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Transport in Gases: An Alternative Treatment

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The treatment of the transport of mass, momentum, charge, and energy in dilute gases traditionally employed in undergraduate physical chemistry is based on the molecular mean free path. This method has historical significance and readily leads to simple expressions for the transport coefficients. However, the values of the transport coefficients so obtained are not particularly accurate, either on an absolute or relative basis. The ad hoc assumption that molecules reach some local equilibration in temperature or momentum after one collision, which is employed in the elementary derivation, is difficult to justify. In order to obtain the standard results, care must be taken to combine the proper unidirectional flux ($n\bar{v}/6$ in some derivations, $n\bar{v}/4$ in others, where n and $\bar{v}$ are the molecular concentration and mean speed) with the proper average distance traveled in one direction between collisions (λ in some derivations, $2\lambda/3$ in others). While the mean free path has its uses, it is a concept which does not appear in the rigorous treatment of transport processes. Perhaps the most important pedagogic defect of the mean free path method is that it does not call attention to the essence of a transport process: its non-equilibrium nature. On the contrary, mean molecular speeds calculated with an equilibrium distribution function are employed, and a justification is rarely if ever given.

Considering the deficiencies of the mean free path treatment of transport processes, and the fact that students usually have been exposed to it in previous introductory physics courses, it would seem desirable to introduce an alternate, more satisfactory, treatment in physical chemistry courses. The rigorous theory based on the Chapman-Enskog or Grad solutions to the Boltzmann transport equation is far too complicated for an undergraduate course. However, a greatly simplified version of this approach, known as the relaxation approximation, is within the abilities of the physical chemistry student, and offers some pedagogical advantages. The relaxation approximation is discussed briefly in a few physics texts.¹⁻³ In order to make the method more readily available in a form appropriate for physical chemistry courses, we will derive here the relaxation approximation to the Boltzmann transport equation, and obtain from it the coefficients for diffusion, viscosity, electrical conductivity, and thermal conductivity in gases.

The Boltzmann Equation

The single particle distribution function $f(\mathbf{v}, \mathbf{r}, t)$ is such that $f(\mathbf{v}, \mathbf{r}, t) d^3v$ is the concentration of particles in the element of velocity space d^3v at $\mathbf{r}$ at time t . In general, it is a function of position and time. However, in the case of a gas at equilibrium it depends only on velocity and the parameters of the system, and has the well-known Maxwell-Boltzmann form:

$$f^0 = n \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-mv^2/2kT}. \quad (1)$$

It is essential to know the distribution function in order to be able to calculate the fluxes of particles, charge, momentum, and energy, which are, respectively,

$$J_z = \int v_z f d^3v, \quad (2)$$

$$j_z = e \int v_z f d^3v, \quad (3)$$

$$P_{zx} = \int (mv_x) v_z f d^3v, \quad (4)$$

$$Q_z = \int \left(\frac{mv^2}{2}\right) v_z f d^3v. \quad (5)$$

We note that these fluxes all vanish for a gas at equilibrium, since then $f = f^0$ is an even function of all velocity components, and all integrands contain a factor which is an odd function of a velocity component. Thus it is the deviation of the distribution function from its equilibrium form which is responsible for nonzero fluxes.

The foregoing makes it clear that a method for finding the distribution function for nonequilibrium situations is needed. To this end, we now formulate the relaxation approximation to the Boltzmann transport equation. Note that

$$dN = f(\underline{y}, \underline{r}, t) d^3v d^3r$$

is the number of molecules in an element of six-dimensional velocity-coordinate space at time t . If no collisions occur, these molecules will progress under the influence of their velocities and any external forces, and at time $t + dt$ will be at $\underline{y}' = \underline{y} + \underline{v} dt$ and $\underline{r}' = \underline{r} + \underline{v} dt$. The size of the volume element will not change, so at this latter time the number of

molecules in the element is

$$dN' = f(\underline{v}', \underline{r}', t+dt) d^3v d^3r.$$

If no collisions occur, no molecules are lost or gained from the volume element, and $dN' = dN$. However, if collisions do occur, some of the molecules originally in d^3v will acquire new velocities and be lost from the element, and molecules not in the volume element may enter it after undergoing collisions. Thus

$$dN' - dN = dN_{\text{coll}} \quad (6)$$

will be zero only in the special case of equilibrium.

We can develop an equation which can be solved for the distribution function from eqn. 6. We note that

$$\begin{aligned} dN' - dN &= [f(\underline{v}', \underline{r}', t+dt) - f(\underline{v}, \underline{r}, t)] d^3v d^3r \\ &= \frac{df}{dt} dt d^3v d^3r. \end{aligned}$$

Since the distribution function is a function of $\underline{r}$, $\underline{v}$, and t ,

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \frac{\partial f}{\partial \underline{r}} \cdot \frac{d\underline{r}}{dt} + \frac{\partial f}{\partial \underline{v}} \cdot \frac{d\underline{v}}{dt}.$$

Noting that the acceleration of the molecules can be written as $\underline{F}/m$, and performing the obvious substitutions, we find

$$\left[\frac{\partial f}{\partial t} + \underline{v} \cdot \frac{\partial f}{\partial \underline{r}} + \frac{\underline{F}}{m} \cdot \frac{\partial f}{\partial \underline{v}} \right] dt d^3v d^3r = dN_{\text{coll}} \quad (7)$$

To complete the derivation of the Boltzmann transport equation, we must find an expression for dN_{coll} . We can write

$$dN_{\text{coll}} = \left[\left(\frac{\partial f}{\partial t} \right)_{\text{coll}}^+ - \left(\frac{\partial f}{\partial t} \right)_{\text{coll}}^- \right] dt d^3v d^3r \quad (8)$$

where the first and second terms represent respectively the increase and decrease of the number of particles in the volume element $d^3v d^3r$ due to collisions in the interval dt . The loss term can be written out readily in terms of the collision cross section σ . If $\underline{v}$ is the velocity of a molecule in the volume element, and $\underline{w}$ is the velocity of any other molecule, their relative speed is $|\underline{v} - \underline{w}| = g$ and the rate of collisions between them is

$$g\sigma f(\underline{v}) f(\underline{w}) d^3v d^3w.$$

The number of collisions in d^3r during dt which involve $\underline{v}$ -molecules and any value of $\underline{w}$ is

$$\left(\frac{\partial f}{\partial t} \right)_{\text{coll}}^- dt d^3v d^3r = dt d^3v d^3r f(\underline{v}) \int f(\underline{w}) g\sigma d^3w$$

The integral is simply the collision rate of one $\underline{v}$ -molecule averaged over the velocity distribution of $\underline{w}$ -molecules, so we can write

$$\left(\frac{\partial f}{\partial t} \right)_{\text{coll}}^- dt d^3v d^3r = dt d^3v d^3r f(\underline{v}) n\langle g\sigma \rangle \quad (9)$$

In principle, the collision rate $n\langle g\sigma \rangle$ is still a function of v , but in our applications we shall ignore this.

The formulation of the rate of increase of molecules in d^3v is more difficult, since collisions involving all types of initial conditions of both collision partners must be considered in order to find which lead to scattering into d^3v .

Use of the conservation laws allows the initial conditions for these inverse collisions to be found.⁴ Rather than pursue this exact but somewhat lengthy analysis, we shall adopt a heuristic approach. We note that the rate of increase of particles in d^3v must involve an average collision rate per particle $n\langle g\sigma \rangle$, and that at equilibrium the rate of gain equals the rate of loss. When the system is not far from equilibrium, the rate of gain must be very close to the equilibrium rate of loss. Therefore, we shall approximate the number gained in $d^3v d^3r$ during dt under all conditions by eqn. 9 evaluated at equilibrium; that is, with f replaced by f^0 . Thus

$$\left(\frac{\partial f}{\partial t}\right)_{\text{coll}}^+ dt d^3v d^3r \approx dt d^3v d^3r f^0(\underline{v}) n\langle g\sigma \rangle.$$

Using these expressions to find dN_{coll} , substituting the result in eqn. 7, and cancelling differentials leads us to

$$\frac{\partial f}{\partial t} + \underline{v} \cdot \frac{\partial f}{\partial \underline{v}} + \frac{F}{m} \cdot \frac{\partial f}{\partial \underline{v}} = (f^0 - f) n\langle g\sigma \rangle \quad (10)$$

which is the approximate form of the Boltzmann transport equation we were seeking.

The quantity $n\langle g\sigma \rangle$, which appears on the right side of eqn. 10, has the units of reciprocal time. Indeed, the right side of eqn. 10 is most frequently written as $(f^0 - f)/\tau$, where $\tau = 1/n\langle g\sigma \rangle$ is the average time between collisions of a molecule with velocity $\underline{v}$, and is known as the relaxation time of the system. The origin of the term becomes more obvious

if we consider a gas of uniform density which is not subject to external forces, but which has a nonequilibrium velocity distribution. Then eqn. 10 becomes

$$\frac{\partial f}{\partial t} = - \frac{f-f^0}{\tau}$$

which can be integrated to give

$$f-f^0 = (f_i-f^0) e^{-t/\tau}$$

where f_i is the distribution function at zero time. We see that τ is the time constant for the exponential relaxation of the system towards equilibrium. Accordingly, eqn. 10 is known as the relaxation approximation to the Boltzmann transport equation.

The Transport Coefficients

We shall now use eqn. 10 to determine an approximate expression for the diffusion coefficient. For simplicity, we assume that steady-state conditions have been reached, so that $\partial f/\partial t = 0$, there are no external forces, and that a concentration gradient of an isotopically labeled atom exists in the z -direction. The Boltzmann equation becomes

$$v_z \frac{\partial f}{\partial z} = (f^0 - f)/\tau. \quad (11)$$

We shall assume that the distribution function f can be written as the sum of two terms:

$$f = f^0(r) + f^1.$$

The first term $f^0(r)$ represents a "local" equilibrium. That is, $f^0(r)$ is the equilibrium Maxwell-Boltzmann function evaluated for the conditions which hold at each differential volume element in the gas. In the case of diffusion, this merely means that the f^0 of eqn. (1) is used, but with the concentration n taken as a function of position. The term f^1 represents the small departures from local equilibrium. We substitute for the distribution function in eqn. 11 and ignore the very small quantity $\partial f^1 / \partial z$. The result is

$$v_z \frac{\partial f^0(z)}{\partial z} = - \frac{f^1}{\tau}$$

or

$$f^1 = -v_z \tau \frac{\partial f^0(z)}{\partial z} = -v_z \tau \frac{f^0}{n} \frac{\partial n}{\partial z} \quad (12)$$

where n is the concentration of the diffusing species. We see that the perturbation to the local equilibrium distribution function is proportional to the relaxation time and to the concentration gradient.

With the distribution function available, we can calculate the diffusive flux:

$$J_z = \int v_z f d^3v = \int v_z (f^0 + f^1) d^3v.$$

The integral which involves f^0 vanishes, since f^0 is an even function of velocity, and v_z is an odd function. Thus the flux simplifies to

$$J_z = \int v_z f^1 d^3v = - \frac{\tau}{n} \left[\int f^0 v_z^2 d^3v \right] \frac{\partial n}{\partial z}.$$

The right side has the form of the usual phenomenological diffusion equation, with

$$D = \frac{\tau}{n} \left[\int f^0 v_z^2 d^3v \right]$$

as the diffusion coefficient. The integral is just equal to the local concentration of diffusing species n times the mean square velocity component. Thus

$$D = \tau kT/m = kT/(n_t \langle g\sigma \rangle m). \quad (13)$$

We note that the relaxation time involves the total gas concentration n_t .

It is of interest to compare eqn. 13 to the conventional expression from mean free path theory:

$$D = \frac{1}{3} \bar{v} \ell$$

where ℓ is the mean free path. Since $\ell = \tau \bar{v}$, we have

$$D = \frac{1}{3} (\bar{v})^2 \tau = \frac{8kT}{3\pi m} \tau.$$

Thus the two approaches give very similar results, with the relaxation expression larger by a factor of $3\pi/8 = 1.18$.

We can now treat the electrical conductivity which results from a dilute solution of univalent positive ions in an excess of background gas. The system is in a steady state, the charge concentration is uniform, but each charge carrier is subject to an external force $e\xi_z$, where ξ_z is the electric field. The Boltzmann equation becomes

$$\frac{e\xi_z}{m} \frac{\partial f}{\partial v_z} = \frac{f^0 - f}{\tau}.$$

Again we assume that f can be written as $f^0 + f^1$, where f^0 is the equilibrium distribution function, and f^1 is small enough so that its velocity derivative is negligible. Then we find

$$f^1 = \frac{\tau e \xi_z}{m} \frac{\partial f^0}{\partial v_z}.$$

The current density is

$$j_z = e \int v_z (f^0 + f^1) d^3v = e \int f^1 v_z d^3v.$$

Since

$$\frac{\partial f^0}{\partial v_z} = \frac{mv_z}{kT} f^0$$

the current density becomes

$$\begin{aligned} j_z &= \frac{e^2 \xi_z}{kT} \int f^0 v_z^2 d^3v \\ &= \frac{ne^2 \xi_z}{m} \end{aligned}$$

where n is the concentration of charge carriers.

The electrical conductivity σ_e is the current density per unit field, so

$$\sigma_e = ne^2 \tau / m = ne^2 / (n_t m \langle g \sigma \rangle) \quad (14)$$

where n is the concentration of charge carriers. Again, the relaxation time τ is determined by the total concentration of gas molecules n_t . The mobility of an ion is the drift velocity per unit field, or the conductivity per unit concentration of charge. Thus we have for the mobility

$$\mu = \sigma_e / ne = e\tau / m.$$

The ratio of the mobility to the diffusion coefficient found earlier is

$$\frac{\mu}{D} = \frac{2\tau m}{m\tau kT} = \frac{e}{kT},$$

a result which is more general and accurate than our treatment of either diffusion or mobility.

To calculate the viscosity coefficient, we assume that the gas is in a steady state with a mass flow velocity u_x in the x-direction whose value is a function only of the z-coordinate. We assume that relative to this mass flow velocity, the velocity distribution of the molecules has its equilibrium form. Thus if we define

$$\underline{U} = \underline{v} - \underline{u}$$

and in particular

$$U_x = v_x - u_x, \quad U_y = v_y, \quad U_z = v_z,$$

we can write the local distribution function as

$$f^0(\underline{U}) = n \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-mU^2/2kT}.$$

Again, this local distribution function is perturbed by f^1 , due to the fact that the flow velocity u_x is a function of z . Thus substituting $f = f^0 + f^1$ into the Boltzmann equation leads to

$$f^1 = -\tau v_z \frac{\partial f^0}{\partial z} = -\tau v_z \left(\frac{\partial f^0}{\partial U_x} \right) \left(\frac{\partial u_x}{\partial z} \right).$$

The flux of the x-component of momentum in the z-direction is

$$\begin{aligned} P_{zx} &= m \int f v_z u_x d^3v = m \int (f^0 + f^1) U_z U_x d^3v \\ &= m \int f^1 U_z U_x d^3v \\ &= - \tau m \left(\frac{\partial u_x}{\partial z} \right) \int \frac{\partial f^0}{\partial U_x} v_z U_z U_x d^3v. \end{aligned}$$

The factors which multiply $\partial u_x / \partial z$ comprise the viscosity coefficient:

$$\eta = - \tau m \int \frac{\partial f^0}{\partial U_x} U_z^2 U_x d^3v.$$

Since $d^3v = d^3U$, and

$$\frac{\partial f^0}{\partial U_x} = - \frac{m U_x}{kT} f^0$$

we have

$$\eta = \frac{\tau m^2}{kT} \int U_z^2 U_x^2 f^0 d^3U.$$

The integration gives the product of two factors of the mean square velocity component multiplied by n , so

$$\eta = \frac{n \tau m^2}{kT} \left(\frac{kT}{m} \right)^2 = n \tau kT. \quad (15)$$

The result from the elementary mean free path method is

$$\begin{aligned} \eta &= \frac{1}{3} n m \bar{v} \ell = \frac{1}{2} n m (\bar{v})^2 \tau \\ &= \frac{8 k T \tau n}{3 \pi} \end{aligned}$$

so that again the relaxation result is larger by a factor of $3\pi/8 = 1.18$.

To find the thermal conductivity coefficient we again assume that the distribution function can be written as

$$f = f^0(z) + f^1$$

where f^1 is a small perturbing term and f^0 is a local equilibrium function of the form

$$f^0(z) = n(z) \left(\frac{m}{2\pi kT} \right)^{3/2} \exp[-mv^2/2kT(z)].$$

We note that both the temperature and the particle density are now functions of position, since the pressure is uniform. The Boltzmann equation gives

$$f^1 = -\tau v_z \frac{\partial f^0}{\partial z}.$$

Evaluation of the derivative, taking into account that $\partial n / \partial T = -n/T$, gives

$$\frac{\partial f^0}{\partial z} = \frac{f^0}{T} \left(\frac{mv^2}{2kT} - \frac{5}{2} \right) \frac{\partial T}{\partial z},$$

so the distribution function is known in terms of the temperature gradient and the relaxation time.

The energy flux for monatomic particles is

$$Q = \int v_z \frac{mv^2}{2} f d^3v = \int v_z \left(\frac{mv^2}{2} \right) f^1 d^3v.$$

Substituting for the distribution function leads to

$$Q = -\frac{\tau}{T} \left(\frac{\partial T}{\partial z} \right) \int \left(\frac{mv^2}{2kT} - \frac{5}{2} \right) \left(\frac{mv^2}{2} \right) v_z^2 f^0 d^3v.$$

The factors which multiply $-(\partial T/\partial z)$ constitute the thermal conductivity coefficient κ . The integrations can be carried out by converting to spherical polar velocity coordinates by

$$d^3v = v^2 dv \sin\theta d\theta d\phi, \quad v_z = v \cos\theta.$$

The integrals are found in standard tables, and the final result for the thermal conductivity coefficient is

$$\kappa = \frac{5}{2} \tau \frac{nk^2T}{m}. \quad (16)$$

Since τ is inversely proportional to n , the thermal conductivity coefficient is independent of concentration.

The elementary mean free path method gives

$$\kappa = \frac{1}{3} n c_v \bar{v} \ell$$

for the thermal conductivity coefficient, where c_v is the heat capacity per molecule. For atoms, $c_v = 3/2 k$, so the mean free path result is

$$\kappa = \frac{1}{2} n (\bar{v})^2 \tau = \frac{4nk^2T\tau}{\pi m}.$$

The relaxation method gives a result which is larger than this by a factor of $5\pi/8 = 1.96$. The relaxation result is significantly closer to the exact result for hard spheres.

Summary

The relaxation approximation to the Boltzmann transport equations provides a procedure for obtaining the transport coefficients of dilute gases. It is somewhat more complicated than the elementary mean free path method, but is well within

the capabilities of students in undergraduate physical chemistry courses. It has the pedagogical advantages of emphasizing the nonequilibrium nature of transport, avoiding suspect geometric arguments, and providing an indication of how transport coefficients are obtained in rigorous treatments.

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