3 Random walk and all that

3.1 Diffusion in the momentum space

If the particle momentum changes only slightly in a single collision, one can conveniently describe the evolution of the particle distribution as diffusion in the momentum space. For example, the Coulomb collisions in plasma may be considered as **diffusion in angles**. The electron free path is found as follows. The deviation angle of an electron passing the ion at the impact parameter b is given by eq. (2.2). At the distance l, the electron passes $2\pi n_i bdbl$ ions at the impact parameters between b and $b+db$. Here n_i is the ion number density. In each collision, the velocity turns by the angle (2.2) . The rms deviation angle, Θ, is estimated as

$$\Theta^2 = 2\pi n_i l \int \theta^2 bdb = 2\pi n_i l \frac{4Z^2e^4}{m^2v^4} \int \frac{db}{b} = 8\pi n_i l \left(\frac{Ze^2}{mv^2}\right)^2 \ln \frac{b_{\rm max}}{b_{\rm min}}. \tag{3.1}$$

The minimal impact parameter is estimated as that corresponding to $\theta \sim 1$, which yields $b_{\rm min} \sim Ze^2/m_e v^2$. The maximal impact parameter is chosen as the Debye radius, $r_{\rm max} = r_D \equiv \sqrt{k_BT/4\pi e^2 n}$. Now one can define the electron mean free path as the distance over which the electron deviates by the angle $\Theta \sim 1$:

$$l_{ei} = \frac{1}{8\pi n_i \Lambda} \left(\frac{mv^2}{Ze^2}\right)^2. \tag{3.2}$$

Here

$$\Lambda = \ln\left(\frac{r_D m_e v^2}{Ze^2}\right) \sim 10 \tag{3.3}$$

is the so called Coulomb logarithm. One can conveniently define the effective collision cross-section,

$$\sigma_{ei} = 8\pi\Lambda \left(\frac{Ze^2}{mv^2}\right)^2, \tag{3.4}$$

such that $l_{ei} = (\sigma_{ei} n_i)^{-1}$. The mean collision frequency is $\nu_{ei} = v/l_{ei}$. For thermal electrons, one can substitute mv^2 by k_BT.

Another example is the energy exchange between heavy and light particles (e.g., ions and electrons). When a light and a heavy particles collide, the momentum of the light particle could change significantly however, the energy of the heavy particle changes only a little bit. Therefore the energy exchange may be considered as **diffusion in energies**. For example in an admixture of heavy and light gases, the collisions between the particles of the same sort rapidly establish thermal equilibrium in each of the two subsystems however, the temperature equilibration between the subsystems requires much larger time.

Let us consider the energy relaxation of heavy particles in the gas of light particles. Denote the quantities describing the heavy particles by index h and the light particles by index l. Let us consider separately the cases when the heavy particle velocity is larger and smaller than the light particle velocities.

If $v_h \gg v_l$, light particles acquire the momentum $\delta\mathbf{p}_l \sim m_l\mathbf{v}_h$ in each collision. The heavy particle looses the same momentum, $\delta\mathbf{p}_h = -\delta\mathbf{p}_l$, thus loosing the energy with the rate

$$\frac{dE_h}{dt} = -\delta\mathbf{p}_l \cdot \mathbf{v}_h \nu \sim -m_l v_h^2 \nu \sim -\frac{m_l}{m_h} E_h \nu; \qquad v_h \gg v_l; \tag{3.5}$$

where $\nu = \sigma v n_l$is the collision rate, v the relative velocities. For estimates, one can conveniently use $v = \max(v_l, v_h)$.

Now let us consider the case $v_l \gg v_h$. Then in a single collision, $\delta p_l \sim p_l$, whereas the energy of the heavy particle changes by

$$\delta E_h = \left[(\mathbf{p}_h + \delta\mathbf{p}_h)^2 - \mathbf{p}_h^2\right]/2m_h = \left[(\delta\mathbf{p}_h)^2 + 2\delta\mathbf{p}_h \cdot \mathbf{p}_h\right]/2m_h. \tag{3.6}$$

In the simplest case $p_h \ll p_l$, the first term, $(\delta\mathbf{p}_h)^2 = (\delta\mathbf{p}_l)^2 \sim p_l^2$, dominates so that the heavy particle gains the energy in each collision. When $p_h \gg p_l$ (but still $v_h \ll v_l$), the second term dominates but this term changes sign therefore in this case, one can describe the process as diffusion in energies.

The average rate of the energy gain/loss by a heavy particle may be written as

$$\frac{d\overline{E}_h}{dt} = \left(\frac{\overline{(\delta\mathbf{p}_l)^2}}{2m_h} + \frac{\overline{\delta\mathbf{p}_h} \cdot \mathbf{p}_h}{m_h}\right)\nu \tag{3.7}$$

where the averaging is over the collisions with isotropically distributed light particles. The first term may be estimated as

$$\frac{\overline{(\delta\mathbf{p}_l)^2}}{2m_h} \sim \frac{\overline{p_l^2}}{2m_h} = \frac{m_l}{m_h}\overline{E_l} \tag{3.8}$$

The second term in (3.7) does not vanish after averaging because the scattering on a moving heavy particle is not symmetric. Namely in the frame of the heavy particle, the distribution of the light particles is anisotropic: the momentum of head-on particles, as well as their number, exceed those of rear-end ones by the factor of $\sim v_h/v_l \ll 1$. Therefore one can write $\overline{\delta\mathbf{p}_h} = -a\mathbf{v_h}$, where the scalar factor a could be found from the condition, that according to the energy equipartition theorem, the rhs of eq. (3.7) should vanish at $\overline{E}_h = \overline{E}_l$. Taking into account this and eq. (3.8), one finds finally

$$\frac{d\overline{E}_h}{dt} \sim \frac{m_l}{m_h}\nu\left(\overline{E}_l - \overline{E}_h\right). \tag{3.9}$$

Note that even though this equation is obtained at the condition $v_h < v_l$, it remains correct in the general case (see eq. (3.5)); one has just to substitute the larger velocity in ν and σ. In most cases, the gas is thermal; then $\overline{E}_l = (3/2)k_B T_l$.

The energy gain/loss by a light particle in the gas of heavy particles is small if, as it is commonly happens, the light particle moves faster than the heavy ones, even though the energy of heavy particles could exceed the light particle energy. Then the transition to the energy equipartition is described similarly.

3.2 Scattering of light

Consider an object of size L hit by light of wavelength λ such that $n^{-1/3} \ll L \ll \lambda$, where $n \sim N/L^3$ is the density of molecules, each with a scattering cross section σ_0. What is the power scattered if the object is subject to Poynting flux S?
Here each particle j generates a field $E_j \propto \cos(\omega t + \phi_j)$, but as all particles oscillate with the same phase ϕ, the scattering constructively interferes, and the emitted radiation is $P \propto |\sum E_j|^2 \propto N^2$. This is coherent scattering.

Consider the case $n^{-1/3} \ll \lambda \ll L$, where the object is much larger than the wavelength. For a wide range of angles θ, we can find for each particle scattering at phase ϕ, another particle scattering with the opposite phase, so the interference is destructive. So how can a dense medium scatter light? It seems we found that the sky cannot scatter light - could this be true?

This would indeed be the case, if the medium were homogeneous. If the radiation wavelength exceeds the distance between the particles, $\lambda \gg n^{-1/3}$, the scattering occurs on the density fluctuations. Let us consider scattering from two small equal volumes positioned such that the incident wave reaches them with the same phase but the distance from them to the observer differs by $\lambda/2$. At the point of observation, the field of the wave scattered by a molecule from the region 1 is $E_1 = A\cos(\omega t + \phi)$ and by a molecule from the region 2 is $E_2 = -A\cos(\omega t + \phi)$. Therefore the total field from both regions is $E = (N_1 - N_2)A\cos(\omega t + \phi)$. The average intensity of the scattered radiation is

$$I = \frac{c}{4\pi}\overline{E^2} = \overline{(N_1 - N_2)^2} I_0; \tag{3.10}$$

where $I_0 = cA^2/8\pi$ is the intensity of the radiation scattered by one molecule, N_1 and N_2 the numbers of molecules in the chosen volumes. One sees that a strictly homogeneous medium does not scatter at all. If the characteristic fluctuation scale is less than the wavelength so that fluctuations at different points are independent, one can write

$$\overline{(N_1 - N_2)^2} = \overline{(\delta N_1 - \delta N_2)^2} = \overline{\delta N_1^2} + \overline{\delta N_2^2}. \tag{3.11}$$

In an ideal gas, $\overline{(\delta N)^2} = \bar{N}$ therefore $I = \left(\bar{N}_1 + \bar{N}_2\right) I_0$ so that the scattering occurs as if each molecule scatters independently of others even though the wavelength exceeds the distance between the molecules. Generally, the scattering cross section (always per particle) in the case when the wavelength exceeds the fluctuation size is

$$\sigma = \sigma_0 \frac{\overline{\delta N^2}}{\bar{N}}, \tag{3.12}$$

where σ_0 is the cross section for an isolated molecule.

3.3 Density fluctuations as gas of phonons

Pressure fluctuations in the thermodynamical equilibrium may be presented as phonon gas with Planckian distribution and the energy per mode

$$\mathcal{E}_{\mathbf{k}} = \frac{\hbar\omega}{\exp(\hbar\omega/kT) - 1} = \begin{cases} k_B T; & \hbar\omega = \hbar v_s k \ll k_B T \\ 0 & \hbar\omega \gg k_B T \end{cases} \tag{3.13}$$

Recall that phonons with $\hbar\omega \gg k_B T$ exist only if the temperature is below the Debye temperature.

Phonons are in fact the sound waves. The corresponding density fluctuations are presented as a superposition of waves

$$\delta n = \sum \delta n_{\mathbf{k}} \cos(\mathbf{k} \cdot \mathbf{r} + \phi_{\mathbf{k}} - \omega t), \tag{3.14}$$

where $\phi_{\mathbf{k}}$ are random phases. Let us first consider a single mode with the wave vector $\mathbf{k}$. The energy per unit volume is

$$\frac{1}{V}\mathcal{E}_{\mathbf{k}} = B\overline{\delta\xi^2} = \frac{1}{2}B\left(\frac{\delta n_{\mathbf{k}}}{n}\right)^2, \tag{3.15}$$

where B is the bulk modulus (of the order of the Young modulus in solids), or the inverse of the compressibility, n the unperturbed particle number density. Comparing this expression with Eq. (3.13), one finds the density fluctuation amplitude as

$$\left(\frac{\delta n_{\mathbf{k}}}{n}\right)^2 = \begin{cases} \frac{2k_BT}{BV}; & \hbar v_s k \ll k_BT \\ 0 & \hbar v_s k \gg k_BT \end{cases} \tag{3.16}$$

The fluctuations at the scale l are characterized by the fluctuation of the particle number in a region of the size l:

$$\delta N = \int \delta n dV \sim l^3 \sum_{|\mathbf{k}|\leq 2\pi/l} \delta n_{\mathbf{k}} \cos(\mathbf{k}\cdot\mathbf{r} + \phi_{\mathbf{k}} - \omega t). \tag{3.17}$$

Here we take into account that the terms with $k > 2\pi/l$ vanish when integrated over the volume V. The rms amplitude of the fluctuations at the scale $l > \hbar v_s/k_BT$ is now estimated as

$$\overline{\delta N^2} \sim l^6 \sum_{|\mathbf{k}|\leq 2\pi/l} (\delta n_{\mathbf{k}})^2 = \int_{|\mathbf{k}|\leq 2\pi/l} (\delta n_{\mathbf{k}})^2 \frac{d^3k}{(2\pi)^3} V l^6 \sim l^3 \frac{k_BTn^2}{B} \sim \frac{nk_BT}{B} N. \tag{3.18}$$

For an ideal gas, $B \sim p = nk_BT$ therefore one gets the Poisson fluctuations[2]. In the condensed matter, $B \sim \epsilon n$, where ϵ is the binding energy, therefore fluctuations in the condensed matter are suppressed as compared with the Poissonian one:

$$\overline{(\delta N)^2} \sim \frac{k_BT}{\epsilon} N. \tag{3.19}$$

If the temperature exceeds the Debye temperature, the relative fluctuations, $\delta N/N$, are maximal at the scale of the order of the interatomic distance; at smaller temperatures, the strongest fluctuations occur at the scale $l \sim \hbar v_s/k_BT$.

3.4 Electron conductivity in metals

According to the Drude model, the electron conductivity is estimated as

$$\kappa = \frac{e^2 n\tau}{m_e} = \frac{\omega_p^2 \tau}{4\pi}, \tag{3.20}$$

where e and m_e are the electron charge and mass, respectively, n the density of free electrons, τ the relaxation time. In the quantum theory, the Drude model remains roughly valid, one has just take into account that free electrons propagate as Bloch waves. The dispersion law of these waves may be very complicated but for estimates, one can use $\varepsilon = p^2/2m_e = (\hbar k)^2/2m_e$. The electrons in metals are strongly degenerate; the Fermi wave-vector is

$$k_F = (3\pi^2 n)^{1/3}. \tag{3.21}$$

[2]Strictly speaking, the Poisson distribution describes the total density fluctuations whereas phonons produce only density fluctuations related to the pressure fluctuations. The total density fluctuations include also isobaric (entropy) fluctuations, in which the local temperature fluctuations are compensated by thermal expansion/contraction. Even in an ideal gas, the contribution of isobaric fluctuations is less than 50%; in the condensed matter, it is negligibly small because of a small thermal expansion coefficient.

Since only one-two free electrons are available for a cell, the Fermi wavelength is comparable with the interatomic separation, $k_F a \sim 1$, whereas the Fermi energy, $\varepsilon_F = (\hbar k_F)^2/2m_e$, is roughly equal to the characteristic binding energy, a few eV. Bloch waves propagate freely in an ideal crystal. Scattering occur either on impurities or on density fluctuations (phonons). At not too low temperatures, the second process dominates and determines τ.

Let us estimate τ due to the scattering on large scale fluctuations,

$$lk_F \gg 1. \tag{3.22}$$

The notion of the density fluctuations has physical sense only at scales not less than the interatomic distance, therefore $l \geq a$. In metals, the Fermi wavelength is of the order of the interatomic distance, $k_F \sim a^{-1}$, therefore generally the above condition is satisfied only at temperatures smaller than the Debye temperature. If the temperature exceeds the Debye temperature, $l \sim a \sim k_F^{-1}$. In this case, one could just extrapolate the estimates in the limits $l >> a$ to $l \sim a$.

Fluctuations in the density imply fluctuations in the Fermi energy:

$$\delta\varepsilon_F \sim \varepsilon_F \frac{\delta n}{n}. \tag{3.23}$$

The total energy on the equilibrium remains constant therefore fluctuations of the (electric) potential energy arise:

$$U \sim -\delta\varepsilon_F. \tag{3.24}$$

The physical reason is that in the regions with a larger Fermi energy, the electrons move faster. Therefore they escape from the region until the the positive electric potential is build up preventing the escape. After passing the region, the electron deviates from the initial direction by an angle

$$\theta \sim \frac{U}{\varepsilon_F} \sim \frac{\delta n}{n}. \tag{3.25}$$

The rms deviation angle after passing the distance x is estimated. as it was done in sect. 3.1:

$$\overline{\Theta^2} \sim \theta^2 \frac{x}{l} \sim \left(\frac{\delta n}{n}\right)^2 \frac{x}{l}. \tag{3.26}$$

Therefore, the free path is estimated from the condition that $\Theta \sim 1$ as

$$L \sim l\left(\frac{n}{\delta n}\right)^2. \tag{3.27}$$

This result was obtained by using of the classical mechanics. Let us show that he quantum approach gives the same. When the Bloch wave propagates through a lattice with a fluctuating density, the wave front becomes corrugated because the wavevector varies with the density according to (3.21). After the wave traverses a fluctuation of the size l with the density excess/deficiency δn, the phase difference arises between the regions of the wave front spaced by $\sim l$:

$$\delta\phi \sim \delta k_F l \sim \frac{\delta n}{n} k_F l. \tag{3.28}$$

Therefore the normal to the wave front turns by the angle

$$\delta\theta \sim \frac{\delta\phi}{k_F l} \sim \frac{\delta n}{n} \ll 1, \tag{3.29}$$

which is compatible with the classical estimate (3.25).

Making use of the estimate (3.19), one finds (recall that in metals, the binding energy is of the order of the Fermi energy)

$$\left(\frac{\delta n}{n}\right)^2 = \left(\frac{\delta N}{N}\right)^2 = \frac{k_B T}{\epsilon_F n l^3}; \tag{3.30}$$

which yields

$$L \sim \frac{\epsilon_F n l^4}{k_B T}. \tag{3.31}$$

One sees that the electron free path is determined by the smallest possible fluctuation size. At the temperatures exceeding the Debye temperature, $l \sim a$; then one gets

$$\tau = \frac{L}{v_F} \sim \frac{\hbar}{k_B T}. \tag{3.32}$$

Now one finds that above the Debye temperature, the conductivity of metals may be estimated as

$$\kappa \sim \frac{\hbar e^2 n}{m_e k_B T}. \tag{3.33}$$