

LECTURE NOTES

METHODS
of
QUANTUM STATISTICAL MECHANICS

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Chapter 1

Kinetic Theory

1.1 Introduction

This chapter deals with the kinetic theory of quantum gases consisting of fermions, bosons or a mixture of both. The theory is concerned with non-equilibrium states and processes in particle systems whose constituents are in some way weakly coupled. That is to say, it is assumed that the interaction between the particles can be characterized by a small parameter. This can be a dimensionless coupling constant, or the ratio of the mean distance between the particles and their size or the range of the interaction. However, it is not assumed that the quantum effects arising from the Fermi or Bose statistics are small.

The value of kinetic theory is that it enables one to explicitly calculate the transport coefficients for a variety of physically interesting systems, which include dilute gasses, plasmas and electrons in metals. Despite the restriction of weak coupling and rarefaction, the theory can also be applied to dense liquids by taking quasi-particles, instead of bare ones, as the fundamental constituents of matter.

The number of applications in physics, astrophysics and, especially, in the technical sciences, is enormous, and we have to confine ourselves to the most general subjects which exhibit the basic kinetic phenomena, and the methods of treating them. Most attention will be given to neutral quantum gasses as the simplest example treated by kinetic theory. However, the presentation will be kept as general as possible to bring the general features and basic reasoning to the forefront.

For the following we will borrow some notations from relativity theory. We will often indicate a point of space-time as $x = x^\mu = (t, \mathbf{x})$, $\mu = 0, 1, 2, 3$, and particle energy-momentum by $p = p^\mu = (p_0, \mathbf{p})$. In the present chapter the energy p_0 will always be equal to $\epsilon(\mathbf{p}) = \mathbf{p}^2/2m$, except where indicated differently. Gradient operator and time derivative may also be combined: $\partial_\mu = (\partial_t, \nabla)$, $\partial^\mu = (\partial_t, -\nabla)$. Furthermore, we will often write $x \cdot p = x_\mu p^\mu = x^\mu p_\mu$ for $tp_0 - \mathbf{x} \cdot \mathbf{p}$. We will use natural units $\hbar = c = k_B = 1$ throughout.

1.2 Distribution function

On the macroscopic level the state of a many-particle system is described by the conserved charge densities $N_A(x)$, the energy density $E(x)$, and the momentum density $\mathbf{G}(x)$. Furthermore, one may define a space- and time-dependent entropy density $S(x)$. Since entropy always increases, $S(x)$ satisfies a balance equation of the form

$$\partial_t S(x) + \nabla \cdot J_S(x) = \sigma(x), \quad (1.1)$$

where J_S is the entropy flow, and σ the entropy production (per unit volume and unit time) which is never negative:

$$\sigma(x) \geq 0. \quad (1.2)$$

These two formulae above constitute the local formulation of the second law of thermodynamics. It applies under the same restrictions as the continuum model of macroscopic physics [5].

Exercise 1.1

Show by integrating over all space that (1.1) implies that the total entropy never decreases.

A non-equilibrium state of a system is characterized by a non-zero entropy production. However, at this stage we do not yet know how the entropy production is related to the irreversible processes which may occur in the system. Therefore, we shall use for now a more heuristic criterion for non-equilibrium behaviour: we shall declare a system to be outside equilibrium if the distribution function

$$f_k(x, p) = n_k(p) + \delta f_k(x, p) \quad (1.3)$$

differs by a non-zero amount δf_k from the equilibrium distribution function $n_k(p)$ to be determined. Since, in general, the properties of a non-equilibrium system are non-stationary and non-uniform, the distribution function is space and time dependent. To keep the discussion general we assume that there are a number $k = 1, 2, \dots$, of different particle species in the system. However, we shall confine ourselves to systems only slightly out of equilibrium which means that δf_k is small, and that quadratic terms may be neglected.

Let us now write down the particle density of component k :

$$N_k(x) = \int d\omega_k f_k(x, p), \quad (1.4)$$

where we introduced the notation

$$d\omega_k := g_k \frac{d^3 p}{(2\pi)^3}. \quad (1.5)$$

with g_k the spinweight factor. It is customary to regard f_k as giving the distribution of the particles in μ -space:

$\triangleright g_k f_k(x, p) \Delta^3 p \Delta^3 x$ = the number of particles of species k which at time t are situated in the small volume $\Delta^3 x$ at the point x with momenta lying in the range $(\mathbf{p} - \frac{1}{2} \Delta \mathbf{p}, \mathbf{p} + \frac{1}{2} \Delta \mathbf{p})$.

However, it must be stressed that this definition is not really necessary. It is sufficient to assume that the density can be expressed in terms of an ancillary quantity $f_k(x, p)$ which in equilibrium reduces to the Fermi or Bose distribution function. In terms of this ancillary quantity the energy density and entropy density of species k take the forms

$$E_k(x) = \int d\omega_k \varepsilon_k f_k(x, p), \quad (1.6)$$

$$S_k(x) = \int d\omega_k [f_k \log f_k - \eta(1 + \eta f_k) \log(1 + \eta f_k)], \quad (1.7)$$

where $\eta = +1$ for bosons, and -1 for fermions. Because of the absence of any interaction terms, the expressions are only valid for weakly coupled or dilute particle systems. Nevertheless, this theory of nonequilibrium "ideal" gases is very important as a model and guideline for the construction of more complicated theories.

1.3 Conservation laws

Let us now go back to the particle densities (1.4). In general these densities will not correspond to a conservation law, because of chemical, nuclear or other reactions taking place in the system. First we must ask ourselves which particle properties are conserved, i.e. what charges are carried by the particles. Assume, for instance, that the particles carry an electromagnetic charge q_k . The conserved charge density is then

$$N(x) = \sum_k q_k N_k(x), \quad (1.8)$$

and the corresponding current density

$$\mathbf{J}(x) = \sum_k q_k \mathbf{J}_k(x), \quad (1.9)$$

$$\mathbf{J}_k(x) = \int d\omega_k \mathbf{v}_k f_k(x, p), \quad (1.10)$$

with

$$\mathbf{v}_k(\mathbf{p}) = \frac{\partial \varepsilon_k(\mathbf{p})}{\partial \mathbf{p}} \quad (1.11)$$

the velocity of the particles.

In general, particles will carry more than one conserved charge q_{Ak} , $A = 1, 2, \dots$, like atomic weight, lepton charge, baryon charge, etc. Moreover, for non-relativistic systems, total mass is strictly conserved which means that the mass number m_k/m , with m some

convenient reference mass, is one of the conserved quantum numbers. We take this into account by defining

$$J_A^\mu(x) = \sum_k q_{Ak} J_k^\mu(x), \quad (1.12)$$

For the sake of a compact notation, we combined charge and current density into one four-vector $J_A^\mu = (N_A, \mathbf{J}_A)$. This allows us to write the continuity equation

$$\partial_\mu J_A^\mu(x) = 0. \quad (1.13)$$

Any conserved quantum number implies the existence of a conserved macroscopic current density.

Exercise 1.2

Consider a ν npe system. Electromagnetic charge, lepton number and baryon number are conserved. Write down the corresponding quantum numbers and conserved currents, and tabulate the allowed two-particle reactions.

Momentum and energy are always conserved because of the translational invariance of space-time. This means that we must have

$$\partial_t E + \nabla \cdot \mathbf{J}_E = 0, \quad (1.14)$$

Where $E = \sum_k E_k$ is the total energy density, and

$$\mathbf{J}_E = \sum_k \int d\omega_k \epsilon_k \mathbf{v}_k f_k \quad (1.15)$$

the energy flow (density). Similarly, the momentum conservation law reads

$$\partial_t \mathbf{G} + \nabla \cdot \mathbf{P} = 0 \quad (1.16)$$

with

$$\mathbf{G} = \sum_k \int d\omega_k \mathbf{p} f_k \quad (1.17)$$

the momentum density, and

$$\mathbf{P} = \sum_k \int d\omega_k \mathbf{p} \mathbf{v}_k f_k \quad (1.18)$$

the pressure tensor.

Energy-momentum conservation may be combined into one single conservation law

$$\partial_\mu T^{\mu\nu} = 0 \quad (1.19)$$

by defining the energy-momentum tensor as

$$T^{\mu\nu} = \sum_k \int d\omega_k p_k^\mu v_k^\nu f_k. \quad (1.20)$$

In this expression one should read $v_k^\mu = (1, \mathbf{v}_k)$ and $p_k^\mu = (\epsilon_k, \mathbf{p})$. Notice that in the non-relativistic case the energy-momentum tensor is not symmetric: $T^{0i} \neq T^{i0}, i = 1, 2, 3$.

1.4 Kinetic equation

A kinetic equation, also called transport equation, is an equation of motion for the space-time behaviour of the distribution function. The derivation and justification of such equations for various systems and circumstances is one of the tasks of statistical mechanics. However, we do not wish to discuss this in any detail. Instead, we shall rely on consistency and plausibility arguments. Our starting point will be the conservation laws. Take, for example, the energy conservation law (1.14). After substitution of (1.6) and (1.15), this equation may be written as

$$\sum_k \int d\omega_k \epsilon_k (\partial_t f_k + \mathbf{v}_k \cdot \nabla f_k) = 0. \quad (1.21)$$

This implies that the kinetic equation must be of the form

$$\partial_t f_k(x, p) + \mathbf{v}_k \cdot \nabla f_k(x, p) = C_k(x, p), \quad (1.22)$$

with a source term such that

$$\sum_k \int d\omega_k \epsilon_k C_k = 0. \quad (1.23)$$

The physical significance of C_k may not be clear at this point, but it seems intuitively obvious that C_k will involve the interaction between the particles. The constraint (1.23) expresses then the fact that in any particle interaction energy is strictly conserved.

By a similar reasoning we arrive at the conclusion that we also must have

$$\sum_k \int d\omega_k \mathbf{p} C_k = 0, \quad (1.24)$$

and

$$\sum_k \int d\omega_k q_{Ak} C_k = 0, \quad (1.25)$$

which reflect the conservation laws of momentum and charge on the microscopic level.

The quantities q_{Ak} , ϵ_k , and \mathbf{p}_k are often called the collision invariants, or also summational invariants, because in an arbitrary n -particle collision they are additively conserved. For example, in a typical two-particle event (see figure 1) we have

$$q_{Ak} + q_{Al} = q_{Ai} + q_{Aj}, \quad (1.26)$$

$$p_k^\mu + p_l^\mu = p_i^\mu + p_j^\mu. \quad (1.27)$$

If the particles before and after a collision are the same, one calls the collision elastic, and inelastic otherwise. In the simplest case of a one-component system, there are five collisional invariants: particle number (mass), momentum, and energy. This number five appears everywhere in kinetic theory as some kind of magic number.

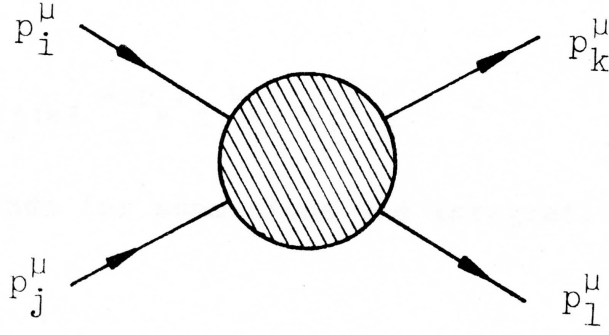


Figure 1.1: Two-particle collision

1.5 Collision integral

The kinetic equation (1.22) becomes meaningful only when the form of the source term, called the collision integral, has been established. To obtain an explicit expression we follow a reasoning originally due to Boltzmann (1872), the founder of kinetic theory. We see from its definition that C_k gives the nett increase of particles of species k with a given momentum per unit volume and unit time. Let us denote by $W_{ij|kl}(p_i, p_j|p_k, p_l)$ the probability that two particles with initial four-momenta p_i^μ, p_j^μ collide and produce two particles with four-momenta p_k^μ, p_l^μ (per unit volume and per unit time). For a given interaction this rate can be calculated with the aid of quantum-mechanical scattering theory. In terms of this transition rate the collision integral looks schematically like

$$C_k = \sum_{i,j,l} \left[\begin{array}{c} i \quad k \\ \diagdown \quad \diagup \\ \text{---} \text{---} \\ \diagup \quad \diagdown \\ j \quad l \end{array} - \begin{array}{c} k \quad i \\ \diagdown \quad \diagup \\ \text{---} \text{---} \\ \diagup \quad \diagdown \\ l \quad j \end{array} \right] \quad (1.28)$$

The first term counts the ‘gain’ collisions, and the second one the ‘loss’ collisions of particles with four-momenta p_k^μ .

The transition rate is normalized to two particles per unit volume. Since the actual number of pairs available is proportional to the product $f_i f_j$ we have to multiply by this factor. Thus, the collision term reads more explicitly:

$$C_k[f] = \int [f_i f_j W_{ij|kl} - f_k f_l W_{kl|ij}]. \quad (1.29)$$

The integral sign stands for summations and integrations over all irrelevant variables

$$\int := \frac{1}{2} \sum_{l,i,j} \int d\omega_l d\omega_i d\omega_j. \quad (1.30)$$

The factor one-half compensates for the double counting of the two identical states (i,j) and (j,i).

Exercise 1.3

Write out the collision integral for a one-component gas. Indicate explicitly the x and p dependences of the various quantities.

The above reasoning is quite general and applies to non-relativistic as well as relativistic particles, irrespective of their interaction (barring the long-range Coulomb force). The specifics of the interaction are hidden in the transition rate. Because of energy and momentum conservation (1.27) in a collision, this quantity must contain an four-momentum conserving delta-function. This guarantees that the two requirements (1.23) and (1.24) are always identically satisfied.

Moreover $W_{ij|kl}$ can only be different from zero for collisions in which the appropriate quantum numbers are conserved. Hence, the collision integral also satisfies requirement (1.27). Detailed proofs of these statements may be found in the standard textbooks [2, 3, 4]

In deriving the Boltzmann collision integral (1.29), we have overlooked one important aspect, namely, the statistics of the particles. Suppose the particles are fermions. Then, these particles cannot scatter into states that are already occupied. The average occupancy of a one-particle state k is given by f_k . Hence, we must reduce the probability for scattering into this state by multiplying the transition rate with the so called blocking factor $1 - f_k$. The collision term which takes this quantum effect into account was first given by Nordheim (1928) and Uehling and Uhlenbeck (1933). It has the form [1]:

$$C_k[f] = \int [f_i f_j W_{ij|kl} (1 + \eta f_k) (1 + \eta f_l) - f_k f_l W_{kl|ij} (1 + \eta f_i) (1 + \eta f_j)]. \quad (1.31)$$

In contrast to fermions, bosons are stimulated to scatter into states which are already occupied. Below we shall see that these additional factors are rather essential: without them the equilibrium distribution function would not be a solution of the transport equation.

1.6 Linearized collision operator

The collision integral (1.31) is a non-linear functional of the distribution functions, and usually too difficult to handle in practical calculations. The standard procedure is to linearise around equilibrium by substitution of (1.3) and by expansion up to first order in δf . In this way one gets:

$$C_k[f] = \int [n_i n_j (1 + \eta n_k) (1 + \eta n_l) - n_k n_l (1 + \eta n_i) (1 + \eta n_j)] W_{ij|kl} - L_k[\delta f], \quad (1.32)$$

if also use is made of the detailed balance property

$$W_{ij|kl} = W_{kl|ij}, \quad (1.33)$$

which need not always be valid, but usually is due to time-reversal invariance. We first consider the term written out explicitly. It should vanish identically because in equilibrium the collision integral must be zero. This implies the relationship

$$\frac{n_i}{1 + \eta n_i} \frac{n_j}{1 + \eta n_j} = \frac{n_k}{1 + \eta n_k} \frac{n_l}{1 + \eta n_l}. \quad (1.34)$$

We know that these special combinations of distribution functions have the form of exponentials:

$$\frac{n_i}{1 + \eta n_i} = e^{-\psi_i}. \quad (1.35)$$

Hence, condition (1.34) implies

$$\psi_i + \psi_j = \psi_k + \psi_l, \quad (1.36)$$

which is the generic form of a conservation law. As a consequence, ψ_k can only be a linear combination of the collision invariants

$$\psi_k = \sum_A q_{Ak} \alpha_A + \beta \epsilon_k - \boldsymbol{\beta} \cdot \mathbf{p} + \gamma. \quad (1.37)$$

For a system in rest one may show that $\boldsymbol{\beta}$ and γ are zero. Then the equilibrium distributions take the standard form

$$n_k = \frac{1}{e^{\psi_k} - \eta}. \quad (1.38)$$

These are characterized by the inverse temperature $\beta = 1/T$, and the independent chemical potentials $\mu_A = -\alpha_A/\beta$ corresponding to the conserved charges. This shows that there exists an intimate connection between the equilibrium distribution function and the form of the collision integral.

Exercise 1.4

Under a Galilei transformation $\mathbf{p} \rightarrow \mathbf{p} + m\mathbf{v}$ the distribution function transforms as a scalar. Use this fact to show that β behaves as a scalar, $\boldsymbol{\beta}$ as a velocity, and that $\gamma = \frac{1}{2}m_k\boldsymbol{\beta}^2/\beta$.

Now the second term of (1.32). We write $\delta f_k = n_k(1 + \eta n_k)\phi_k$. We then get, collecting terms linear in ϕ_k , using also detailed balance (1.33) and the product rule (1.34), the linearised collision operator

$$L_k[\delta f_k] = \frac{1}{2} \sum_{l,i,j} \int d\omega_l d\omega_i d\omega_j n_k n_l (1 + \eta n_i)(1 + \eta n_j) (\phi_k + \phi_l - \phi_i - \phi_j) W_{ij|kl}, \quad (1.39)$$

where the summations and integrations have been made explicit. This symmetrical form makes it immediately clear that the collision integral vanishes for any deviation function

ϕ_k that satisfies (1.36), i.e. for any collision invariant ψ_k . It is also easy to show that one has

$$\sum_k \int d\omega_k \psi_k L_k[\delta f] = 0 \quad (1.40)$$

by interchanging dummy variables. As it should be, the linearised collision operator preserves the conservation laws.

Exercise 1.5

Verify (1.40).

After linearisation the kinetic equation for the deviation function δf_k becomes

$$(\partial_t + \mathbf{v}_k \cdot \nabla) \delta f_k = -L_k[\delta f]. \quad (1.41)$$

It is still rather hard to solve, in general. For the purpose of a qualitative treatment it is convenient to estimate the collision operator by means of the mean free time τ_k which is defined as follows:

$$(1 + \eta n_k) \tau_k^{-1} = \frac{1}{2} \sum_{l,i,j} \int d\omega_l d\omega_i d\omega_j n_l (1 + \eta n_i) (1 + \eta n_j) W_{ij|kl}. \quad (1.42)$$

For a first estimate we can then put

$$L_k[\delta f] \sim \tau_k^{-1} \delta f_k. \quad (1.43)$$

This is called the relaxation-time approximation because τ_k acts as a relaxation time for the establishment of equilibrium in each volume element of the gas.

Exercise 1.6

Consider a one-component system and ignore the statistics and spin factors. Calculate τ_k^{-1} given that

$$W_{ij|kl} = \frac{(2\pi)^6}{m} |\mathbf{p}_i - \mathbf{p}_j| \sigma \delta^{(4)}(p_i + p_j - p_k - p_l)$$

with the so-called cross-section σ a constant.

The relaxation time still depends on the energy e_k . However, various average relaxation times can now be defined by

$$\langle \tau \rangle^r = (N^r)^{-1} \sum_k \int d\omega_k n_k (1 + \eta n_k) (\epsilon_k)^r \tau_k, \quad (1.44)$$

where the normalization factor N^r is the same integral without τ_k . These averages, when employed with care, are useful for estimating the value of transport coefficients; the value of r varies according to which transport phenomenon is under consideration.

We close with a few general remarks about the limitation of the kinetic equation (1.41) with (1.39). In the first place it is obvious that only two-particle events have been taken into account which seems to restrict the treatment to dilute gasses. However, there is a way around this problem which in practice works quite well. It consists in using for the transition rate W an effective transition rate which describes scattering of particles in a medium rather than in vacuum. In this way many-body correlation effects can be taken into account. A second remark is that we have regarded collisions as essentially instantaneous and occurring at a particular point in space. It is therefore clear that the equation allows us in principle to follow the variation of the distribution function only over times long compared with the duration and extension of a collision. The typical distance is of the order of the range of the interaction. Such a value gives a lower limit of distances that can be dealt with by means of the transport equation. In practice, however, there is usually no need for a more detailed account of the behaviour of the system.

Finally we mention that there exist collision integrals other than the Boltzmann one, to suit special purposes especially in plasma physics. For the following this is hardly relevant because the only essential property we will use is (1.40), which is the immediate consequence of the existence of conservation laws.

1.7 Local equilibrium

A gas left to itself, like any macroscopic system, will tend to a state of thermal and chemical equilibrium. In this state the entropy of the system reaches its maximum value. A necessary condition for complete equilibrium is, therefore, that the entropy production vanishes everywhere in space-time. If we define an entropy density and flux $S^\mu = (S, \mathbf{J}_S)$ according to

$$S^\mu = - \sum_k \int d\omega_k v_k^\mu [f_k \log f_k - \eta(1 + \eta f_k) \log(1 + \eta f_k)], \quad (1.45)$$

we can write the entropy law (1.1) as

$$\partial_\mu S^\mu = \sigma, \quad (1.46)$$

and with the help of the kinetic equation (1.22) we find for the entropy production

$$\sigma = - \sum_k \int d\omega_k C_k \log \frac{f_k}{1 + \eta f_k}. \quad (1.47)$$

Since the establishment of statistical equilibrium in a gas is brought about by collisions, the increase of entropy arises from the collision integral which must be such that $\sigma \geq 0$. The proof that this is indeed the case is known as the H-theorem. This was the great success of Boltzmann (1872) who provided the proof for the collision integral (1.29). By an analogous reasoning the H-theorem for the Uehling-Uhlenbeck collision integral (1.31) can be established.

Exercise 1.7

Write down the entropy production (1.47) in the linear approximation, and verify the H-theorem for this case.

It is remarkable that the condition

$$\sigma(x) = 0 \quad (1.48)$$

is in itself not sufficient for complete equilibrium. The reason is, what else, the existence of conservation laws. Indeed, if we substitute in (1.47) a distribution function $f_k^{(0)}(x, p)$ such that

$$\log \frac{f_k^{(0)}}{1 + \eta f_k^{(0)}} = -\psi_k \quad (1.49)$$

with ψ_k a linear combination of collision invariants

$$\psi_k(x, p) = \sum_A q_{Ak} \alpha_A(x) + \beta(x) \epsilon_k - \boldsymbol{\beta}(x) \cdot \mathbf{p} + \gamma(x), \quad (1.50)$$

then equation (1.48) is satisfied identically in virtue of the integral constraints (1.23) through (1.25). The parameters $\alpha_A(x)$ etc. can be arbitrary functions of space and time. One calls $f_k^{(0)}$ a local-equilibrium distribution function. By using the fact that distribution functions transform as scalars under Galilei (as well as Lorentz) transformations, one may show that the vector field

$$\mathbf{v}(x) = \boldsymbol{\beta}(x) / \beta(x) \quad (1.51)$$

transforms as a velocity (see exercise 1.4), and that the parameter γ is equal to $\beta \frac{1}{2} m v^2$. For convenience we shall always neglect such non-linear terms.

It may seem puzzling that there exists a distribution function $f_k^{(0)}$ different from n_k , for which the entropy production vanishes. However, one should keep in mind that $f_k^{(0)}$ is not a solution of the kinetic equation and, as a consequence, does not represent a real state of the system. The actual distribution function always deviates from $f_k^{(0)}$, although close to equilibrium the deviation may be small. Therefore, a clear distinction must be made between the deviation from total (global) equilibrium:

$$\delta f_k = f_k - n_k = n_k (1 + \eta n_k) \phi_k, \quad (1.52)$$

and the deviation from local equilibrium

$$\delta \bar{f}_k = f_k - f_k^{(0)} = n_k (1 + \eta n_k) \bar{\phi}_k. \quad (1.53)$$

If we assume that deviations like $\delta \alpha_A(x) = \alpha_A(x) - \alpha_A$, $\delta \mathbf{v}(x) = \mathbf{v}(x)$, etc. are small, we find that the two deviation functions are connected by

$$\bar{\phi}_k(x, p) = \phi_k(x, p) + \sum_A q_{Ak} \delta \alpha_A(x) + \delta \beta(x) \epsilon_k - \beta \delta \mathbf{v}(x) \cdot \mathbf{p}. \quad (1.54)$$

The difference is a linear combination of collision invariants.

The local-equilibrium distribution function may be regarded as a zeroth-order approximation in an expansion with respect to $\bar{\phi}_k$, called the Chapman-Enskog expansion. This raises the question what significance should be attributed to the arbitrary functions. How are these functions related to the actual state of the system? In analogy with equilibrium, it seems natural to consider these functions as Lagrange multipliers, that is, to choose them such that the conserved densities are locally determined by $f_k^{(0)}$:

$$N_A(x) = \sum_k q_{Ak} \int d\omega_k f_k^{(0)}(x, p), \quad (1.55)$$

$$E(x) = \sum_k \int d\omega_k \epsilon_k f_k^{(0)}(x, p), \quad (1.56)$$

$$\mathbf{G}(x) = \sum_k \int d\omega_k \mathbf{p} f_k^{(0)}(x, p). \quad (1.57)$$

Of course, other quantities, especially the flows, are not correctly given by $f_k^{(0)}$. One may look upon the above equations as definitions of the local chemical potentials $\mu_A(x)$, temperature $T(x)$, and hydrodynamic velocity $\mathbf{v}(x)$ in terms of the hydrodynamic variables. By this construction the non-equilibrium thermodynamic parameters are uniquely defined. Since $f_k^{(0)}$ has the equilibrium form, local thermodynamic relationships have the same form as in full equilibrium, provided that the non-equilibrium entropy density can also be defined in terms of $f_k^{(0)}$. This will be investigated next.

Exercise 1.8

Show that \mathbf{v} is indeed the hydrodynamic velocity: $\mathbf{G}(x) = \rho(x)\mathbf{v}(x)$.

1.8 Entropy production

We go back to the entropy four-flow (1.45), which we decompose as follows:

$$\begin{aligned} S^\mu = & - \sum_k \int d\omega_k v_k^\mu \left[f_k \log f_k^{(0)} - \eta(1 + \eta f_k) \log(1 + \eta f_k^{(0)}) \right] \\ & - K^\mu \left[f, f_k^{(0)} \right]. \end{aligned} \quad (1.58)$$

The last term is simply the difference of (1.45) and the first terms at the right-hand side of (1.58). The quantity K^μ vanishes when $\delta\bar{f}_k$ vanishes. In fact, an expansion of the integrand shows that K^μ is quadratic in the deviation from local equilibrium:

$$K^\mu = O \left[(\delta\bar{f}_k)^2 \right]. \quad (1.59)$$

Like before such terms will be neglected. So we are left with the first term at the right-hand side of (1.58).

Let us substitute (1.49) with (1.50). We then recognize the expression for the current density (1.12) and energy-momentum tensor (1.20), so that we can write

$$S^\mu(x) = \sum_A \alpha_A(x) J_A^\mu(x) + \beta_\nu(x) T^{\mu\nu}(x) + \beta^\mu(x) P^{(0)}(x), \quad (1.60)$$

with $\beta^\mu = (\beta, \boldsymbol{\beta})$. In equilibrium this expression reduces to the familiar Euler relation. The last term is the local-equilibrium pressure defined by

$$\beta(x) P^{(0)}(x) = \eta \sum_k \int d\omega_k \log \left[1 + \eta f_k^{(0)}(x, p) \right]. \quad (1.61)$$

Notice that the integral is invariant for a shift $\mathbf{p} \rightarrow \mathbf{p} + m_k \mathbf{v}$ of the integration variable. Using this fact, it follows by explicit calculation that we may write

$$\delta (\beta^\mu P^{(0)}) = - \sum_A J_A^{(0)\mu} \delta \alpha_A - T^{(0)\mu\nu} \delta \beta_\nu, \quad (1.62)$$

where the superscript (0) indicates that the currents and energy-momentum tensor are calculated with $f_k^{(0)}$. Because of the "conditions of fit" (1.56)-(1.57), we have

$$N_A - N_A^{(0)} = 0, \quad (1.63)$$

$$T_{\mu 0} - T_{\mu 0}^{(0)} = 0. \quad (1.64)$$

No such restrictions are imposed on the other components, and these determine, in fact, the entropy production as we shall see now.

Exercise 1.9

Make sure that the Gibbs and the Gibbs-Duhem relations are valid outside equilibrium if quadratic deviations from local equilibrium are neglected.

We calculate the entropy production by taking the four-divergence of (1.60). On account of the conservation laws (1.13) and (1.19), and the above equations (1.62) through (1.64), we obtain

$$\partial_\mu S^\mu = \sum_A \left(\mathbf{J}_A - \mathbf{J}_A^{(0)} \right) \cdot \nabla \alpha_A + \left(\mathbf{J}_E - \mathbf{J}_E^{(0)} \right) \cdot \nabla \beta \quad (1.65)$$

$$- \beta \left(\mathbf{P} - P^{(0)} \mathbf{l} \right) : \nabla \mathbf{v}. \quad (1.66)$$

Hence, the entropy production is a bilinear expression in terms of gradients and so-called irreversible flows

$$\mathbf{I}_A = \mathbf{J}_A - \mathbf{J}_A^{(0)}, \quad (1.67)$$

$$\mathbf{I}_q = \mathbf{J}_E - \mathbf{J}_E^{(0)}, \quad (1.68)$$

$$\Pi = \mathbf{P} - P^{(0)} \mathbf{l}. \quad (1.69)$$

In equilibrium and local equilibrium these flows are zero. Note especially the definition of the viscous pressure tensor (1.69) which is the difference between the pressure tensor (1.18), and the local equilibrium pressure as defined in (1.61).

Exercise 1.10

The requirement that the viscous pressure tensor (1.69) vanishes in local equilibrium may be used to define the ‘hydrostatic’ pressure $P^{(0)}$. Is this definition compatible with the ‘thermodynamic’ definition (1.61)?

1.9 Irreversible flows

The irreversible flows may be expressed in terms of δf_k , the deviation from global equilibrium. Take e.g. the heat flow (1.69). The first term can be written, see (1.15),

$$\mathbf{J}_E = \sum_k \int d\omega_k \epsilon_k \mathbf{v}_k \delta f_k, \quad (1.70)$$

since the energy flow vanishes in equilibrium. Furthermore, the zeroth-order flow may be calculated by a shift of integration variables as

$$\mathbf{J}_E^{(0)} = (E + P)\mathbf{v}, \quad (1.71)$$

where the factor in front is the equilibrium enthalpy density. For the hydrodynamic velocity we can write

$$\rho \delta \mathbf{v} = \delta \mathbf{G} = \sum_k \int d\omega_k \mathbf{p} \delta f_k. \quad (1.72)$$

So we finally arrive at the heat flow

$$\mathbf{I}_q = \sum_k \int d\omega_k \mathbf{j}_{qk} \delta f_k, \quad (1.73)$$

expressed in terms of δf_k and the so-called dissipative current

$$\mathbf{j}_{qk} = [\epsilon_k - m_k \rho^{-1} (E + P)] \mathbf{v}_k, \quad (1.74)$$

in which the enthalpy flow is subtracted from the energy flow.

With regard to the viscous pressure we follow a similar reasoning and we find the sum

$$\Pi = \overset{\circ}{\Pi} + \Pi \text{ I} \quad (1.75)$$

of a shear tensor part

$$\overset{\circ}{\Pi} = \sum_k \int d\omega_k \overset{\circ}{\pi}_k \delta f_k, \quad (1.76)$$

$$\overset{\circ}{\pi}_k = \mathbf{p} \mathbf{v}_k - \frac{1}{3} (\mathbf{p} \cdot \mathbf{v}_k) \mathbf{l}, \quad (1.77)$$

and the scalar volume, or bulk, viscous pressure

$$\Pi = \frac{1}{3} \sum_k \int d\omega_k \mathbf{p} \cdot \mathbf{v}_k f_k - P^{(0)}, \quad (1.78)$$

i.e. the difference between the ‘mechanical’ and the ‘hydrostatic’ pressure. In general, Π is non-vanishing for fluids, but for the ideal non-relativistic gases we consider here, one finds

$$\Pi = \frac{2}{3} (E - E^{(0)}) = 0, \quad (1.79)$$

in virtue of the condition of fit (1.64), and the equation of state $P^{(0)} = \frac{2}{3}E^{(0)}$.

Exercise 1.11

Show that ultra-relativistic ideal gases have no volume viscosity.

Lastly, there are the flows (1.68) which describe diffusion. Without derivation we write

$$\mathbf{I}_A = \sum_k \int d\omega_k \mathbf{j}_{Ak} \delta f_k, \quad (1.80)$$

$$\mathbf{j}_{Ak} = (q_{Ak} - m_k \rho^{-1} N_A) \mathbf{v}_k. \quad (1.81)$$

The thermodynamic quantities between the parenthesis refer to equilibrium.

Exercise 1.12

Derive (1.80), (1.81).

Exercise 1.13

Show that $\mathbf{I}_A = 0$ for a simple non-relativistic gas.

The three dissipative currents (1.74), (1.77), and (1.81) have one property which is very important for the following, namely, they are orthogonal to the collision invariants in the sense

$$\sum_k \int d\omega_k \psi_k \left(\mathbf{j}_{Ak}, \mathbf{j}_{qk}, \overset{\circ}{\pi}_k \right) n_k (1 + \eta n_k) = 0. \quad (1.82)$$

For $\psi_k = q_{Ak}, \epsilon_k$ the proof is trivial. To see the truth of the statement for $\psi_k = \mathbf{p}$ one needs the identities

$$N_A = \frac{1}{3} \beta \sum_k q_{Ak} \int d\omega_k \mathbf{p} \cdot \mathbf{v}_k n_k (1 + \eta n_k), \quad (1.83)$$

$$E + P = \frac{1}{3} \beta \sum_k \int d\omega_k \epsilon_k \mathbf{p} \cdot \mathbf{v}_k n_k (1 + \eta n_k), \quad (1.84)$$

which are proved with the aid of a partial integration.

1.10 Transport coefficients

After these preliminaries, we shall now construct a solution of the linearised kinetic equation (1.41) for the purpose of calculating the irreversible flows, which, as we recall, are nothing but the non-equilibrium parts of the charge flows and the energy-momentum tensor. We follow the Chapman-Enskog method and write

$$(\partial_t + \mathbf{v}_k \cdot \nabla) f_k^{(0)} = -L_k[\phi], \quad (1.85)$$

with the linearised collision operator given by (1.39), here and henceforth denoted as $L_k[\phi]$. At the left-hand side we have replaced f_k by its zeroth-order approximation. However, one should note that for consistency with (1.40) we must have

$$\sum_k \int d\omega_k \psi_k (\partial_t + \mathbf{v}_k \cdot \nabla) f_k^{(0)} = 0. \quad (1.86)$$

With the help of this equation the time derivative can be eliminated in favour of the gradients of the thermodynamic parameters.

The details of this procedure, which may be pictured as a projection orthogonal to the collision invariants, are rather involved. Nevertheless, the final answer is easy to guess. Let us take a look at the gradient part in (1.85). Neglecting as usual quadratic terms we get with (1.49), (1.50)

$$\mathbf{v}_k \cdot \nabla f_k^{(0)} = -n_k(1 + \eta n_k) \left[\sum_A q_{Ak} \mathbf{v}_k \cdot \nabla \alpha_A + \epsilon_k \mathbf{v}_k \cdot \nabla \beta - \beta \mathbf{p} \mathbf{v}_k : \nabla \mathbf{v} \right]. \quad (1.87)$$

If we now compare the various factors multiplying the gradients with the dissipative currents (1.74), (1.77), and (1.81), we observe that we can satisfy the orthogonality requirement by merely replacing these factors with the appropriate dissipative currents. This suggests that we should write

$$n_k(1 + \eta n_k) \left[\sum_A \mathbf{j}_{Ak} \cdot \nabla \alpha_A + \mathbf{j}_{Ak} \cdot \nabla \beta - \beta \overset{\circ}{\pi}_k : \nabla \mathbf{v} \right] = L_k[\phi]. \quad (1.88)$$

Exactly the same answer is obtained by the standard elimination procedure.

We can now cast the kinetic equation (1.88) into an elegant and convenient form by defining the inner product

$$(\chi|\phi) = \sum_k \int d\omega_k n_k(1 + \eta n_k) \chi_k \phi_k \quad (1.89)$$

for two sets of momentum dependent functions χ_k and ϕ_k . One may verify that this definition fulfils the basic axioms of an inner product. Furthermore, we define a so-called collision bracket

$$(\chi|L|\phi) = \sum_k \int d\omega_k \chi_k L_k[\phi], \quad (1.90)$$

for arbitrary ϕ 's and χ 's.

It is tempting to read (1.90) as the matrix element of an operator L in an abstract Hilbert space of states $|\phi\rangle$, and nothing prevents us from doing this. The kinetic equation can then be represented as

$$|X\rangle = L|\phi\rangle, \quad (1.91)$$

$$|X\rangle = \sum_A |\mathbf{j}_A\rangle \cdot \nabla \alpha_A + |\mathbf{j}_q\rangle \cdot \nabla \beta - |\overset{\circ}{\pi}\rangle : \overset{\circ}{\nabla} \mathbf{v}, \quad (1.92)$$

where the last symbol denotes the traceless strain rate

$$\overset{\circ}{\nabla} \mathbf{v} = \frac{1}{2} (\nabla \mathbf{v} + \mathbf{v} \overleftarrow{\nabla}) - \frac{1}{3} (\nabla \cdot \mathbf{v}) \mathbf{l}. \quad (1.93)$$

In the new notation the irreversible flows appear as

$$\mathbf{I}_q = (\mathbf{j}_q|\phi\rangle, \quad (1.94)$$

$$\mathbf{I}_A = (\mathbf{j}_A|\phi\rangle, \quad (1.95)$$

$$\overset{\circ}{\Pi} = (\overset{\circ}{\pi}|\phi\rangle. \quad (1.96)$$

Exercise 1.14

Check the equivalence of (1.88) and (1.92).

Now suppose that the kinetic equation has a solution, which means that the collision operator is invertible:

$$|\phi\rangle = L^{-1}|X\rangle. \quad (1.97)$$

This implies then for the flows

$$\mathbf{I}_q = (\mathbf{j}_q|L^{-1}|X\rangle, \quad (1.98)$$

etc.

Let us first assume that there is only a temperature gradient in the system. Then we get for the heat flow the linear law

$$\mathbf{I}_q = -\lambda \frac{\nabla T}{T}. \quad (1.99)$$

In deriving this, one uses that a gas in equilibrium is isotropic so that inner products between vectors and tensors can only be expressed in terms of the unit tensor, e.g.

$$\beta(\mathbf{j}_q|L^{-1}|\mathbf{j}_q\rangle) = \lambda \mathbf{l}. \quad (1.100)$$

This relation defines the heat conductivity coefficient which also can be written as

$$\lambda = \frac{1}{3} \beta(\mathbf{j}_q|L^{-1}|\mathbf{j}_q\rangle), \quad (1.101)$$

where now a contraction of vector indices is understood.

Similarly, one finds for the viscous pressure

$$\overset{\circ}{\Pi} = -2\eta \overset{\circ}{\nabla} \mathbf{v}, \quad (1.102)$$

with the viscosity coefficient given by

$$\eta = \frac{1}{10} \beta (\overset{\circ}{\pi} | L^{-1} | \overset{\circ}{\pi}), \quad (1.103)$$

where again a contraction of tensor indices is meant.

Because of the isotropy of the system only the phenomena with the same tensor character couple to each other. This is called Curie's principle. In the present case this implies that there is no coupling between viscosity, on the one hand, and heat conduction and diffusion, on the other. However, the latter are both vector phenomena so that diffusion couples to heat flow and vice versa. These phenomena are called the Soret (thermal diffusion) and Dufour effects, respectively.

Exercise 1.15

Show that the complete set of linear laws for heat conduction and diffusion has the form

$$\begin{aligned} \mathbf{I}_q &= \lambda \frac{\nabla \beta}{\beta} + \sum_{\mathbf{B}} D_{q\mathbf{B}} \nabla \alpha_{\mathbf{B}} \\ \mathbf{I}_A &= \sum_{\mathbf{B}} D_{\mathbf{A}\mathbf{B}} \nabla \alpha_{\mathbf{B}} + D_{\mathbf{A}q} \frac{\nabla \beta}{\beta} \end{aligned}$$

and write down expressions for the transport coefficients figuring here.

Without going into more detail the general structure of an arbitrary transport coefficient should be clear by now. Apart from a numerical factor, they have the form

$$\kappa = \beta (j | L^{-1} | j) \quad (1.104)$$

of the collision operator sandwiched between the relevant dissipative currents. We can also write

$$\kappa = \beta \int_0^\infty dt (j | e^{-Lt} | j). \quad (1.105)$$

The exponential operator is the evolution operator associated with the linearised kinetic equation. This suggests that we write the integrand as

$$(j | e^{-Lt} | j) = (j(t) | j). \quad (1.106)$$

Such an inner product of dynamical variables at different times is called a time-correlation function. It is a measure for the memory of the system. Hence, transport coefficients are time integrals of time-correlation functions. General expressions of the kind (9.18) are referred to as Green-Kubo formulae [5].

1.11 Variational principle

The formal appearance of the transport coefficients may be simple, but, in general, their actual calculation is not. The collision integral, even the linearised version, is a formidable operator, and already the proof that L^{-1} exists in the Hilbert space orthogonal to the collision invariants is a non-trivial mathematical problem. It is therefore of some importance to know that there exists a variational method whereby explicit inversion can be avoided.

We need the result that the collision operator is non-negative. This is an immediate consequence of the fact that the - linearised - entropy production (1.47) is non-negative (see exercise 7):

$$\sigma = (\phi|L|\phi) \geq 0. \quad (1.107)$$

One can check this explicitly for the linear operator (1.39), but one should be aware that this positivity property is an essential ingredient of any kinetic theory which ensures, in particular, that the (direct) transport coefficients are always positive.

Let now $|\phi\rangle$ be a solution of the transport equation

$$L|\phi\rangle = |j\rangle, \quad (1.108)$$

with $|j\rangle$ a given dissipative current. And suppose that we wish to calculate the transport coefficient

$$\kappa = \beta^{-1}(j|L^{-1}|j) = \beta(j|\phi). \quad (1.109)$$

Let us consider states $|\chi\rangle$ such that

$$(\chi|L|\chi) = (\chi|j). \quad (1.110)$$

The variational principle now states that the solution of (1.108) gives a maximum

$$(\phi|L|\phi) \geq (\chi|L|\chi) \quad (1.111)$$

within the class of functions that satisfy (1.110). The validity of this principle is shown by considering

$$(\chi - \phi|L|\chi - \phi) \geq 0. \quad (1.112)$$

Hence, any trial function $|\chi\rangle$, subject to the constraint (1.110), gives a value for the transport coefficient that is certainly less than would follow from the exact solution:

$$\kappa = \beta(j|\phi) \geq \beta(\chi|L|\chi). \quad (1.113)$$

This may be used in a systematic approximation scheme, sometimes called the Ritz method, wherein the trial function is expanded with respect to some convenient basis set, and the first few terms are retained. If the set is chosen with care, one term of ten suffices to get an accuracy of a few percent.

A drawback of the variational method as presented above is the constraint that has to be satisfied by $|\chi\rangle$. However, this constraint is fulfilled automatically if we set

$$|\chi\rangle = \frac{(j|\alpha)}{(\alpha|L|\alpha)} |\alpha\rangle. \quad (1.114)$$

with $|\alpha\rangle$ arbitrary. Then the variational principle becomes

$$\kappa \geq \beta \frac{(j|\alpha)^2}{(\alpha|L|\alpha)} \quad (1.115)$$

and any choice for $|\alpha\rangle$ will lead to an estimate for κ .

Finally, we should mention the relaxation time approximation for the transport coefficients which may be obtained by writing

$$\kappa = \beta(j|j)\langle L^{-1}\rangle, \quad (1.116)$$

where the average

$$\langle L^{-1}\rangle = \frac{(j|L^{-1}|j)}{(j|j)} \quad (1.117)$$

has the dimension of time. Recalling our discussion of the mean free time in section 5, we see that the average times (1.44) can be useful for an estimate of the order of magnitude.

Exercise 1.16

Give an expression for the heat conductivity of a one-component system in terms of the relaxation times (1.44).

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