

Physics 127b: Statistical Mechanics

Boltzmann Equation II: Binary Collisions

Binary collisions in a classical gas

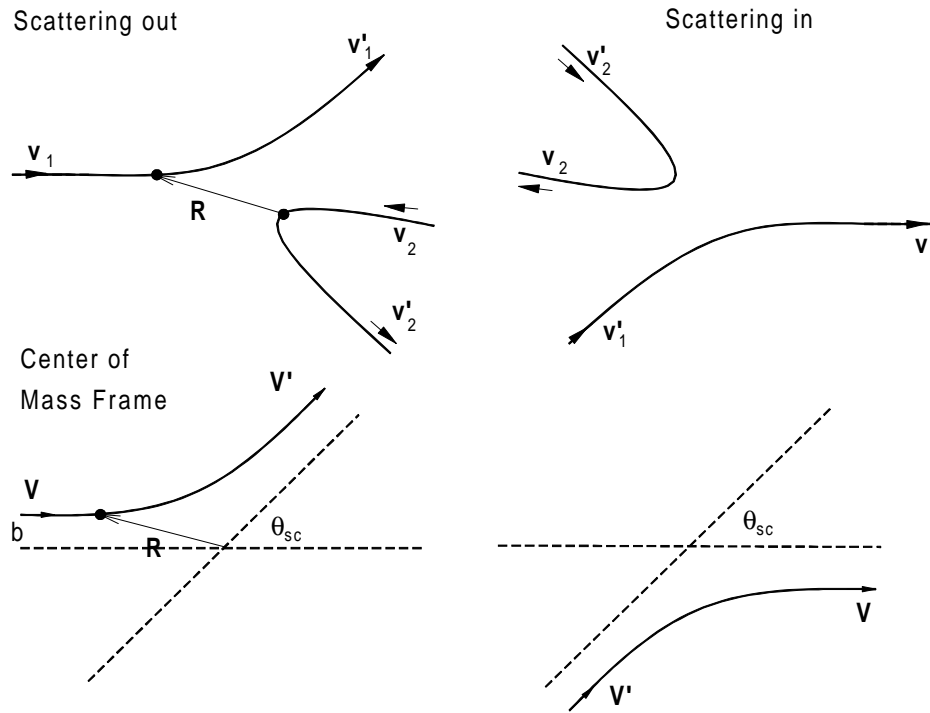


Figure 1: Binary collisions in a gas: top—lab frame; bottom—centre of mass frame

Binary collisions in a gas are very similar, except that the scattering is off another molecule. An individual scattering process is, of course, simplest to describe in the center of mass frame in terms of the relative velocity $\vec{V} = \vec{v}_1 - \vec{v}_2$. However the center of mass frame is different for different collisions, so we must keep track of the results in the lab frame, and this makes the calculation rather intricate. I will indicate the main ideas here, and refer you to *Reif* or *Landau and Lifshitz* for precise discussions.

Lets first set things up in the lab frame. Again we consider the pair of scattering in and scattering out processes that are space-time inverses, and so have identical cross sections. We can write abstractly for the scattering out from velocity \vec{v}_1 due to collisions with molecules with all velocities \vec{v}_2 , which will clearly be proportional to the number $f(\vec{v}_1)$ of molecules at \vec{v}_1 (which we write as f_1 —sorry, not the same notation as in the previous sections where f_1 denoted the deviation of f from the equilibrium distribution!) and the number $f_2 d^3 v_2 \equiv f(\vec{v}_2) d^3 v_2$ in each velocity volume element, and then we must integrate over all possible outgoing velocities \vec{v}'_1 and \vec{v}'_2

$$\left. \frac{df(\vec{v}_1)}{dt} \right|_{\text{out}} = - \int \int \int w(\vec{v}'_1, \vec{v}'_2; \vec{v}_1, \vec{v}_2) f_1 f_2 d^3 v_2 d^3 v'_1 d^3 v'_2. \quad (1)$$

Similarly for the scattering in from collisions between molecules with velocities \vec{v}'_1 and \vec{v}'_2 which collide to

give outgoing velocities \vec{v}_1 and \vec{v}_2

$$\left. \frac{df(\vec{v}_1)}{dt} \right|_{\text{in}} = \int \int \int w(\vec{v}_1, \vec{v}_2; \vec{v}'_1, \vec{v}'_2) f'_1 f'_2 d^3 v_2 d^3 v'_1 d^3 v'_2 \quad (2)$$

(with $f'_1 = f(\vec{v}'_1)$ etc.). The space-time inversion symmetry tells us that

$$w(\vec{v}'_1, \vec{v}'_2; \vec{v}_1, \vec{v}_2) = w(\vec{v}_1, \vec{v}_2; \vec{v}'_1, \vec{v}'_2), \quad (3)$$

so that

$$\left. \frac{df(\vec{v}_1)}{dt} \right|_{\text{coll}} = \int \int \int w(\vec{v}'_1, \vec{v}'_2; \vec{v}_1, \vec{v}_2) (f'_1 f'_2 - f_1 f_2) d^3 v_2 d^3 v'_1 d^3 v'_2. \quad (4)$$

These expressions are good for setting up the problem and making general arguments, but there is a 9 dimensional integral to do, and the scattering function w is comprised of many delta functions that express the conservation of energy and momentum (only a *very* limited set of \vec{v}'_1 and \vec{v}'_2 are consistent with the incoming velocities) that are complicated to write down directly in terms of the lab-frame velocities. We consequently transform to the center of mass frame, defining center of mass and relative coordinates

$$\vec{r}_c = \frac{m_1 \vec{r}_1 + m_2 \vec{r}_2}{m_1 + m_2}, \quad \vec{R} = \vec{r}_1 - \vec{r}_2, \quad (5)$$

the corresponding velocities

$$\vec{c} = d\vec{r}_c/dt, \quad \vec{V} = d\vec{R}/dt, \quad (6)$$

and similar primed expressions in terms of the outgoing velocities. The conservation laws are now easy to state

$$\vec{c} = \vec{c}', \quad |\vec{V}| = |\vec{V}'|, \quad (7)$$

and we can simply describe the scattering rate, which in the CM frame is entirely analogous to scattering off a fixed center, in terms of a differential (angular) cross section

$$\text{scattering rate into solid angle } d\Omega_{sc} = n_{sc} V \sigma(\theta_{sc}, V) d\Omega_{sc}, \quad (8)$$

with n_{sc} the density of scatterers, here the particles of velocity v_2 .

Thus we can write the collision term:

$$\left. \frac{df(\vec{v}_1)}{dt} \right|_{\text{coll}} = \int_{\vec{v}_2} \int_{\Omega_{sc}} [f(\vec{v}'_1) f(\vec{v}'_2) - f(\vec{v}_1) f(\vec{v}_2)] |\vec{v}_1 - \vec{v}_2| \sigma(|\vec{v}_1 - \vec{v}_2|, \theta_{sc}) d\Omega_{sc} d^3 \vec{v}_2 \quad (9)$$

with the geometry as shown in Fig. 1 and σ the differential cross section in the center of mass frame. So now we are doing the integral in the centre of mass frame for each \vec{v}_2 —a much simpler integration—but must evaluate \vec{v}'_1 and \vec{v}'_2 in terms of \vec{v}_1 , \vec{v}_2 and θ_{sc} . Thus the collision term can be evaluated as a four dimensional integral

For more details consult *Reif*, chapter 14 and particularly §14.8.

Boltzmann's H-theorem

An interesting application of the Boltzmann equation is *Boltzmann's H-theorem*. Boltzmann showed from the Boltzmann equation that the quantity H (not the Hamiltonian!) defined by

$$H = \int d^3 v f \ln f \quad (10)$$

never increases

$$\frac{dH}{dt} \leq 0. \quad (11)$$

Thus, within the limitations of the Boltzmann equation, $-H$ plays the role of a generalization of the entropy (actually S/kT) to *arbitrary* distributions, not restricted to ones characterized by macroscopic thermodynamic variables.

A sketch of the derivation is as follows. The time derivative of H is

$$\frac{dH}{dt} = \int d^3v_1 \left. \frac{df_1}{dt} \right|_{\text{coll}} (1 + \ln f_1) \quad (12)$$

$$= \int \int \int \int w(\vec{v}'_1, \vec{v}'_2; \vec{v}_1, \vec{v}_2) (f'_1 f'_2 - f_1 f_2) (1 + \ln f_1) d^3v_1 d^3v_2 d^3v'_1 d^3v'_2 \quad (13)$$

Using the symmetry of the scattering process under spatial inversions, time reversal, and interchange of the two incoming (and outgoing) molecules this can be written in four different ways, with all terms the same except $(1 + \ln f_1)$ is replaced by $(1 + \ln f_2)$, $-(1 + \ln f'_1)$, $-(1 + \ln f'_2)$ respectively. Summing these four expressions then gives

$$\frac{dH}{dt} = -\frac{1}{4} \int \int \int \int w(\vec{v}'_1, \vec{v}'_2; \vec{v}_1, \vec{v}_2) (\ln f'_1 f'_2 - \ln f_1 f_2) (f'_1 f'_2 - f_1 f_2) d^3v_1 d^3v_2 d^3v'_1 d^3v'_2 \quad (14)$$

But for any positive x and y it can be seen that

$$(\ln y - \ln x) (y - x) \geq 0 \quad (15)$$

with the equal sign only valid for $y = x$. Hence $dH/dt \leq 0$, and the equality only holds if $f'_1 f'_2 = f_1 f_2$.

The equilibrium condition $f'_1 f'_2 = f_1 f_2$ is equivalent to

$$\ln f'_1 + \ln f'_2 = \ln f_1 + \ln f_2 \quad (16)$$

i.e. the sum of quantities before the collision equals the sum of corresponding quantities after the collision, for all collisions. Since the equilibrium distribution must also be isotropic, so that the momentum vector cannot occur in the distribution, this shows that the equilibrium distribution must be the exponential of a term proportional to the kinetic energy of the particle, i.e. the distribution must be the Maxwell distribution, and then the proportionality constant is β .

Conservation laws and hydrodynamic equations

For quantities that are conserved in the collisions, such as mass, momentum and energy, if we sum these quantities over all the molecules, we can derive macroscopic conservation laws which are the equations of hydrodynamics and heat transport. The conservation laws take the form of the time derivative of a density given by the divergence of the corresponding current or flux. These currents can then be evaluated first using the equilibrium distribution function f_0 and then using the correction f_1 coming from deviations from equilibrium driven by gradients of the temperature, pressure or chemical potential, and velocity.

Conservation laws

First consider the mass. Then

$$\int d^3v m f(\vec{x}, \vec{v}, t) = n(\vec{x}, t) m = \rho(\vec{x}, t) \quad (17)$$

with ρ the mass density. We can use the Boltzmann equation

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \frac{\partial f}{\partial \vec{x}} + \frac{\vec{F}}{m} \cdot \frac{\partial f}{\partial \vec{v}} = \left. \frac{df}{dt} \right|_{\text{coll}} \quad (18)$$

to derive the equation of motion for the density

$$\frac{\partial \rho}{\partial t} = - \int d^3v m \vec{v} \cdot \frac{\partial f}{\partial \vec{x}} - \int d^3v \vec{F} \cdot \frac{\partial f}{\partial \vec{v}} + \int d^3v m \left. \frac{df}{dt} \right|_{\text{coll}}. \quad (19)$$

The last term on the right hand side is zero because mass is conserved in the collisions, the second term $-\vec{F} \cdot \int d^3v \vec{\nabla}_v f$ is also zero, and the first term is $-\vec{\nabla} \cdot \vec{g}$ with $\vec{g} = \rho \vec{u}$ the momentum density

$$\vec{g}(\vec{x}, t) = \int d^3v m \vec{v} f(\vec{x}, \vec{v}, t) \quad (20)$$

and \vec{u} the average velocity

$$\vec{u}(\vec{x}, t) = \frac{\int d^3v \vec{v} f(\vec{x}, \vec{v}, t)}{\int d^3v f(\vec{x}, \vec{v}, t)} \quad (21)$$

Thus we have derived the macroscopic conservation law for mass

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot (\rho \vec{u}) = 0. \quad (22)$$

Now we investigate the consequence of the conservation of momentum $m\vec{v}$ in the collision. Integrating over the velocity distribution gives

$$\frac{\partial(\rho \vec{u})}{\partial t} = \int d^3v m \vec{v} \frac{\partial f(\vec{x}, \vec{v}, t)}{\partial t} = - \int d^3v m \vec{v} \vec{v} \cdot \frac{\partial f}{\partial \vec{x}} - \int d^3v \vec{v} \vec{F} \cdot \frac{\partial f}{\partial \vec{v}} \quad (23)$$

where again the collision term drops out. This simplifies to

$$\frac{\partial(\rho \vec{u})}{\partial t} = -\vec{\nabla} \cdot \left(m \int d^3v \vec{v} \vec{v} f \right) + \vec{\Phi} \quad (24)$$

(you might want to write this in component notation if the double vector is confusing) where integration by parts is used in the last term, and $\vec{\Phi}(\vec{x}, t) = \vec{F}(\vec{x}, t)n(\vec{x}, t)$ is the force per unit volume. Now write the molecular velocity in terms of the mean velocity \vec{u} and a correction \vec{V} with zero mean

$$\vec{v} = \vec{u} + \vec{V}, \quad (25)$$

with $\int d^3v \vec{V} f = 0$. Then

$$\int d^3v \vec{v} \vec{v} f = n \vec{u} \vec{u} + \int d^3v \vec{V} \vec{V} f, \quad (26)$$

since the cross term gives zero. Thus Eq. (24) reduces to

$$\frac{\partial(\rho \vec{u})}{\partial t} + \vec{\nabla} \cdot (\rho \vec{u} \vec{u}) = \vec{\Phi} - \vec{\nabla} \cdot \overleftrightarrow{\Sigma} \quad (27)$$

or in component form

$$\frac{\partial(\rho u_i)}{\partial t} + \frac{\partial}{\partial x_j} (\rho u_i u_j) = \Phi_i - \frac{\partial}{\partial x_j} \Sigma_{ij} \quad (28)$$

(repeated index j summed over) with $\overleftrightarrow{\Sigma}$ the *momentum flux* or *stress tensor*

$$\Sigma_{ij} = m \int d^3V V_i V_j f(\vec{x}, \vec{u} + \vec{V}, t) = mn \frac{\int d^3V V_i V_j f(\vec{x}, \vec{u} + \vec{V}, t)}{\int d^3V f(\vec{x}, \vec{u} + \vec{V}, t)} = \rho \langle V_i V_j \rangle. \quad (29)$$

If in Eq. (29) $f = f_m(V)$ the equilibrium Maxwell-Boltzmann distribution for the velocity shifted about the mean velocity \vec{u} , then the off diagonal terms of Σ_{ij} are zero, and the diagonal terms involve the mean square molecular velocity fluctuation which just gives us the pressure P : $\Sigma_{ij} = P \delta_{ij}$ with $P = \frac{1}{3}nm \langle V^2 \rangle = nk_B T$.

Note that Eq. (22) can be used to rewrite Eq. (28) in a form that might be more familiar

$$\rho \frac{d\vec{u}}{dt} = \vec{\Phi} - \vec{\nabla} \cdot \overleftrightarrow{\Sigma}, \quad (30)$$

with

$$\frac{d\vec{u}}{dt} = \frac{\partial \vec{u}}{\partial t} + (\vec{u} \cdot \vec{\nabla}) \vec{u} \quad (31)$$

the *advective* or *Langrangian* derivative of \vec{u} .

A similar result can be derived for the energy density, since energy is conserved in the binary collisions, but I will not go through the calculation here.

Transport Coefficients

There are corrections to the stress tensor if the gas is not in equilibrium. In particular if the mean velocity \vec{u} is not uniform, there are *viscous forces* that tend to eliminate velocity gradients. These correspond to terms in the stress tensor depending on spatial derivatives of the velocity. We can calculate these terms by evaluating the correction terms f_1 to distribution function that are proportional to the velocity gradient (for small enough gradients) using the Boltzmann equation, and then substituting into Eq. (29). The calculation of f_1 follows the same approach as in the calculation of the thermal conductivity example in the previous lecture, except here we are considering binary collisions and there collisions off impurities. And now the local equilibrium to which the collisions tend to restore the distribution (momentum is conserved in the collisions!) is the Maxwell distribution at fixed temperature about a mean velocity $\vec{u}(\vec{x}, t)$ that is a function of position and time in general.

We calculate f_1 as the solution to

$$\frac{\partial f_0}{\partial t} + \vec{v} \cdot \frac{\partial f_0}{\partial \vec{x}} \simeq \left. \frac{df_1}{dt} \right|_{\text{coll}} \quad (32)$$

where to lowest order we use the equilibrium distribution on the left hand side, and we have set the external force to zero. In full generality the equilibrium distribution is

$$f_0(\vec{v}, \vec{x}, t) \propto e^{\beta \mu} e^{-\beta \varepsilon_{\text{int}}(T)} e^{-\beta m(\vec{v} - \vec{u})^2/2} \quad (33)$$

where $\varepsilon_{\text{int}}(T)$ is the internal energy of the molecule (rotation and vibration etc.). The \vec{x}, t dependence of f_0 arises because μ, T , and \vec{u} defining the local equilibrium are functions of position and time. Thus we can evaluate the left hand side of Eq. (32). When doing this, it is convenient to make a Galilean transformation to a frame of reference moving with the local mean velocity \vec{u} , i.e. set \vec{u} to zero (but not derivatives of \vec{u}) after taking the derivatives.

Let's first look at the time derivative term. We use P and T as the variables defining the local state of the gas, rather than μ and T . Then taking logs of Eq. (33) and differentiating gives

$$\frac{k_B T}{f_0} \frac{\partial f_0}{\partial t} = \left[\left(\frac{\partial \mu}{\partial T} \right)_P - \frac{\mu - \varepsilon_v}{T} \right] \frac{\partial T}{\partial t} + \left(\frac{\partial \mu}{\partial P} \right)_T \frac{\partial P}{\partial t} + m \vec{v} \cdot \frac{\partial \vec{u}}{\partial t}, \quad (34)$$

with $\varepsilon_v = \varepsilon_{\text{int}} + \frac{1}{2}mv^2$, the energy of a particle of speed v . This expression can be simplified using the thermodynamic identities $(\partial\mu/\partial T)_P = -s$ and $(\partial\mu/\partial P)_T = 1/n$, with s the entropy per particle and n^{-1} the volume per particle, and then introducing the enthalpy per particle $h = \mu + Ts$, to give

$$\frac{k_B T}{f_0} \frac{\partial f_0}{\partial t} = \frac{\varepsilon_v - h}{T} \frac{\partial T}{\partial t} + \frac{1}{n} \frac{\partial P}{\partial t} + m\vec{v} \cdot \frac{\partial \vec{u}}{\partial t}. \quad (35)$$

Processing the spatial derivative in the same way gives the corresponding result

$$\frac{k_B T}{f_0} \vec{v} \cdot \frac{\partial f_0}{\partial \vec{x}} = \frac{\varepsilon_v - h}{T} \vec{v} \cdot \vec{\nabla} T + \frac{1}{n} \vec{v} \cdot \vec{\nabla} P + m v_\alpha v_\beta u_{\alpha\beta} \quad (36)$$

with $u_{\alpha\beta}$ the shear in the velocity

$$u_{\alpha\beta} = \frac{1}{2} \left(\frac{\partial u_\alpha}{\partial u_\beta} + \frac{\partial u_\beta}{\partial u_\alpha} \right), \quad (37)$$

(it is convenient to write the expression in terms of this symmetrized derivative).

The time derivatives in Eq. (35) result from the energy, mass, and momentum currents flowing due to the spatial derivatives of T , P , and \vec{u} . Since these terms appear as the driving terms in the Boltzmann equation, to leading order in the departure from equilibrium we can evaluate these currents for the equilibrium distribution f_0 . For the velocity term this corresponds to using just the pressure term in Σ , i.e.

$$\frac{\partial \vec{u}}{\partial t} = -\vec{u} \cdot \vec{\nabla} \vec{u} - \frac{1}{nm} \vec{\nabla} P \rightarrow -\frac{1}{nm} \vec{\nabla} P \quad (38)$$

where the last step is because we are in the frame of the local velocity, so that $\vec{u} = 0$. The temperature and pressure time derivatives are evaluated from the density conservation equation Eq. (22) (again setting $\vec{u} \rightarrow 0$)

$$\frac{\partial n}{\partial t} = -n \vec{\nabla} \cdot \vec{u}, \quad (39)$$

and from the entropy equation (remember we are evaluating these derivatives in equilibrium so the entropy is constant)

$$\frac{\partial s}{\partial t} = 0 = \left(\frac{\partial s}{\partial P} \right)_T \frac{\partial P}{\partial t} + \left(\frac{\partial s}{\partial T} \right)_P \frac{\partial T}{\partial t}. \quad (40)$$

Using $(\partial s/\partial T)_P = c_p/T$ with c_p the specific heat per particle at constant pressure, the Maxwell relation $(\partial s/\partial P)_T = -(\partial v/\partial T)_P$, and then $n = v^{-1} = P/k_B T$ and $c_p - c_v = k_B$ for the ideal gas, Eqs. (39) and (40) together give

$$\frac{\partial P}{\partial t} = -nk_B T (c_p/c_v) \vec{\nabla} \cdot \vec{u}, \quad (41)$$

$$\frac{\partial T}{\partial t} = -(k_B T/c_v) \vec{\nabla} \cdot \vec{u}, \quad (42)$$

with c_v the specific heat per particle at constant volume. Finally combining Eqs. (35, 36, 38, 41, 42) gives the driving term in the Boltzmann equation

$$\frac{\partial f_0}{\partial t} + \vec{v} \cdot \frac{\partial f_0}{\partial \vec{x}} = \frac{f_0(v)}{k_B T} \left[\frac{\varepsilon_v - h}{T} (\vec{v} \cdot \vec{\nabla}) T + m v_\alpha v_\beta (u_{\alpha\beta} - \frac{1}{3} \delta_{\alpha\beta} \vec{\nabla} \cdot \vec{u}) + \frac{h - T c_p - \varepsilon_v + (c_v/k_B) \frac{1}{3} m v^2}{(c_v/k_B)} \vec{\nabla} \cdot \vec{u} \right]. \quad (43)$$

Note that the velocity gradient matrix has been written in terms of a transverse part (with zero trace) $u_{\alpha\beta} - \frac{1}{3} \delta_{\alpha\beta} \vec{\nabla} \cdot \vec{u}$ and a longitudinal part (the trace) $\vec{\nabla} \cdot \vec{u}$.

Using Eq. (32) and some treatment of the collisions, we can calculate $f_1(\vec{v})$, which will have contributions proportional to the gradients $\vec{\nabla} T$, $u_{\alpha\beta} - \frac{1}{3} \delta_{\alpha\beta} \vec{\nabla} \cdot \vec{u}$, and $\vec{\nabla} \cdot \vec{u}$ appearing in Eq. (43). (Note that the $\vec{\nabla} P$ terms

actually cancel, and do not appear.) These may then contribute to the expressions for the stress tensor Eq. (29), and energy flux (not written down).

For example consider the stress tensor (we evaluate the integral at $\vec{u} = 0$, so $\vec{V} \rightarrow \vec{v}$)

$$\Sigma_{ij} = P\delta_{ij} + m \int d^3v v_i v_j f_1(\vec{v}). \quad (44)$$

For illustration we evaluate the collision term in the relaxation time approximation, so that the Boltzmann equation gives

$$f_1 = -\tau \frac{f_0(v)}{k_B T} \left[\frac{\varepsilon_v - h}{T} (\vec{v} \cdot \vec{\nabla}) T + m v_\alpha v_\beta (u_{\alpha\beta} - \frac{1}{3} \delta_{\alpha\beta} \vec{\nabla} \cdot \vec{u}) + \frac{h - T c_P - \varepsilon_v + (c_V/k_B) \frac{1}{3} m v^2}{(c_V/k_B)} \vec{\nabla} \cdot \vec{u} \right]. \quad (45)$$

The term in f_1 from the temperature gradient is odd in \vec{v} and so does not contribute in the integral for Σ_{ij} . The velocity gradients lead to viscous contributions to the stress tensor. For example the second term in Eq. (43) will give a contribution

$$\Sigma_{ij}^{\text{shear}} = -2\eta(u_{ij} - \frac{1}{3} \delta_{ij} \vec{\nabla} \cdot \vec{u}), \quad (46)$$

with η the coefficient of *shear viscosity*. In addition there is a contribution from $\vec{\nabla} \cdot \vec{u}$

$$\Sigma_{ij}^{\text{longitudinal}} = -\zeta \vec{\nabla} \cdot \vec{u} \quad (47)$$

where ζ is known as the coefficient of *second viscosity*.

Using similar methods, the equation resulting from the conservation of energy can be derived. The derivation is complicated because many terms, including the kinetic energy of the mean velocity $\frac{1}{2} \rho u^2$, contribute to the energy density that is carried along by the flow velocity. The additional dissipative energy current coming from the nonequilibrium correction f_1 on the other hand is quite simple, arising just from the $\vec{v} \cdot \vec{\nabla} T$ term in Eq. (43), since the other terms have the wrong symmetry in \vec{v} . This leads to a term in the energy current (heat flow) proportional to $-\kappa \vec{\nabla} T$ with κ the thermal conductivity that again is readily evaluated using the simple relaxation time approximation, and that in principle can be evaluated using more realistic descriptions of the collisions.

Thus we may completely derive the fluid dynamic equations for the gas with a prescription for how to calculate the *transport coefficients* such as the viscosity that arise in the equations in terms of the solution to the Boltzmann equation. This solution may still be hard to do accurately, and simple approximations, such as the relaxation time approximation, are often used. However, in principle, knowing the two particle molecular scattering cross-section allows a complete calculation of the transport coefficients. The form of the equations, e.g. the expressions for the viscous contributions to the stress tensor Eqs. (46,47) are actually valid more generally, applying to dense gases and liquids. However in these cases the Boltzmann equation cannot be used to evaluate the transport coefficients.

The full derivation of the hydrodynamic equations from the Boltzmann equation is quite involved, but the most important results can be derived relatively simply. For example, of the coefficient of shear viscosity it is clear from symmetry arguments, that the time derivative terms $\partial f_0 / \partial t$ do not contribute in Eq. (32)—these terms do not have the right symmetry in \vec{v} to contribute to the stress tensor. It is then straightforward to extract the contribution to f_1 resulting from a particular velocity gradient, e.g. $\partial u_x / \partial z$, and then to calculate the contribution to the stress tensor. This is the subject of a problem in the homework. Similarly the thermal conductivity can be extracted by focussing on the temperature gradient term.