1 Elementary processes

1.1 Introduction

To understand matter on a macroscopic scale, it is necessary to pay attention to its molecular makeup and also that the dynamical equations which describe the change of macroscopic systems, have thermodynamics built into them. This is the basic content of Boltzmann's H-theorem and it's also apparent in the Onsager theory which is based on the observation that thermodynamic forces are responsible for the relaxation to equilibrium. All this suggests that both thermodynamics and fluctuations are imbedded in a deeper formalism - a formalism which is based on a picture of molecular events like the Boltzmann equation.

The 3rd chapter aims to develop a mechanistic statistical theory of nonequilibirum thermodynamics for two special cases:

1. First, in this lecture, we'll examine the Boltzmann equation and show how to interpret the effect of molecular collisions stochastically.

2. Second, left for the future lectures, is the stochastic description of the μ- space number density and the coupled nonlinear equations which we refer to as the fluctuating Boltzmann equation. We show that near equilibrium the fluctuating Boltzmann equation reduces to the μ-space stochastic description of Onsager.

The stochastic formulation of the Boltzmann equation depends in a fundamental way on Boltzmann's picture of molecular collisions.

1.2 The Stochastic Description of the Boltzmann Equation

In the previous chapter the Boltzmann level of description was conceived by breaking the μ-space into small cellular volume elements. In the stochastic picture operating with many small cells translates to the fact that collisions cause unpredictable transitions from one cell to another. The reason these transitions are unpredictable is that in μ-space we keep track only of the number of molecules in a given μ-space volume element. This does not provide sufficient information to determine the number of binary clusters of molecules, which is required to describe the effect of collisions. Thus the μ-space density provides only a contracted picture of a molecular system which implies that the variables are random and that we are reduced to considering an ensemble of related systems.

It is the collisions, not the streaming motion in μ-space, that make the μ-space description unpredictable. In his original work, Boltzmann ignored these fluctuations and used a concept of molecular scattering processes to describe the effect of collisions. Consider a direct collision between two molecules with velocities in the range $\mathbf{v}$ to $\mathbf{v}+d\mathbf{v}$ and $\mathbf{v_1}$ to $\mathbf{v_1}+d\mathbf{v_1}$ in the spatial volume element $d\mathbf{r}$ located at position $\mathbf{r}$. This is a *conditional* event as far as changing the μ-space number density. To clarify this, consider $N(\mathbf{r},\mathbf{v},t) = \rho(\mathbf{r},\mathbf{v},t)d\mathbf{r}d\mathbf{v}$, which is the number of molecules in the volume element $d\mathbf{r}d\mathbf{v}$. The scattering event describes what occurs *if* there is a partner molecule which is *poised*

for collision in the volume $d\mathbf{r}d\mathbf{v_1}$. If a collision occurs, both $N(\mathbf{r},\mathbf{v},t)$ and $N(\mathbf{r},\mathbf{v_1},t)$ decrease by one whereas $N(\mathbf{r},\mathbf{v}',t)$ and $N(\mathbf{r},\mathbf{v_1'},t)$ increase by one. Thus the effect on the macroscopic observable $N(\mathbf{r},\mathbf{v},t)$ is perfectly deterministic *if* such a sollision occurs.

If each volume element in μ-space is labeled by its occupancy number $N(\mathbf{r},\mathbf{v},t)$, then a single collision of type $\mathbf{v},\mathbf{v}_1 \rightarrow \mathbf{v}',\mathbf{v}_1'$ is a jump process in which the occupancy number of the two volume elements at $\mathbf{r}$, $\mathbf{v}$ and $\mathbf{r}$, $\mathbf{v}_1$ decreases by one and the occupancy of the two volume elements at $\mathbf{r}$, $\mathbf{v}'$ and $\mathbf{r}$, $\mathbf{v_1'}$ increases by one. Analogy can be drawn with coin tossing, consider n coins which are either heads or tails and for which we keep track of only the number of heads, n_+. If we toss a single coin which was originally tails and heads comes up, symbolically $T \rightarrow H$, then n_+ changes by $+1$. The event $T \rightarrow H$ is an allowed process in tossing a coin and if it occurs, there will be a predictable change in the number of heads and tails.

We will refer to any molecular process which causes a deterministic change in an extensive variable as an *elementary process*. For a dilute gas the elementary processes that cause change in the occupancy numbers in μ-space are all the possible binary collisions. Elementary collision processes come in pairs for every direct collision, $\mathbf{v},\mathbf{v_1}\rightarrow \mathbf{v}',\mathbf{v_1'}$ there is an inverse collision $\mathbf{v},\mathbf{v_1}\leftarrow \mathbf{v}',\mathbf{v_1'}$, which restores the initial velocities. This is typical for all elementary processes and for that reason the elementary process and its inverse are considered as a single elementary process, $\mathbf{v},\mathbf{v_1}\rightleftharpoons \mathbf{v}',\mathbf{v_1'}$.

To determine how the elementary processes affect the extensive variables, it is necessary to know the probability that each elementary process occurs in dt. This probability is not given in the Boltzmann picture, what we can get instead, is an expression for the rate of change of the occupancy number due to an elementary collision process. The rate of change of $N(\mathbf{r},\mathbf{v},t)$ due to process $\mathbf{v},\mathbf{v_1}\rightleftharpoons \mathbf{v}',\mathbf{v_1'}$ is seen to be

$$R_\kappa = -V_\kappa \tag{1}$$

The factor -1 represent the fact that exactly one molecule is lost from $d\mathbf{r}d\mathbf{v}$ at every collision, the other factor

$$V_\kappa = \hat{\sigma}_T g[\rho\rho_1 - \rho'\rho_1']d\mathbf{v}_1 d\mathbf{v} \tag{2}$$

is called the *rate* of the elementary processes, $\mathbf{v},\mathbf{v}_1 \rightleftharpoons \mathbf{v}',\mathbf{v}_1'$, the first term represents the direct collision and the second term is the restoring collision. The contributions to the overall rate of the elementary process arise from the direct and restoring collisions - we will call them the forward and reverse *transition rates*. The forward transition rate is

$$V_\kappa^+ = \hat{\sigma}_T g\rho\rho_1 d\mathbf{v}_1 d\mathbf{v} d\mathbf{r} \tag{3}$$

and the reverse transition rate is

$$V_\kappa^- = \hat{\sigma}_T g\rho'\rho_1' d\mathbf{v}_1 d\mathbf{v} d\mathbf{r}. \tag{4}$$

These expressions can be interpreted as the number of direct or restoring collisions that occur per unit time. To explain this we label the occupancy numbers in every μ-space

volume element $i = 1, \ldots, k$,

$$\mathbf{n}(t) = \begin{matrix} N_1(t) \\ N_2(t) \\ \vdots \\ N_k(t) \end{matrix} \tag{5}$$

The vector of occupancy numbers $\mathbf{n}(t)$ is stochastic process whose time evolution we want to determine. Since it is a random variable, the best we can do is to specify the probability that its value will change by any specified amount in the interval dt. Now the specific amounts by which $\mathbf{n}$ can change are completely determined by the elementary processes, labeled by κ. For the forward part of the elementary process only four occupancy numbers in the vector $\mathbf{n}$ change by plus or minus one and all other occupancy numbers stay fixed. This vector of changes will be written $\overrightarrow{\omega}^{+}_{\kappa}$. For the reverse process there is a corresponding vector of changes $\overrightarrow{\omega}^{-}_{\kappa}$, but

$$-\overrightarrow{\omega}^{-}_{\kappa} = \overrightarrow{\omega}^{+}_{\kappa} \equiv \overrightarrow{\omega}_{\kappa} \tag{6}$$

because the reverse process restores the effect of the direct collision. Thus the set $\{\overrightarrow{\omega}_{\kappa}\}$ for all κ summarizes the possible changes in $\mathbf{n}$ which can occur due to collision. In addition to these collisional changes, which may or may not occur, a change in $\mathbf{n}(t)$ is caused by the inevitable streaming motion in μ-space. If the change in $\mathbf{n}$ in the intrerval dt due to streaming in $d\mathbf{n}_s$, then the probability of the total change of $\mathbf{n}, d\mathbf{n} + d\mathbf{n}_s$, is calculated according to

$$P_2(\mathbf{n}, t|\mathbf{n}' = \mathbf{n} + d\mathbf{n}_s + d\mathbf{n}, t + dt) = \begin{cases} V^{\pm}_{\kappa} dt + \mathcal{O}(dt), & \text{if } d\mathbf{n} = \pm\overrightarrow{\omega}_{\kappa} \\ 1 - \sum (V^{+}_{\kappa} + V^{-}_{\kappa}) dt + \mathcal{O}(dt), & \text{if } d\mathbf{n} = \mathbf{0} \\ 0 \text{ otherwise.} \end{cases} \tag{7}$$

The left-hand side of the equation above indicates the conditional probability for $\mathbf{n}$ changing in the time interval dt, and κ can be any elementary process. This equation states that in addition to streaming, only the elementary collision processes cause the occupancy numbers to change. Further, the probability of a collisional change occuring is given by the number of collisions that occur in dt. In the absence of collisions, when all the rates $V^{\pm}_{\kappa} = 0$, the above equation states that streaming occurs with probability one. The *ansatz* in equation (7) produces a stochastic process which is, essentially a diffusion process. Stochastic diffusions satisfy the following conditions on their transition moments which measure the average increment of change of $\mathbf{n}$ from its value at t (Section 1.5)

$$\lim_{\tau \to t} \frac{1}{\tau - t} \int P_2(\mathbf{n}, t|\mathbf{n}', \tau)(\mathbf{n}' - \mathbf{n}) d\mathbf{n}' = \mathbf{h}(\mathbf{n}, t), \tag{8}$$

$$\lim_{\tau \to t} \frac{1}{\tau - t} \int P_2(\mathbf{n}, t|\mathbf{n}', \tau)(\mathbf{n}' - \mathbf{n})(\mathbf{n}' - \mathbf{n})^T d\mathbf{n}' = \gamma(\mathbf{n}, t) \tag{9}$$

$$\lim_{\tau \to t} \frac{1}{\tau - t} \int P_2(\mathbf{n}, t|\mathbf{n}', \tau) \prod_{l=1}^{k} (n'_{i_l} - n_{i_l}) d\mathbf{n} = 0. \tag{10}$$

The first transition moment is

$$\int P_2(\mathbf{n}, t|\mathbf{n}', t+dt)(\mathbf{n}' - \mathbf{n})d\mathbf{n}' \equiv \mathbf{M}^1(\mathbf{n}). \tag{11}$$

This can be calculated directly from Eq. (7), which gives

$$\mathbf{M}^1(\mathbf{n}) = \langle d\mathbf{n}_s + d\mathbf{n}\rangle^{\mathbf{n}} = \sum_\kappa \overrightarrow{\omega}_\kappa (V_\kappa^+ - V_\kappa^-)dt + d\mathbf{n}_s + \mathcal{O}(dt) \tag{12}$$

Thus the limit

$$\lim_{dt\to 0} \frac{\mathbf{M}^1(\mathbf{n})}{dt} = \sum_\kappa \overrightarrow{\omega}_\kappa (V_\kappa^+ - V_\kappa^-) + \frac{d\mathbf{n}_s}{dt} \equiv \mathbf{h}(\mathbf{n}, t) \tag{13}$$

exists as required by Eq. (8) since $d\mathbf{n}_s$, the streaming change, is proportional to dt. Similarily the second transition moment is

$$\begin{aligned} M^2(\mathbf{n}) &= \langle (d\mathbf{n}_s + d\mathbf{n})(d\mathbf{n}_s + d\mathbf{n})^T\rangle^{\mathbf{n}} && (14)\\ &= d\mathbf{n}_s d\mathbf{n}_s^T + d\mathbf{n}_s \left[\sum_\kappa \overrightarrow{\omega}_\kappa^T (V_\kappa^+ - V_\kappa^-)\right] dt + \left[\sum_\kappa \overrightarrow{\omega}_\kappa (V_\kappa^+ - V_\kappa^-)\right] d\mathbf{n}_s^T dt && (15)\\ &+ \sum_\kappa \overrightarrow{\omega}_\kappa \overrightarrow{\omega}_\kappa^T V_\kappa^+ dt + \sum_\kappa \overrightarrow{\omega}_\kappa^T V_\kappa^- dt + \mathcal{O}(dt) && (16) \end{aligned}$$

Since all the terms which involve streaming contributions are of order $(dt)^2$, the limit required in Eq. (9) exists and

$$\lim_{dt\to 0} \frac{\mathbf{M}^2(\mathbf{n})}{dt} = \sum_\kappa \overrightarrow{\omega}_\kappa (V_\kappa^+ + V_\kappa^-) \overrightarrow{\omega}_\kappa^T \equiv \gamma(\mathbf{n}, t). \tag{17}$$

To verify that the higher-order transitions moments vanish, as in Eq. (10), we need to examine quantities such as

$$M^3_{ijk}(\mathbf{n}) = \langle dn_i dn_j dn_k\rangle = \sum_\kappa \omega_{\kappa i}\omega_{\kappa j}\omega_{\kappa k}(V_\kappa^+ - V_\kappa^-)dt + \mathcal{O}(dt) \tag{18}$$

since each term $(dn_i)_s$ contributes a factor of dt it is easy to see that Eq. (10) is *not* valid for the extensive variables n_i, since the first term in the above equation is proportional to dt. The stochastic process $\mathbf{n}$ is not strictly a stochastic diffusion process except in the limit that a large number of molecules make up the system. For the Eq. (7) to be valid the occupancy numbers n_i must be large and consequently the total number of molecules $n = \sum_{i=1}^k n_i$ must be infinite. We introduce the scaled extensive variables $\hat{n}_i = n_i/\sqrt{m}$ where $m = n/k$. The number of subvolumes, k, should be chosen such that the n_i are the order of m and such that $m \gg 1$. The changes in $\hat{n}_i$ during an elementary process κ are

$\hat{\omega}_{\kappa i} = \omega_{\kappa i}/\sqrt{m}$. For the scaled variables $\hat{n}_i$ the moment conditions in Eqs. (12), (14) and (18) become

$$\begin{aligned} \mathbf{M}^1(\hat{\mathbf{n}}) &= \sum_\kappa \hat{\overrightarrow{\omega}}_\kappa (V_\kappa^+ - V_\kappa^-)dt + d\hat{\mathbf{n}}_s + \mathcal{O}(dt) \\ M^2(\hat{\mathbf{n}}) &= \sum_\kappa \hat{\overrightarrow{\omega}}_\kappa (V_\kappa^+ - V_\kappa^-)\hat{\overrightarrow{\omega}}_\kappa^T dt + \mathcal{O}(dt) \qquad (19) \\ M^3_{ijk}(\hat{\mathbf{n}}) &= \sum_\kappa \omega_{\kappa i}\omega_{\kappa j}\omega_{\kappa k}(V_\kappa^+ - V_\kappa^-)dt + \mathcal{O}(dt). \qquad (20) \end{aligned}$$

The limiting values of these expressions for large m and n depend on the scaling of the rate of the e lementary processes, $V_\kappa^\pm$. These rates are extensive quantities given by the collision rates in Eqs. and (4). Thus $V_\kappa^\pm$ are the order of n_i, i.e., the order of m. Since $\omega_{\kappa i} = +1, 0, -1$ and $\hat{\omega}_{\kappa i} = \omega_{\kappa i}/\sqrt{m}$ the expressions for the first two moments are unchanged as $dt \to 0$. The first moment $\mathbf{M}^1$ is of order $\sqrt{m}$, the second moment M^2 is of order unity, the third moment is of order $1/\sqrt{m}$ and in general the lth moments are of order $m^{(2-l)/2}$. Since $m = n/k$ is much larger than one, this means that

$$M^3_{ijk}(\hat{\mathbf{n}}, t) = \mathcal{O}(dt) \qquad (21)$$

with similar results for higher order moments. These considerations show that in the thermodynamic limit at least the scaled extensive variables, $\hat{n}_i$ become a stochastic diffusion process.

Now to explore the properties of this stochastic diffusion further we remember that in Section 1.5 it was shown that a stochastic diffusion process satisfies a Fokker-Planck equation

$$\frac{\partial P_2(\mathbf{n}_1, t_1|\mathbf{n}, t)}{\partial t} = -\frac{\partial h_i(\mathbf{n}, t) P_2(\mathbf{n}_1, t_1|\mathbf{n}, t)}{\partial n_i} + \frac{1}{2}\frac{\partial^2 \gamma_{ij}(\mathbf{n}, t) P_2(\mathbf{n}_1, t_1|\mathbf{n}, t)}{\partial n_i \partial n_j} \qquad (22)$$

using Eq. (13) we get

$$\begin{aligned} \frac{\partial P_2(\hat{\mathbf{n}}_1, t_1|\hat{\mathbf{n}}, t)}{\partial t} &= -\frac{\partial \left[\sum_\kappa \hat{\omega}_{\kappa i}(V_\kappa^+ - V_\kappa^-) + \hat{s}\right] P_2(\hat{\mathbf{n}}_1, t_1|\hat{\mathbf{n}}, t)}{\partial \hat{n}_i} \\ &+ \frac{1}{2}\frac{\partial^2 \left[\sum_\kappa \hat{\omega}_{\kappa i}(V_\kappa^+ + V_\kappa^-)\hat{\omega}_{\kappa j}\right] P_2(\hat{\mathbf{n}}_1, t_1|\hat{\mathbf{n}}, t)}{\partial \hat{n}_i \partial \hat{n}_j} \end{aligned} \qquad (23)$$

where the streaming term $d\hat{\mathbf{n}}_s/dt = \hat{\mathbf{s}}$ and the summation on repeated indices is used for i and j. The first term of the right hand side of the Eq. (23) is the drift term and the second is the diffusion term. The drift term is proportional to $\sqrt{m}$ whereas the diffusion is independent of m. Thus for the scaled occupancy numbers $\hat{\mathbf{n}}$ the drift term dominates. If the diffusion term is neglected in Eq. (23) the equation can be written

$$\frac{\partial P_2(\hat{\mathbf{n}}_1, t_1|\hat{\mathbf{n}}, t)}{\partial t} = -\frac{\partial h_i(\hat{\mathbf{n}}) P_2(\hat{\mathbf{n}}_1, t_1|\hat{\mathbf{n}}, t)}{\partial \hat{n}_i}. \qquad (24)$$

To find the solution to Eq. (24) recall that the conditional probability density P_2 satisfies the intial condition $P_2(\hat{\mathbf{n}}_1, t_1|\hat{\mathbf{n}}, t_1) = \delta(\hat{\mathbf{n}}_1 - \hat{\mathbf{n}})$. Then if $\overline{\hat{\mathbf{n}}}(\mathbf{n}_1, t)$ is the solution to the scaled Boltzmann equation

$$\frac{d\overline{\hat{n}}_i}{dt} = \sum_\kappa \hat{\omega}_{\kappa i}(\overline{V}_\kappa^+ - \overline{V}_\kappa^-) + \overline{\hat{s}}_i = h_i(\overline{\hat{\mathbf{n}}}), \tag{25}$$

then using the chain rule and the properties of the delta function

$$\begin{aligned} \frac{\partial \delta[\hat{\mathbf{n}} - \overline{\hat{\mathbf{n}}}(t)]}{\partial t} &= \frac{\partial \delta[\hat{\mathbf{n}} - \overline{\hat{\mathbf{n}}}(t)]}{\partial \hat{n}_i}\left(-\frac{d\overline{\hat{n}}_i}{dt}\right) \\ &= -\frac{\partial \delta[\hat{\mathbf{n}} - \overline{\hat{\mathbf{n}}}(t)]}{\partial \hat{n}_i} h_i(\overline{\hat{\mathbf{n}}}) \\ &= -\frac{\partial h_i(\hat{\mathbf{n}})\delta[\hat{\mathbf{n}} - \overline{\hat{\mathbf{n}}}(t)]}{\partial \hat{n}_i} \end{aligned} \tag{26}$$

the solution the Eq. (24) is just

$$P_2(\hat{\mathbf{n}}_1, t_1|\hat{\mathbf{n}}, t) = \delta(\hat{\mathbf{n}} - \overline{\hat{\mathbf{n}}}(\hat{\mathbf{n}}_1, t)). \tag{27}$$

In other words, neglecting the diffusion term in the Fokker-Planck equation implies that the conditional probability remains a delta function, peaked at the solution to the Boltzmann equation. This means that the occupancy numbers in μ-space satisfy the Boltzmann equation on the conditional average and that, to a first approximation, fluctuations are negligible. Seen in this way, the statistical interpretation of the collision terms in Eq. (7) implies that for a large system the Boltzmann equation is true on the average.