attention from individual trajectories $\mathbf{X}(t)$ to functions $\varrho(\mathbf{X}, t)$ that describe probability distributions over $\mathbf{X}$. The continuity equation reads

$$\begin{aligned} & \frac{\partial \varrho(\mathbf{X}, t)}{\partial t} + \nabla \cdot [\varrho(\mathbf{X}, t)\mathbf{V}(\mathrm{x}, t)] \\ = \; & \frac{\partial \varrho(\mathbf{X}, t)}{\partial t} + \mathbf{V}(\mathbf{X}, t) \cdot \nabla \varrho(\mathbf{X}, t) \equiv \frac{\partial \varrho}{\partial t} - iL\varrho = 0 \end{aligned} \tag{4}$$

where we used (2) in the first transformation. The operator L, given by

$$L = -i\mathbf{V} \cdot \partial/\partial\mathbf{X} \; or \; Lf = i\{H, f\} \tag{5}$$

with $\{\ ,\ \}$ denoting the Poisson bracket, is called the Liouville operator. If we introduce a Hilbert space of phase functions with the weighted scalar product

$$\langle A|B\rangle_w = \int A(\mathbf{X})B(\mathbf{X})w(\mathbf{X})d^{6N}\mathbf{X}, \tag{6}$$

then L is hermitian when $w(\mathbf{X})$ in invariant under time evolution, i.e. if $Lw = 0$. Hence, L has a spectral representation with real eigenvalues,

$$Lf = \sum_i \lambda_i |i\rangle\langle i|f\rangle_w, \tag{7}$$

where, as in quantum mechanics, $\sum_i$ denotes a sum over the discrete spectrum and an integral over the continuous spectrum. For most of our applications we shall use averages over the energy surface :

$$w_E(\mathbf{X}) \sim \delta(H(\mathbf{X}) - E)$$

and denote the corresponding inner product with $\langle A|B\rangle_E$. We shall further always use distributions $\varrho(\mathbf{X})$ that are concentrated on the energy shell :

$$\varrho(\mathbf{X}, t) = \varrho_E(\mathbf{X}, t)\delta(H(\mathbf{X}) - E). \tag{8}$$

Next we consider averages over $\varrho(\mathbf{X}, t)$ of some phase function $A(\mathbf{X})$. These can be written as :

$$\begin{aligned} \langle A \rangle_{\varrho(t)} &\equiv \int \varrho(\mathbf{X}, t) A(\mathbf{X}) d\mathbf{X} \\ &= \sum_i \langle A | i \rangle_E e^{-i\lambda_i t} \langle i | \varrho \rangle_E. \end{aligned} \tag{9}$$

If we average this quantity over a long time, i.e. if we consider

$$\bar{A} = \frac{1}{T} \int_0^T \langle A \rangle_{\varrho(t)} dt, \tag{10}$$

then only the eigenvectors with $\lambda_i = 0$ contribute. There is at least one such eigenvector, the constant function $|1\rangle$. Hence, we may distinguish two types of systems :

1. ergodic systems, for which $|1\rangle$ is the only eigenvector with $\lambda_i = 0$. For such systems one has
$$\bar{A} = \langle A | 1 \rangle,$$
which means the time average equals the average over the energy shell.
2. nonergodic systems. These have additional eigenvectors for $\lambda_i = 0$, i.e. additional constants of the motion that lie within the Hilbert space generated by (6), which means that they must be at least square integrable, and thus be reasonably smooth functions of $\mathbf{X}$.

The ergodic property was first postulated by Boltzmann to justify calculating equilibrium values of physical quantities by means of averages over the energy shell (equilibrium values are by definition time independent, hence equal to their time average). Gibbs, in his discussion of the foundations of statistical mechanics, used a stronger property, namely :

$$\lim_{t \to \infty} \langle A \rangle_{\varrho(t)} = \langle A | 1 \rangle_E, \tag{11}$$

which he called the *mixing* property, If one analyses (9) one may distinguish two contributions : the *discrete spectrum* leads to a quasi-periodic contribution that oscillates around the time average, but returns arbitrarily close to any value it has once assumed. On the other hand, the contribution of the continuous spectrum does approach zero, as a consequence of the Riemann-Lebesgue lemma (I shall not discuss complications caused by the presence of a singular continuous spectrum). Hence, mixing is equivalent to : $|1\rangle$ is the only eigenfunction of L belonging to a *discrete* eigenvalue. It is clear that a mixing system is always ergodic.

In a mixing system, "information" about the system, that manifests itself e.g. in values of phase functions A different from their equilibrium values, gradually disappears from the system. However, the mixing property itself does not imply anything about the rate of disappearance of information. For that purpose one may use the concept of informational entropy production, introduceed by Kolmogorov and Sinai. They start by consideuring *partitions* R of the energy surface into N cells r_i and define the entropy H of that partition as

$$H = \sum_{i=1}^{N} -\mu(r_i)\ {}^2log\mu(r_i), \tag{12}$$

where $\mu(r_i)$ is the measure of the cell r_i, normalized to a measure unity for the entire energy surface. For the case of a partition into 2^s cells of equal measure 2^{-s}, one finds $H = s$, so H roughly equals the number of bits necessary to specify in which cell a point is located. Next one considers the partitions $R^{m\tau}$, the i-th set of which consists of all those points that *were* in r_i at the point $t = -m\tau$, as well as the common refinement

$$R^0_{n\tau} \equiv R \cap R^{\tau} \cap R^{2\tau} \cap \cdots \cap R^{n\tau}. \tag{13}$$

This partition consists of at most N^{n+1} sets, and to determine in which cell of $R^0_{n\tau}$ a point lies one must know in which cell of R it was at all $n+1$ points in time $-n\tau, \cdots, \tau, 0$. For the entropy of $R^0_{n\tau}$ one may consider two extreme cases : when the r_i are determined by the value of some conserved quantity, all $R^{m\tau}$ and $R^0_{n\tau}$ are identical to R and one has $H\left(R^0_{n\tau}\right) = H(R)$. On the other hand, when there is no correlation between the values of the cell index at different (discretized) times, one has $H\left(R^0_{n\tau}\right) = (n+1)H(R)$. Hence the limiting value,

$$h(R, L, \tau) = \lim_{n\to\infty} \frac{1}{n} H\left(R^0_{n\tau}\right), \tag{14}$$

gives an impression, how much new information is obtained by learning a trajectory is in a given cell of R, when its "coarse-grained history" (its cell numbers at all previous times $-m\tau$) is known ; the ratio $H(R)/h(R)$ tells one how long (in units of τ) the system "remembers" in which cells it has been. A system is called a *K-System*, when h is positive for all R (further theorems show that is suffices to prove positivity for just one R of a particular type). Then also the supremum $h_{KS}(L, \tau)$ of $h(R, L, \tau)$ over all R exists and is called the Kolmogorov-Sinai entropy of the system. A K-system is clearly ergodic and mixing (the value taken by a function f that is an eigenvector of L to a discrete eigenvalue can be used to construct a partition R with vanishing $h(r, L, \tau)$. For systems simpler than Hamiltonian systems (one-dimensional or low dimensional maps) there is an interesting connection between the KS entropy and the Lyapunov exponents : h_{KS} equals the sum of all positive Lyapunov exponents. For Hamiltonian systems, this property has not yet been proved, except for very simple systems. However, there are strong indications that for K-systems (and even for mixing systems) almost the entire phase space is chaotic ; the regular regions must have negligible measure.

The theory presented in this chapter gives us an idea about how irreversibility, the appearance of a unique direction in time, perceived as an approach towards equilibrium, may be understood. If the initial state of a system is not known exactly, but only approximately, we may represent it by a $\varrho(\mathbf{X}, 0)$ that is confined to one cell in phase space, say with volume Δ. For all later t, $\varrho(\mathbf{X}, t)$ still has the value Δ^{-1} in a total volume of size Δ and zero elsewhere, due to the incompressibility of the flow in phase space. However, the originally regular volume is constantly expanding in the directions associated with Lyapunov exponents with positive real parts and contracting in directions associated with exponents with negative real parts. Hence, it develops into ever longer and ever finer "threads" that spread over the entire energy surface. When calculating averages of phase functions $A(\mathbf{X})$ that are smooth functions of $\mathbf{X}$, this fine structure does not matter much, and $\varrho(\mathbf{X}, t)$ becomes equivalent to a uniform distribution over the energy shell (mathematically : it approaches this uniform distribution in a weak sense), at least for mixing systems. From the description of a K-system we also see that, while precise knowledge of the initial state allows a precise prediction of the entire future, a knowledge that is only approximate may rapidly become worthless for the purpose of predictions. The source of the uncertainty about the initial state should not, at least in my opinion, be ascribed to psychological factors ("physics does not describe nature, but our knowledge of nature"), but to the fact that no physical system can be completely isolated from its surroundings. The uncontrollable external perturbations cause a certain fuzzines in the state of the system that not only justifies, but requires the use of statistical methods to describe it. The success of these methods may be regarded as indirect evidence for the ergodic properties.

3 Master equation and Fokker-Planck equation ; the Brownian particle as a model system for statistical mechanics.

In this chapter we consider specific systems, for which the eigenvalues of the Liouville operator can be divided into two groups, a slow group λ_i and the remaining ones μ_j, where we assume

$$\lambda_i \ll \tau^{-1} \ll \mu_j \qquad (15)$$

for all i and j and some suitably chosen τ. We treat the eigenvalues as discrete for simplicity of notation, though in practice they will be continuous ; in particular we shall assume that the subsystem of fast variables is mixing, even that it is a K-system with an information decay time much faster than τ. We shall divide the phase space of the system into cells, characterized by the values taken by the slow variables $a_i(\mathbf{X})$, determined by the coefficients of the eigenfunctions belonging to the λ_i. Now, if one considers a distribution $\varrho(\mathbf{X})$ that is at $t = 0$ concentrated entirely within a single cell i of this partition, then for times small compared to τ virtually none of the trajectories will have left the cell, but the probability distribution will have smeared out uniformly over the entire cell (in the weak sense, as discussed at the end of the previous chapter).

Once we pass to the time scale τ, the possibility that a trajectory that is in cell i at time 0 ends up in cell j at time τ is no longer negligible. The starting points of those trajectoies form the cell r_{ji} of the partition $R^{-\tau} \cap R$ in the notation of the previous chapter :

$$r_{ji} \equiv (\mathbf{X}|\mathbf{X}(\tau) \in r_j, \mathbf{X} \in r_i)\,. \qquad (16)$$

Now the fact that any distribution within r_i is practically smeared out over the entire cell in a time much less than τ means, that the probability, that a point belongs to r_{ji} cannot depend significantly on its previous history, and that we can define a probability

$$\tilde{w}_{ji}(\tau) = \mu(r_{ji})/\mu\,(r_i) \qquad (17)$$

that a transition from i to j occurs in the time $(0, \tau)$. By the same argument, consecutive jumps are uncorrelated (this is known as the *Markov property* : $\tilde{w}_{ji}(2\tau) = \sum_k \tilde{w}_{jk}(\tau)\tilde{w}_{ki}(\tau)$, (this equation is called the Chapman-Kolmogorov equation) and from the choice (15) for τ it follows, that all $\tilde{w}_{ij}(\tau)$ for $j \neq i$ are small compared to unity, thus one sees that $\tilde{w}_{ij}(2\tau) = 2\tilde{w}_{ij}(\tau)$ for $j \neq i$. Hence $\tilde{w}_{ij}(\tau)$ is proportional to τ and one may write $\tilde{w}_{ij}(\tau) = \tau W_{ij}$. This in turn implies that the development of the occupation probabilities $p_i(t)$ of the cells on a time scale long

compared to τ can be described by the *master equation*

$$\frac{dp_i}{dt} = \sum_{j \neq i} [W_{ij}p_j(t) - W_{ji}p_i(t)] \equiv \sum_j M_{ij}p_j(t). \qquad (18)$$

The matrix M has positive off-diagonal elements W_{ij} and non-positive diagonal elements $M_{ii} = -\sum_j W_{ij}$. This means $\sum_i M_{ij} = 0$, hence the vector $\mathbf{I} = (1, \cdots, 1)$ is a left eigenvector of M with eigenvalue zero. It is also easy to write down a right eigenvector to $\lambda = 0$, namely the equilibrium distribution $p_i^{(0)} = \mu_i$ (when the sum of all μ_i is talken to be unity). A number of further properties is easy to prove :

1. Any solution of (18) with $p_i(0) \geq 0$ for all i has $p_i(t) \geq 0$ for all i and $t > 0$.
2. All eigenvalues of M unequal to zero have negative real parts ; the eigenvalue $\lambda = 0$ is nondegenerate for ergodic systems.
3. For ergodic systems the distribition $p_i(t)$ approaches $p_i^{(0)}$ *monotonically* in the sense that there exist Lyapunov-functions that are positive, nonincreasing, and vanishing for the equilibrium distribution. These properties are obeyed by all functions of the form

$$H(t) = \sum_i p_i^{(0)} f\left(p_i(t)/p_i^{(0)}\right) \tag{19}$$

with

$$f(x) \geq 0_j \; f"(x) > 0 \; forx > 0. \tag{20}$$

The most usual, but not the only possible, choice is

$$f(x) = x \; ln \; x. \tag{21}$$

This choice has the advantage that it is additive when one considers systems built up from noninteracting or weakly interacting parts, a property shared by the thermodynamic entropy, to which (19) can be related.

An interesting further property, called *detailed balance*, holds when two additional conditions are satisfied :

1. The microscopic evolution is invariant under time reversal (see Ch.1).
2. All slow quantities are even in the particle velocities; this means that $\{\mathbf{r}_i, \mathbf{v}_i\}$ and $\{\mathbf{r}_i, -\mathbf{v}_i\}$ always lie in the same cell.

Then, for every trajectory with $\{\mathbf{r}_i(0), \mathbf{v}_i(0)\} \in r_i$, $\{\mathbf{r}_i(\tau), \mathbf{v}_i(\tau)\} \in r_j$, that goes from r_i to r_j in τ, one has a "matching trajectory" $\{\tilde{\mathbf{r}}_i(0) = \mathbf{r}_i(\tau), \tilde{\mathbf{v}}_i(0) = -\mathbf{v}_i(\tau)\}$ with $\{\tilde{\mathbf{r}}_i(\tau) = \mathbf{r}_i(0), \tilde{\mathbf{v}}_i(\tau) = -\mathbf{v}_i(0)\}$ that goes from cell j to cell i. Using (16) and (17), as well as the relations $\tilde{w}_{ji}(\tau) = \tau W_{ji}$ and $p_i^{(0)} = \mu\left(r_i\right)$, we therefore have

$$\mu\left(r_{ji}\right) = \mu\left(r_{ij}\right) \; ; W_{ji} p_i^{(0)} = W_{ij} p_j^{(0)}, \tag{22}$$

from which one easily proves that W_{ij}, and therefore also M_{ij} in (18), are hermitian with respect to the scalar product

$$(\mathbf{p}, \mathbf{p}') = \sum_i p_i p'_i \left(p_i^{(0)}\right)^{-1} . \tag{23}$$

This hermiticity property has the immediate consequence that *all eigenvalues of M are real.*

One may still obtain a useful symmetry property when not all slow quantities are even in the velocities, but some of them, called A_k, are even, while others, called B_l, are odd. Then, for every cell r_i characterized by the values$\{a_k, b_l\}$ there is a complementary cell $r_{i'}$ with values $\{a_k, -b_l\}$. Moreover, since the equilibrium distribution is even in the velocities, one must have $\mu\left(r_{i'}\right) = \mu\left(r_i\right)$. By the same argument as above, one now sees that for every trajectory leading from r_i to r_j in time τ there is the time-reversed trajectory that leads from $r_{j'}$ to $r_{i'}$. Hence, one has instead of (23)

$$\mu\left(r_{ji}\right) = \mu\left(r_{i'j'}\right); \quad W_{ji} p_i^{(0)} = W_{i'j'} p_j^{(0)} . \tag{24}$$

These are also useful relations : whereas (22) is connected to the Onsager relations, (24) is related to their generalization by Casimir. However, (24) does not lead to hermiticity of M.

Under the conditions (15), transitions may be assumed to occur not between cells with widely different values of the slow variables $\mathbf{a} = (a_1, \cdots, a_s)$, but predominantly between cells whose $\mathbf{a}$ differ only slightly. If we want to exploit this fact, it is convenient to use $\mathbf{a}$ itself as the cell index, and to go over to a continuous notation, in which (18) takes the form

$$\frac{d}{dt} P(\mathbf{a}, t) = \int d^s\mathbf{a}' \left[W\left(\mathbf{a}|\mathbf{a}'\right) P\left(\mathbf{a}', t\right) - W\left(\mathbf{a}', \mathbf{a}\right) P(\mathbf{a}, t)\right] . \tag{25}$$

Next we rewrite $W\left(\mathbf{a}|\mathbf{a}'\right)$ as $W\left(\mathbf{a}; \mathbf{y}\right)$ with $\mathbf{y} \equiv \mathbf{a}' - \mathbf{a}$, which brings (25) into the form

$$\frac{d}{dt} P(\mathbf{a}, t) \equiv \int d^s\mathbf{y} \left[W(\mathbf{a} - \mathbf{y}; \mathbf{y}) P(\mathbf{a} - \mathbf{y}, t) - W(\mathbf{a}; -\mathbf{y}) P(\mathbf{y}, t)\right] . \tag{26}$$

When W and P are smooth functions of $\mathbf{a}$, on the scale of a typical jump length $|\mathbf{y}|$ we can insert a Taylor expansion in $\mathbf{y}$ in the first term of (26) and obtain the Kramers-Moyal expansion of the master equation :

$$\frac{d}{dt} P(\mathbf{a}, t) \quad = \quad -\sum_i \frac{\partial}{\partial a_i} \left[b_i(\mathbf{a}) P(\mathbf{a}, t)\right] + \frac{1}{2} \sum_{i,j} \frac{\partial^2}{\partial a_i \partial a_j} \left[b_{ij}(\mathbf{a}) P(\mathbf{a}, t)\right] + \cdots \tag{27}$$

with

$$b_{i_1}, \cdots i_n(\mathbf{a}) = \int d\mathbf{y} y_{i_1} y_{i_2} \cdots y_{i_n} \, W(\mathbf{a}; \mathbf{y}) . \tag{28}$$

The equation obtained by truncating (27) after the second term, i.e. by omitting the $+\cdots$, is called the Fokker-Planck equation. As pointed out by van Kampen, just truncating the formal series (27) is not a valid derivation of the Fokker-Planck equation ; one has to give an argument, that the terms omitted are small compared to the terms retained. A closer analysis shows that the truncation is in general *not* justified ; in special cases, a derivation is possible by means of on expansion in a small parameter, such as the inverse system size. In general, the truncation is only possible for systems with values of $\mathbf{a}$ in the neighborhood of a stable fixed point $\mathbf{a}^{(0)}$. Since one readily sees from (27) that the average $\langle a_i \rangle = \int d\mathbf{a} a_i P(\mathbf{a}, t)$ obeys

$$\frac{d}{dt}\langle a_i \rangle = \langle b_i(\mathbf{a}) \rangle, \tag{29}$$

one sees that a stable fixed point ischaractoerized by

$$b_i(\mathbf{a}) = \sum_j -A_{ij}\left(a_j - a_j^{(0)}\right) + \mathcal{O}\left(\left(a_k - a_k^{(0)}\right)^2\right) \tag{30}$$

with a positive definite matrix A_{ij}. For fluctuations in the vicinity of $\mathbf{a}^{(0)}$, a Fokker-Planck equation can be derived, but consistency requires that the $b_i(\mathbf{a})$ are replaced by their linearized versions and the $b_{ij}(\mathbf{a})$ by their values $B_{ij} = b_{ij}\left(\mathbf{a}^{(0)}\right)$ at the fixpoint. One thus arrives at the *linear* Fokker-Planck equation

$$\frac{dP(\mathbf{a}, t)}{dt} = \left[A_{ij}\frac{\partial}{\partial a_i}\left(a_j - a_j^{(0)}\right) + \frac{1}{2}B_{ij}\frac{\partial^2}{\partial a_i \partial a_j}\right] P(\mathbf{a}, t) \tag{31}$$

(For the remainder of this section we use Einstein's summation convention). However, in special cases, one of which we shall mention at the end of this chapter, nonlinear Fokker-Planck equations may be justified as well. The B_{ij} , or more generally the $b_{ij}(\mathbf{a})$, set the scale of the fluctuations in $\mathbf{a}$ (the width of the distribution P), as can be seen from

$$\frac{\partial}{\partial t}\langle a_i a_j \rangle = \langle a_i b_j(\mathbf{a}) \rangle = \langle a_j b_i(\mathbf{a}) \rangle + \langle b_{ij}(\mathbf{a}) \rangle, \tag{32}$$

which can be solved explicitly for the linear case (31).

Before introducing the special Fokker-Planck equation that will concern us in the rest of these lectures, I mention without derivation the consequences of microscopic reversibility for the hermiticity properties of the Fokker-Planck operator with respect to the scalar product

$$(P, Q) = \int d\mathbf{a} P(\mathbf{a}) Q(\mathbf{a}) P_{eq}(\mathbf{a})^{-1}, \tag{33}$$

the continuous version of (23). When all $\mathbf{a}$ are even in the velocities, the Fokker-Planck operator F should be hermitian with respect to (33), which implies

$$F\left[P_{eq} f\right] = P_{eq}\left[F^{+} f\right], \tag{34}$$

where F^{+} is the formal adjoint (for an unweighted scalar product)

$$F^{+} = b_i(\mathbf{a})\frac{\partial}{\partial a_i} + \frac{1}{2}\, b_{ij}(\mathbf{a})\frac{\partial^2}{\partial a_i \partial a_j}. \tag{35}$$

Working out the hermiticity requuirement, and use of $FP_{eq} = 0$, leads one to the requirement

$$b_i(\mathbf{a}) = \frac{1}{2}P_{eq}^{-1}(\mathbf{a})\frac{\partial}{\partial a_j}b_{ij}(\mathbf{a})P_{eq}(a), \tag{36}$$

which allows one to write F in the manifestly hermitian form

$$F = \frac{1}{2}\frac{\partial}{\partial a_i}P_{eq}(\mathbf{a})b_{ij}(\mathbf{a})\frac{\partial}{\partial a_j}P_{eq}^{-1}(\mathbf{a}). \tag{37}$$

For the case that **a** contains both odd and even variables, the symmetry requirement for $W\left(\mathbf{a}|\mathbf{a}'\right)$ may be written as

$$W\left(\mathbf{a}|\mathbf{a}'\right)P_{eq}(\mathbf{a}') = W\left(\bar{\mathbf{a}}'|\bar{\mathbf{a}}\right)P_{eq}(\mathbf{a}) \tag{38}$$

with $\bar{a}_i = \eta_i a_i$, $\eta_i = \pm 1$ for a_i (even / odd).
If we now write F in the form

$$F = -\frac{\partial}{\partial a_i}c_i(\mathbf{a}) + \frac{1}{2}\frac{\partial}{\partial a_i}P_{eq}(\mathbf{a})b_{ij}(\mathbf{a})\frac{\partial}{\partial a_j}P_{eq}^{-1}(\mathbf{a}) \tag{39}$$

with

$$c_i(\mathbf{a}) \equiv b_i(\mathbf{a}) - \frac{1}{2}P_{eq}^{-1}(\mathbf{a})\frac{\partial}{\partial a_j}\left(b_{ij}(\mathbf{a})P_{eq}(\mathbf{a})\right),$$

then one may derive from (38)

$$\eta_i\eta_i b_{ij}(\bar{\mathbf{a}}) = b_{ij}(\mathbf{a});\ \eta_i c_i(\bar{\mathbf{a}}) = -c_i(\mathbf{a});\ \eta_i c_i(\bar{\mathbf{a}})P_{eq}^{-1}(\mathbf{a})\frac{\partial}{\partial a_i}P_{eq}^{-1}(\mathbf{a}) = \frac{\partial}{\partial a_i}c_i(\mathbf{a}). \tag{40}$$

¿From these relations one may deduce with some algebra, that the part of (39) involving the c_i is antihermitian, and describes a purely reversible evolution, whereas the second term is hermitian and describes a purely irreversible evolution (monotonic approach to equilibrium). In the linear case we obtain, in obvious notation,

$$F = -\frac{\partial}{\partial a_i}C_{ij}\left(a_j - a_j^{(0)}\right) + \frac{1}{2}P_{eq}^{-1}\frac{\partial}{\partial a_i}B_{ij}P_{eq}\frac{\partial}{\partial a_j} \tag{41}$$

and for the case $\mathbf{a}^{(0)} = \bar{\mathbf{a}}^{(0)}$ (no spontaneous breaking of time reversal symmetry in the stationary state) we see that B_{ij} is symmetric and connects only components of **a** with equal time parity, whereas C_{ij} is antisymmetric and connects only components with opposite parity.

The developments presented in this chapter were a first example of a reduction of the description, in this case from $\varrho(\mathbf{X})$, depending on all particle positions and momenta, to $P(\mathbf{a})$, depending only on the slow variables. However, there are some serious disadvantages in our treatment. The main one is that we assumed the $A_i(\mathbf{X})$ to be *exact eigenfunctions* of the Liouville operator. In practice these are never known, and any quantity one writes down will have both rapidly and slowly varying parts, though one may on intuitive grounds select quantities that are *predominantly* slowly varying. Secondly, the condition (15) is certainly extreme, and one wonld like to know which corrections to expect in a system where time scales differ considerably, but not enormously. To obtain some insight into such questions I shall discuss in the next two chapters the transition, not between a microscopic and a mesoscopic description, but between two descriptions on the borderline between mesoscopic and macroscopic. Both are of Fokker-Planck type and they concern a collection of noninteracting Brownian particles. In both descriptions, the variables of the molecules of the fluid in which the Brownian particles move have already been eliminated ; the fluid merely gives rise to friction for the movement of the particles. The first, more mesoscopic, description contains a distribution function for positions and velocities of the Brownian particles ; the second only their distribution in space. The equation governing their evolution, a *nonlinear* Fokker-Planck equation, the Klein-Kramers equation, could in principle be derived, but we shall choose instead to guess it from the known consequences (29) and (32) for average and flucutations.

I would like to add final remark : though in our derivation we started from (15) and the K-property of the subsystem of fast variables, in practice one most often observes that for certain $\mathbf{a}$ chosen on physical grounds, a description by means of (25) or (27) reproduces experimental results well, and hence (15) and the K-property (Markov property) probably hold for that special choice of $\mathbf{a}$. This is true in spite of the fact that the $\mathbf{a}$ chosen with the help of physical intuition are at best approximate eigenvectors of the Liouville operator. I hope the example in the next chapter will shed some light on this last question.

4 Reducing the level of description : coarse graining, adiabatic elimination of fast variables, the Chapman-Enskog procedure

The specific Fokker-Planck equation we shall discuss in this and the remaining chapter was first written down by Klein and Kramers and reads

$$\frac{\partial P(u,x,t)}{\partial t}=\gamma\left[\frac{1}{m\beta}\frac{\partial^2}{\partial u^2}+\frac{\partial}{\partial u}u\right]P-u\frac{\partial P}{\partial x}+\frac{1}{m}\frac{d\Phi}{dx}\frac{\partial P}{\partial u}. \tag{42}$$

Here, u and x are the velocity and position of a Brownian particle, moving in one dimension, m its mass, $\beta=(kT)^{-1}$, γ is the friction coefficient, and $\Phi(x)$ is an external potential acting on the particle. According to (29) the averages obey the expected laws

$$\frac{d}{dt}\langle x\rangle=\langle u\rangle\,;\ \frac{d}{dt}\langle u\rangle=-\gamma\langle u\rangle-\frac{1}{m}\langle\frac{d\Phi}{dx}\rangle, \tag{43}$$

and the equilibrium distribution is the Maxwell-Boltzmann distribution

$$P_{eq}(u,x)=cst.e^{-\frac{1}{2}m\beta u^2-\beta\Phi(x)}, \tag{44}$$

as is easily seen by substitution. The first term in (42) describes the effects of the interaction of the Brownian particle with the fluid. In analogy with the terminology usual in kinetic theory we call it the *collision term*, and the operator in it acting on P is called the collision operator $\mathcal{C}$. Acting on its own, it transforms the velocity distribution into a Maxwellian in a time of the order γ^{-1}. The second and third term in (42) together from the *streaming term.* The corresponding operator $\mathcal{S}$ describes the "free" motion of the particle; it causes the approach to the Boltzmann distribution in space, but it also distorts the Maxwell distribution in the velocities as long as the Boltzmann distribution in space has not yet been reached.

As could have been expected from the discussions in the preceding chapter, $\mathcal{C}$ and $\mathcal{S}$ are hermitian and antihermitian, respectively, with respect to the scalar product (33) with P_{eq} given by (44). This may be brought out clearly by writing

$$\mathcal{C}=-\gamma a^\dagger a;\ \ \mathcal{S}=\frac{1}{\sqrt{m\beta}}\left(da^\dagger-ad^\dagger\right) \tag{45}$$

with

$$a=\frac{1}{\sqrt{m\beta}}\frac{\partial}{\partial u}+\sqrt{m\beta}u\,;\ a^\dagger=-\frac{1}{\sqrt{m\beta}}\frac{\partial}{\partial u}\,; \tag{46}$$

$$d=\frac{\partial}{\partial x}+\beta\frac{d\Phi}{dx}\,;\ d^\dagger=-\frac{\partial}{\partial x}, \tag{47}$$

where a and $a^\dagger$ as well as d and $d^\dagger$ are pairs of hermitian conjugates with respect to (33). The structure of $\mathcal{C}$ is that of the harmonic oscillator Hamiltonian (note that $\left[a, a^\dagger\right] = 1$) ; this can also be shown via the transformation

$$P(u) = exp\left[-\frac{1}{4}m\beta u^2\right]\phi(u). \tag{48}$$

The eigenvalues and eigenfunctions of $\mathcal{C}$ are given by

$$\lambda_n = -n\gamma(n = 0, 1, 2, \cdots); \;\; \varphi_n(u) = N_n H_n\left(\sqrt{m\beta/2u}\right)e^{-\frac{1}{2}m\beta u^2}, \tag{49}$$

with H_n the Hermite polynomials and N_n a normalization constant, that is of no further interest to us but for the fact that the integral over $\varphi_0(u)$ is made to be unity ; hence in the eigenfunction expansion

$$P(u, x) = \sum_{n=0}^{\infty} a_n(x, t)\varphi_n(u) \tag{50}$$

the coefficient function $a_0(u)$ has the physical meaning of the distribution in space. Under the influence of $\mathcal{C}$ alone, $a_0(x, t)$ remains constant, while the other $a_n(x, t)$ obtain a factor $exp[-n\gamma t]$, hence decay to zero without changing their shape. This expresses the fact, that the spectrum of $\mathcal{C}$ is infinitely degenerate, since it does not operate on the variable x at all.

Now we consider the case that $\mathcal{S}$ is nonnegligible, but still small. Of course, since both $\mathcal{C}$ and $\mathcal{S}$ are unbounded operators, this inplies that we concentrate our attention upon special solutions of (42), in particular those for which $P(u, x, t)$ changes slowly on the scale $l = \left[\gamma\sqrt{m\beta}\right]^{-1}$, the distance a typical particle travels during the time its velocity needs to randomize (the velocity persistence length). Of course, such solutions are only to be expected for $\Phi(x)$ that are smooth on that scale. Under this condition we may use perturbation theory ; the eigenfunctions of $\mathcal{F}$ can thus be written as

$$P_n^{[\gamma]}(u, x) = c_n(x)\varphi_n(u) + \gamma^{-1}P^{[n,1]}(u, x) + \gamma^{-2}\cdots, \tag{51}$$

where we used γ^{-1} as a formal expansion parameter. However, the $c_n(x)$ are no longer arbitrary, since the perturbation can be expected to lift the degeneracy. When the degeneracy is lifted in first order, the $c_n(x)$ should be chosen to be eigenfunctions of the part of $\mathcal{S}$ that acts whithin the degenerate subspace in question, which may be written as $\mathcal{P}_n^{(0)}\mathcal{S}\mathcal{P}_n^{(0)}$, with $\mathcal{P}_n^{(0)}$ the projection operator on the subspace of eigenvectors of $\mathcal{C}$ with eigenvalue $-n\gamma$. However, it is clear form (45) that this expression vanishes ($a^\dagger$ and a carry one from one subspace to an other one, with $n\pm1$). Hence, the operator to be diagonalized is the expression for the second order eigenvalue shift

$$\mathcal{E}_n^{(2)} = \sum_{m\neq n}\mathcal{P}_n^{(0)}\mathcal{S}\mathcal{P}_m^{(0)}\frac{1}{E_n^{(0)} - E_m^{(0)}}\mathcal{P}_m^{(0)}\mathcal{S}\mathcal{P}_n^{(0)}. \tag{52}$$

For the special case (45) only $m = n \pm 1$ contribute, and for $n = 1$ we obtain

$$\mathcal{E}_0^{(2)} = \frac{-1}{m\beta\gamma} d^\dagger d = \frac{1}{m\beta\gamma}\frac{\partial}{\partial x}\left(\frac{\partial}{\partial x} + \beta\frac{d\Phi}{dx}\right). \tag{53}$$

Since the operator $\mathcal{E}_0^{(2)}$ is hermitian and nonpositive definite, its eigenvalues are certainly all real and nonpositive, the eigenvalue zero belonging to the equilibrium distribution $e^{-\beta\Phi}$. The operator $\mathcal{E}_0^{(2)}$ is a well-known operator : it was first proposed by Smoluchowski to describe diffusion in an external potential, and the identification $D = (m\beta\gamma)^{-1}$, with D the diffusion coefficient, goes back to Einstein. To bring out the connection more clearly, we consider a linear combination of eigenfunctions of $\mathcal{F} = \mathcal{C} + \mathcal{S}$ that all in zeroth order reduce to a multiple $\chi_m(x)\varphi_0(u)$ of the Maxwellian $\varphi_0(u)$, with $\chi_m(x)$ an eigenfunction of $\mathcal{E}_0^{(2)}$ with eigenvalue $-\mu_n$. Now if one goes through the formalism of perturbation theory, one sees that the correction terms in (51) are always determined only up to a multiple of $\varphi_0(u)$. One may exploit this freedom by prescribing that all corrections in (51) are orthogonal to $\varphi_0(u)$ (in quantum mechanics this is usually not done, since one wants to preserve the norm, but this is of less importance in our problem). Moreover, the corrections can be written in the form

$$P_m(u,x) = \chi_m(x)\varphi_0(u) + \sum_{n=1}^{\infty}\left[\mathcal{R}_n^{(0)}\chi_m(x)\right]\varphi_n(u), \tag{54}$$

where $\mathcal{R}_n^{(0)}$ is an operator, obtained from the perturbation scheme as a series in γ^{-1}, with terms built out of $d, d^\dagger$ and energy denominators, but not depending on $\chi_m \cdot A$ function of type (54) for t=0 keeps the same form but for on overall factor $exp\left[-\mu_m t\right]$. Therefore a linear combination of functions of type (54) evolves like

$$P^{[0]}(u,x,t) = c_0(x,t)\varphi_0(u) + \sum_{n=1}^{\infty}\left[\mathcal{R}_n^{(0)}c_0(x,t)\right]\varphi_n(u), \tag{55}$$

with $c_0(x,t)$ evolving in time according to

$$\frac{\partial}{\partial t}c_0(x,t) = \frac{1}{m\beta\gamma}\frac{\partial}{\partial x}\left(\frac{\partial}{\partial x} + \beta\frac{d\Phi}{dx}\right)c_0(x,t) \tag{56}$$

up to terms of order $\gamma^{-2}t$ (in fact $\gamma^{-3}t$ when further corrections are calculated). Thus, the density in space of the special solutions of the Klein-Kramers equation (42) that evolve slowly in time obeys the Smoluchowski equation. If one wants to obtain a better approximation to the dynamics, one may replace the operator $\mathcal{E}_0^{(2)}$ in (51) by a more complicated expression, involving higher corrections to the eigenvalues. Because of our convention that the corrections to the distribution function should be orthogonal to $\varphi_0(u)$, one may not simply copy the expressions from quantum mechanics textbooks, but the formalism needed was worked out long ago by C. Bloch. I shall only cite some results : As is seen from (45), intermediate states are alternately even and odd, so the next contribution occurs in fourth order in the perturbation scheme. The corrected Smoluchowski equation including these terms reads

$$\frac{d}{dt}c_0(x,t) = \frac{1}{m\beta\gamma}\frac{\partial}{\partial x}\left(1 + \frac{1}{m\gamma^2}\frac{d^2\Phi}{dx^2}\right)\left(\frac{\partial}{\partial x} + \beta\frac{d\Phi}{dx}\right)c_0(x,t) \tag{57}$$

It is again hermitian, but this property is lost in the next order. For the special case $\Phi = 0$, all higher oder corrections to the Smoluchowski equation can be shown to vanish ; the Smoluchowski equation (in this case simply the diffusion equation) is exact to all orders in the perturbation.

To conclude this chapter I would like to point out the relation between the derivation just given and two procedures often encountered in other contexts. The first is *elimination of fast variables.* In a general solution (50) of the Klein-Kramers equation (42) the $a_n(x,t)$ with $n \neq 0$ decay on the fast time scale γ^{-1}, and are therefore called fast variables, whereas $a_0(x,t)$ changes much more slowly, and is called a slow variable. Unless a_n with $n \neq 0$ are excited over the boundary conditions, the only contributions to $a_n(x,t)$ with $n > 0$ that survive after times large compared to γ^{-1} are the correction terms in the slowly varying solutions, as given by (55). These are determined completely by $c_0(x,t)$, which in turn is the only surviving contribution to the slow variable $a_0(x,t)$. Hence, after a "ripening time" of the order of a few γ^{-1}, the a_n with $n > 0$ are completely determined by a_0 ; this fact is also often expressed by saying that the fast variables *adiabatically follow* or are *enslaved* by the slow ones. This means that there must be a description of the dynamics in terms of the slow variables alone. The derivation of such a description, such as our derivation of (56) or (57) from (42), is called the *adiabatic elimination* of the fast variables. We are now also in a position to answer the question raised at the end of the last chapter. Though the actual slow eigenfunctions of the Liouville operator are not $c_0(x,t)$, but expressions of type (54), the coefficients of all $P_m(u,x)$ are found from $c_0(x,t)$, so the function $c_0(x,t)$ contains all information needed to construct the coefficients of the slow eigenfunctions, and may serve equally well to identify the cells in phase space discussed in chapter 3.

A very early example of adiabatic elimination occurred in the kinetic theory of gases. The Boltzmann operator again has the form $\mathcal{F} = \mathcal{C} + \mathcal{S}$, only $\mathcal{S}$ is in general a nonlinear operator. $\mathcal{C}$ again acts on the velocity variables only ; it describes the collisions between particles in which, at least for a pure gas of molecules without inner structure (noble gases or molecular gases at temperatures at which rotations and vibrations are not excited) there are five constants of the motion : particle number, kinetic energy, and the three components of the momentum. Hence there are five slowly varying fields, the densities of these five collision invariants ; all other moments of the velocity distribution decay fast, and one expects them to become enslaved by the slow variables after some ripening time. This is indeed the case, as can be shown by means of the algorithm of *Chapman* and *Enskog*, the oldest known example of what was later recognized as the method of elimination of fast variables. The basic idea is to expand the one-particle distribution $f(\mathbf{u}, \mathbf{r}, t)$ according to

$$f(\mathbf{u}, \mathbf{r}, t) = n(\mathbf{r}, t)\varphi_0\left(\mathbf{u} - \mathbf{v}(\mathbf{r}, t); \beta(\mathbf{r}, t)\right) + \sum_{i=1}^{\infty} \gamma^{-i} f^{[i]}(\mathbf{u}, \mathbf{r}, t), \tag{58}$$

where $\varphi_0(\mathbf{u} - \mathbf{v}; \beta)$ is the Maxwell distribution at temperature $(k\beta)^{-1}$, shifted over $\mathbf{v}$, and the $f^{[i]}$ underly the restraint that their first five velocity moments $\mathbf{s}(\mathbf{r}, t) = (\langle 1\rangle, \langle \mathbf{u}\rangle, \langle u^2\rangle)$ vanish identically ; hence these moments are defined completely by the first term in (58) :

$$\mathbf{s}(\mathbf{r}, t) = \Big(n(\mathbf{r}, t), n(\mathbf{r}, t)v(\mathbf{r}, t), n(\mathbf{r}, t)\left[v(\mathbf{r}, t)^2 + (3/m)\beta(\mathbf{r}, t)^{-1}\right]\Big) \tag{59}$$

For the time evolution of $\mathbf{s}$ one postulates

$$\frac{\partial}{\partial t}\mathbf{s}(\mathbf{r}, t) = \sum_{n=0}^{\infty} \gamma^{-n} \mathcal{D}^{[n]} \mathbf{s}(\mathbf{r}, t), \tag{60}$$

where the $\mathcal{D}^{[n]}$ are (in this case nonlinear) differential operators, which is the direct analogue of a similar series for the Klein-Kramers equation, the first terms of which were shown in (56) and (57). When (58) and (60) are substituted into the Boltzmann equation, a consistent expansion is carried out, and the constraint (59) is observed, one obtains to order 0 the Euler equations, to order 1 the Navier-Stokes equations, and thereafter the Burnett and super-Burnett corrections. The formalism goes just as in the Klein-Kramers case, only the derivation via the eigenvalue problem does not hold since the Boltzmann equation, and the operators in (60) as well, are nonlinear. There even is an analogue to the nonhermiticity of the higher corrections : from Burnett order on, the Onsager-Casimir symmetry relations no longer hold. But that is another story.

5 Connecting two levels of description : initial and boundary layers ; slip coefficients.

In the preceding chapter we discussed the derivation of evolution equations for a system on a coarse grained or contracted level of description. However, to construct solutions of these equations, one also needs initial and boundary conditions. The subject of this chapter is, how to construct such initial and boundary conditions for the contracted description from the conditions on the more detailed level, when the latter are known. Again, we shall treat the problem first for the case of the Klein-Kramers equation, where many of the steps can be carried out explicitly.

Finding the initial condition is rather straightforward for linear equations : one has to project upon the subspace of all solutions of type (54) or (55). If we write the latter in the form $P(u,x,t) + \mathcal{R}_0^{(\gamma)}\left[c_0(x,t)\varphi_o(u)\right]$, then the projector we need is

$$\mathcal{P}_0^{(\gamma)} = \mathcal{R}_0^{(\gamma)}\mathcal{P}_0^{(0)}\mathcal{R}_0^{(\gamma)\dagger}, \tag{61}$$

where $\mathcal{P}_0^{(0)}$, first introduced after (51), is the projection on the multiples of $\varphi_0(u)$. An explicit power series in γ^{-1} for $\mathcal{P}_0^{(\gamma)}$ can also be derived from the perturbation expansion for the resolvent $\left[\gamma\left(\mathcal{C} + \gamma^{-1}\mathcal{S}\right) - z\right]^{-1}$, by contour integration around $z = 0$, with a contour excluding the points $z = -n\gamma$, $n \neq 1$. It is instructive to consider the special case $\Phi(x) = 0$ for an initial distribution of local equilibrium type

$$P(u,x,0) = a_0(x)\varphi_0(u). \tag{62}$$

For this case the series for $\mathcal{R}_0^{(\gamma)}$ can be calculated in closed form and summed exactly ; from the result one sees that

$$c_0(x,0) = exp\left[-\left(m\beta\gamma^2\right)^{-1}\partial^2/\partial x^2\right]a_0(x) \tag{63}$$

and, since the diffusion equation is exact for $\Phi = 0$,

$$c_0(x,t) = exp\left[m\beta\gamma^{-1}\left(t - \gamma^{-1}\right)\partial^2/\partial x^2\right]a_0(x). \tag{64}$$

Thus, $a_0(x)$ may be used as the initial value for the diffusion equation that describes the long time behavior of the density, but not at the "real" time $t = 0$, but at the shifted time $t = +\gamma^{-1}$. This is a clear (and particularly simple) example of *initial slip* : the asymptotic (macroscopic) solution for long times does not connect smoothly to the initial values provided by forming the appropriate integral over the mesoscopic initial distribution, as is to be expected, since the mesoscopic solution consists of both fast and slow components. However, when one is not interested in the fast components, one may "bridge" the transitional region, during which the hydrodynamic regime has not yet been established, and extract the initial value for the macroscopic equation by means of a projection operator. A warning is in order however, as on also sees from (63) : the operator acting on $a_0(x)$ is a highly singular one, since it amounts to letting the diffusion equation act *backwards in time* for a period γ^{-1}, which gives a sensible result only for very smooth $a_0(x)$. This makes sense, since our perturbation parameter, though equal to γ^{-1} in the formal expansion, is in reality the ratio between the velocity persistence length and the length over which $P(u, x, t)$ varies. I have to add, however, that in the particular case under discussion the result (64) can be derived directly from the solution of the Klein-Kramers equation in the limit $exp[-\gamma t] << 1$, hence the result (64) turns out to make sense even if (63) does not, such as for a δ-function as $a_0(x)$. This may not be just a lucky accident : (64) is based on the picture that there is a clear separation in time scales between solutions of type (55) and those of type (51) with $n \neq 0$. This is no longer the case which $c_0(x)$ has components that vary strongly in space. Hewever, exactly those troublesome components will have decayed before the asymptotic regime described e.g. by (64) sets in. The example shows, however, that the separation of time scales that lies at the basis of many of our developments need not be a property of the operator in the finer-grained description as such : the spectrum of the Klein-Kramers operator consists of $\lambda_{nk} = -n\gamma - (m\beta\gamma)^{-1}k^2$, which cover the negative real axis rather uniformly. It is only after one restricts oneself to phase functions that are smooth in space, so that high k-values do not occur, that the gaps in the spectrum and the time scale separation emerge.

The next, and final topic I wish to address in this chapter, and in these lectures, is that of finding *boundary conditions* for the equations on the contracted level of description. This is not always a problem : it may happen, that the boundary conditions on the mesoscopic level are obeyed, exactly or in good approximation, by a solution of type (55), or (58) in kinetic theory, as is e.g. the case for specular or diffuse reflection (the latter only for walls in approximate thermal equilibrium with the particles studied). Then the boundary condition can be expressed naturally in terms of $c_0(x, t)$, or of $\mathbf{s}(\mathbf{r}, t)$ in kinetic theory. However, often the mesoscopic boundary conditions are *not* compatible with local thermodynamic equilibrium. The most obvious case is that of an *absorbing* boundary, where one should have $P(u, 0, t) = 0$ for $u > 0$ at a left wall at $x = 0$; there is no way to reach such a result by means of small corrections to a Maxwellian. Similar effects may occur at *internal* boundaries, such as sudden jumps in the potential (where the derivation of the hydrodynamic equations also breaks down due to the large gradient of Φ).

Near such external or internal boundaries there will occur a *kinetic boundary layer*, in which large deviations from local equilibrium occur. The thickness of this boundary layer is of the order of the typical length that also occurs in the derivation of the hydrodynamic equations, hence the velocity persistence length l for Brownian particles or the mean free path in kinetic theory. We shall discuss the kinetic boundary layer for the simplest case, the *stationary* Klein-Kramers equation without an external potential. Time dependence can be taken into account by passing to the Laplace-transform, and a linearly varying potential can also be included (potentials that cannot be approximated by a linear one over the thickness of the kinetic boudary layer would violate the small r-gradient condition for the validity of the hydrodynamic equations). The solution of the boundary layer problem is possible by considering special solutions of the form

$$\Psi_n(u,x) = exp\left[-q_n x\right]\varphi_n(u). \tag{65}$$

The determination of the λ_n and φ_n leads to the nonhermitian eigenvalue problem (in units with $\gamma = m\beta = 1$)

$$\frac{1}{u}\frac{\partial}{\partial u}\left(u + \frac{\partial}{\partial u}\right)\varphi_{\sigma n}(u) = -q_{\sigma n}\varphi_{\sigma n}(u) \tag{66}$$

where $\sigma = \pm 1$. By substitution one verifies

$$q_{\sigma n} = \sigma\sqrt{n};\ \ \varphi_{\sigma n}(u) = \frac{1}{\sqrt{n!}}e^{-u^2/2}D_n(2q_n - \sigma u), \tag{67}$$

where $D_n(z)$ is the parabolic cylinder function, which for natural numbers n is related to the Hermite polynomials via

$$D_n(z) = 2^{-n/2}e^{z^2/4}H_n(z/\sqrt{2}). \tag{68}$$

However, there is one additional complication : the eigenvalues with $n \neq 0$ occur in pairs, and for finite external force α or Laplace variable s there are also *two* low-lying eigenvalues $\pm(s+\alpha^2)^{1/2}$. For $s = \alpha = 0$ however, we find only a single eigenfuction $\varphi_0(u)$, the equilibrium distribution. However, there is also one *associated* function $\varphi_0'(u) \equiv u\varphi_0(u)$, which obeys

$$\frac{1}{u}\frac{\partial}{\partial u}\left(u + \frac{\partial}{\partial u}\right)\varphi_0'(u) = -\varphi_0(u). \tag{69}$$

The appearance of such associated functions is a wellknown feature of nonhermitian eigenvalue problems, such as the damped harmonic oscillator with critical damping. It implies that the solutions of type (65) are not complete ; they must be supplemented by additional solutions. In our case there is just one such additional solution, namely

$$\Psi_0^c(u,x) = \frac{x-u}{\sqrt{2\pi}}e^{-u^2/2}, \tag{70}$$

which, in contrast to all functions of type (65), carries a *particle current*, with the normalization in (70) a unit of current in the negative x-direction. Thus, it is also clear on physical grounds, that a solution of type (70) is necessary for a complete description of the system : the Smoluchowski or diffusion equation also has two independent stationary solutions, the equilibrium solution and a solution with constant current, and these should have their counterparts on the mesoscopic level. Since we have to do with a non-hermitian eigenvalue problem, the usual orthogonality and completeness theorems cannot be relied upon, and results have to be proved from case to case. Two important properties, which have been proved for many particular cases, are

1. Full-range completeness and quasi-orthogonality : The set $\{\varphi_0(u), \varphi_0'(u), \varphi_{\pm n}(u)\}$ is complete on $-\infty < u < \infty$, and orthogonal with weight function $\sim uexp\,[u^2/2]$ (with complications for n=0). This allows one to construct a unique solution $P(u,x)$ for $x > 0$, that approaches a prescribed function $g(u)$ for $x \to 0$. Unfortunately, this is a type of problem that hardly ever occurs in practice ; the solution, which contains terms with $\Psi_{-n}(u,x)$ that grow exponentially with x, is also not very relevant physically.
2. Half-range completeness : The set $\{\varphi_0(u), \varphi_{+n}(u)\}$ is complete on $0 < u < \infty$. This guarantees the existence of a *unique* solution that approaches a given function $g(u)$ for $x \to 0, u > 0$, and stays finite for $x \to \infty$. Since there is no corresponding orthogonality property, there is no prescription to construct this solution in closed form. However, once we know a unique solution exists, we can devise numerical methods to approximate it. Moreover, for some cases, including the Klein-Kramers case, there are prescriptions that give the result e.g. in terms of infinite (double) series, though badly converging ones.

Some of the problems that can thus be solved are :

(a) The albedo problem : particles are continually injected into the system at $x = 0$ with a velocity distribution $g(u), u > 0$ and leave the system when they first reach $x = 0$ again (with a negative velocity). One asks for the velocity distribution of the outcoming particles. The problem occurs e.g. for a planetary atmosphere, or for a layer of paint, upon which light (described as particles) falls from the outside. Inside the medium the light may be absorbed or scattered elastically (without frequency shift) and one is interested in the intensity and the angular distribution of the outcoming photons.

(b) The Milne problem : a source of particles deep inside the medium causes a constant current towards the surface ; particles reaching the surface leave the system and one is again interested in their angular distribution. This is the problem of light emission by the sun (intensity distribution over the solar disk), or of the neutrons leaving a nuclear reactor. A solution may be postulated in the form

$$P(u,x) = C_0 \left[\Psi_0^c(u,x) + d_0 \varphi_0(u) + \sum_{n=1}^{\infty} d_{+n} \varphi_{+n}(u) e^{-x\sqrt{n}} \right] . \qquad (71)$$

The condition that all particles reaching the surface leave it implies $P(u,0) = 0$ for $u > 0$; hence the problem can be reduced to the albedo proble m for

$$g(u) = -C_0 \Psi_0^c(u,0) = \frac{C_0 u}{\sqrt{2\pi}} e^{-u^2/2}. \qquad (72)$$

For $x >> 1$, the last term in (71) can be neglected and the solution approaches

$$P_{as}(u,x) = C_0 \left[\frac{x + d_0 + u}{\sqrt{2\pi}} e^{-u^2/2} \right] ; \qquad (73)$$

the corresponding density distribution is

$$n_{as}(x) = C_0 \left(x + d_0 \right) \equiv C_0 \left(x + x_M \right) ; \qquad (74)$$

thus d_0, with the dimension of a length, can be interpreted as the distance beyond the surface where the asymptotic density profile extrapolates to zero. In other words, $n_{as}(x)$ is the solution of the problem

$$\frac{d^2 n_{as}(x)}{dx^2} = 0 \, ; \; n_{as}\left(-x_M\right) = 0; \;\; n_{as} \to C_0 x \; for \; x \to \infty. \qquad (75)$$

The first boundary condition is to be compared with the condition $n_{as}(0) = 0$, that is imposed when one wishes to solve the diffusion equation with an absorbing boundary condition in hydrodynamics. Thus, that "naive" boundary condition is to be applied not at the physical surface, but at an imaginary surface, placed at a distance x_M (in units of the velocity persistence length) beyond the real one. The situation is similar to (64), where the "naive" initial condition has to be applied at a time $t = \gamma^{-1}$ instead of $t = 0$. The distance x_M is called the *slip length* of our problem. For the Klein-Kramers case, x_M can be determined exactly by means of the Wiener-Hopf technique ; the result is

$$x_M = -\zeta \left(\frac{1}{2} \right) = 1.46035 \cdots . \qquad (76)$$

(c) Scattering problems. Here, the boudary condition can be expressed in a scattering kernel $\sigma\left(u'|u\right)$ by means of

$$uP(u,0) = \int_{-\infty}^{0} |u'| \, \sigma\left(u|u'\right) P\left(u'\right) du'. \qquad (77)$$

For the Klein-Kramers case one gets nontrivial hydrodynamics only for the case of incomplete scattering (partial absorption) :

$$r\left(u'\right) \equiv \int du\sigma\left(u|u'\right) < 1, \tag{78}$$

where a Milne length dependent on $r\left(u'\right)$ is found.

The solutions of the boundary layer problems yield the complete $P(u,x)$ in addition to these asymptotic results. They are of some independent theoretical interest, since they exhibit an interesting nonanalytic structure at $x = 0$, $u = 0$. For example, the solution of the Klein-Kramers equation for the Milne problem has a square root singularity there, which can be extracted from the asymptotic behavior of the d_{+n} in (71) for $n \to \infty$ (as the singularities of a function can be found from the asymptotic behavior of its Fourier coefficients).

To conclude this chapter I want to make a few remarks on the situation in kinetic theory. For the linearized Boltzmann equation, one is again led to an eigenvalue problem of the type

$$u^{-1}\mathcal{C}\varphi_{\sigma n}(u) = -q_{\sigma n}\varphi_{\sigma n}(u). \tag{79}$$

This time, there are five eigenfunctions with $q = 0$, the five collision invariants, and in addition three solutions of nonseparated type (69), which carry a heat current, and two components of a transverse momentum current (particle current equals a density of longitudinal momentum, and the longitudinal momentum current is associated with the kinetic energy density). The typical problems to be solved (in one dimension) are a gas between two plates at different temperatures and / or with different transverse velocities. The asymptotic temperature and velocity profiles calculated from the solution of the boundary layer problems (one at each plate) again reach their "naive" values (temperature or velocity of the plates themselves) not at the plates, but at certain slip lengths behind the plates. The slip lenghts again are of the order of a mean free path.

Literature

This list of references does not intend to be comprehensive. I tried to give reference to books and review articles, rather than to original papers, except where they are accessible to non-specialists, or when no reviews are available.

Ch.1 : A good source for survey articles on various aspects of statistical mechanics, some of which are addressed in this series of lectures, is the series of summer school proceedings "Fundamental Problems in Statistical Mechanics, I, II, III.···", that have appeared at irregular intervals with different editors and publishers since the early 1960's. Many of the topics discussed in this introduction are also treated in the article by G.E.Uhlenbeck in Vol.II of this series.

Ch.2 : The classic book on this subject is :

œ*B*!!œ(*BV.I.ArnoldandA.Avez,"ErgodicProblemsofClassicalMechanics"(Benjamin, New York,* 1968)*.Thebookisclearlywritten, butinarathermathematicalstyle.*
Reviewarticleswrittenfornonspecialistphysicistsare :
œB!!œ(BO.Penrose, Rep. Progr. Phys. **42**, 1937 (1979)
œ*B*!!œ(*BA.S.Wightmanin"StatisticalMechanicsattheTurnoftheDecade"*,
œB!!œ(BE.G.D. Cohen, Ed. (Dekker, New York, 1971).

Ch.3 : The classic reference on this subject is :

œ*B*!!œ(*BN.G.vanKampen,"StochasticProcessesinPhysicsandChemisty"*
œB!!œ(B(North Holland, Amsterdam, 1981)

The derivation of the master equation follows ideas of van Kampen, which can be found in the first book of the series mentioned with Ch.1.

Ch.4 : Whereas Klein's paper appeared in a rather inaccessible journal, the original paper by Kramers

œ*B*!!œ(*BH.A.Kramers, Physica***7**, 284(1940)
isaccessibleandstillworthreading.Thetreatmentgivenintheselecturescanbefoundinamoredetaile
œB!!œ(BU,M,Titulaer, Physica **91A**, 321 (1978).

A treatment of the more mathematical aspects, which also recapitulates the work by C. Bloch (available only in French) is

œ*B*!!œ(*BU.M.Titulaer, Physica***100A**, 234(1980).
Areviewonadiabaticeliminationoffastvariabesis
œB!!œ(BN.G.van Kampen, Physics Reports **124**, 69 (1985).

A simple case, involving only matrix algebra, is discussed in

œ*B*!!œ(*BU.Geigenmueller, U.M.TitulaerandB.U.Felderhof, Physica***119A**, 41(1983).
TheChapman–Enskogmethodistreatedinallbooksonkinetictheory; aclearandveryprecisetreatm
œB!!œ(BC.Cercignani, "The Boltzmann Equation and its Application" (Springer, Berl in, 1988)

The complications caused by adiabatic elimination of fast variables in the Onsager-Casimir relations, mentioned at the end of the chapter, are discussed in

œ*B*!!œ(*BU.Geigenmueller, U.M.TitulaerandB.U.Felderhof, Physica***119A**53(1983)

Theconsequencesforthecorrectionstothe Smoluchowskiequationandforthe Burnettcorrectionsto
Stokesequationsarediscussedin
œB!!œ(BG.F.Hubmer and U.M.Titulaer, J. Stat. Phys. **49**, 331 (1987)
œ*B*!!œ(*BG.F.HubmerandU.M.Titulaer*, *J.Stat.Phys.***50**, 913(1988)
Ch.5 : *Theinitialslipproblemistreatedinthefirstpaperbymequotedunder Ch*.4; *asimplespecialcas*
œB!!œ(BU.M.Titulaer, J. Chem. Phys. **78**, 1004 (1983).
Boundary layer problems in kinetic theory are treated very clearly in the book by Cercignani quoted under Ch.4 ; examples from other transport equations can be found in
œ*B*!!œ(*BJ.J.DuderstadtandW.R.Martin*, "*TransportTheory*" (*Wiley*, *NewYork*, 1979).
Theboundarylayerproblemforthe Klein−*Kramersequationwasfirsttreatedinarathercompletew*
œB!!œ(BM.A.Burschka and U.M.Titulaer, J. Stat. Phys. **25**, 569 (1981),
œ*B*!!œ(*BM.A.BurschkaandU.M.Titulaer*, *Physica***112A**, 315(1982).
Ashortreview, *inanunfortunatelynotveryaccessiblesource*, *is*
œB!!œ(BU.M.Titulaer in "Coherence, Cooperation and Fluctuations",
œ*B*!!œ(*BF.Haakeetal.*, *eds.*(*CambridgeUniv.Press*, *Cambridge*, 1986).
Themostcompleteexactresultsavailabletodatearefoundin
œB!!œ(BA.J.Kainz and U.M.Titulaer, J. Phys. A (Math.Gen.) **24** 4677 (1991).
Two other papers by the same authors in the same journal treat accurate numerical results and analytical results for the simplified BGK-model, a soluble Boltzmann equation. An application to droplet condensation can be found in
œ*B*!!œ(*BG.F.HubmerandU.M.Titulaer*, *J.Stat.Phys.***63**, 203(1991).œB!!œ(B