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Nonequilibrium Thermodynamics of Multi-component fluids

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1 What is nonequilibrium

An isolated system tends to an equilibrium state, which is macroscopically static and uniform. Chemical reactions tend to an equilibrium state, where forward and backward reactions are in balance.

Suppose a gas is confined in a half region of a box separated by a wall from the other half region of vacuum. When we remove the wall which separates gas and vacuum, the gas diffuses into the vauum region. This transient process is nonequilibrium with the gas flow. If one waits long enough, the whole system will be in an equilibrium state.

In order to keep a nonequilibrium state, we put the system in contact with baths, which have different temperatures or different chemical potentials on both sides of the system. Then heat flow or matter flow is sustained. We may also sustain velocity gradient by the shear of the two boundaries of the fluid.

In this case, viscosity is regarded as the transfer of momentum from a fast-flow region to a slow-flow region.

When we say "nonequilibrium", it implies not only a transient state towards an equilibrium state but also a stationary state, sustained by nonequilibrium boundary conditions. In this lecture, we first generalize entropy in order to include velocity of fluid as an independent variable of entropy. If we formulate nonequilibrium thermodynamics in terms of entropy, we can discuss fluctuations in an equilibrium state, since by Boltzmann-Einstein principle, we have the probability of having fluctuation X in the form of

$$P_{eq}(X) = e^{S(X)/k}$$

This can be extended to nonequilibrium fluctuations by constructing a master equation for the nonequilibrium probability $P(X,t)$ by assuming that the master equation should have the equilibrium state $P_{eq}(X) = e^{S(X)/k}$.

Also, we can give a basis to "fluctuation dissipation theorem"[1] purely phenomenologically. The reason why I insist on phenomenology is that it is the most sound basis of statistical physics and I hope to be able to extend thermodynamics to complex systems.

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[1] This is in principle due to M. S. Green *J. Chem. Phys.* **35** (1956) 836.

2 Nonequilibrium Thermodynamics

Here we extend thermodynamics of equilibrium systems to nonequilibrium systems. We consider particularly multi-component fluids. Nonequilibrum thermodynamics of solid states has not yet been well studied. For the moment, I have no idea how to formulate nonequilibrium thermodynamics of solids which may contain defects, such as point defects, dislocations, surfaces etc. .

An equilibrium system is described in terms of a set of extensive variables; internal energy U, volume V, mass M_k of the k-th component. The Gibbs relation reads

$$TdS = dU + PdV - \sum_{k=1}^{n} \mu_k dM_k$$

The Gibbs Duhem relation, which is derived from the extensivity of entropy, is

$$\begin{cases} U + PV - \sum_{k=1}^{n} \mu_k M_k = TS \\ \\ VdP - \sum_{k=1}^{n} M_k \mu_k = SdT \end{cases}$$

We consider a non-equilibium system, in which there are flows of heat, matter or momentum. These are caused by the spatial gradient of temperature, chemical potential or velocity field. In order to deal with such continuum fluid, it is more convenient to use quantities per unit mass rather than absolute quantities, such as U, V and M_k.

$$s = \frac{S}{M}, \quad u = \frac{U}{M}, \quad v = \frac{V}{M} = \frac{1}{\rho}, \quad c_k = \frac{M_k}{M}$$

Then we need not refer to the size of the local subsystems. By using these quantities per unit mass, we consider the system as a continuum, in which these quantities are spatially distributed. Then the Gibbs-Duhem relation reads,

$$\begin{cases} u + Pv - \sum_{k=1}^{n} \mu_k c_k = Ts \\ \\ vdP - \sum_{k=1}^{n} c_k \mu_k = sdT \end{cases}$$

Of course, for a one-component system, we have

$$\begin{cases} u + Pv - \mu = Ts \\ \\ vdP - \mu = sdT \end{cases}$$

Now we want to consider hydrodynamic phenomena in the framework of thermodynamics. First, we note that the viscosity is an irreversible process, in which the kinetic energy of macroscopic flow is transformed into internal energy. So the viscosity should be related to entropy production. Therefore entropy should contain velocity as an independent variable. Another point is that in the presence of convective flow, internal energy is no more conserved but the sum of internal energy and kinetic energy is conserved. The irreversible transport of a conserved quantity is related to the spatial gradient of the associated intensive parameter. For example, we consider a conserved quantity X.

Before the transport, we have X_A in the box A and X_B in the box B. Thus the total entropy before the transport is $S_A(X_A) + S_B(X_B)$. After the transport of the amount ΔX from A to B, we have the entropy $S_A(X_A - \Delta X) + S_B(X_B + \Delta X)$. Thus the net increase of the total entropy is

$$\Delta S = \Delta X \left(-\frac{dS_A}{dX_A} + \frac{dS_B}{dX_B} \right) = \Delta X \left(F_B - F_A \right)$$

The second law requires that the transport $\Delta X > 0$ takes place in the spatial direction of the increasing intensive parameter. Thus in order to deal with irreversible transport of energy, we express the entropy as a function of total energy and the irreversible energy flow is caused by the gradient of the associated intensive parameter which will be the inverse of temperature. It should be noted that irreversible processes of non-conserved quantities obey different laws. For example, local magnetization or polarization can grow or decrease without any transport. A non-conservative variable evolves in the direction of increasing entropy. So its associated intensive parameter itself is the thermodynamic force.

Let us consider also hydrodymanic phenomena of viscosity. The velocity of fluid is small near the rest boundary. As the distance from the boundary increases, the velocity grows. This causes the spatial gradient of the velocity. From the part with faster velocity to the part with slow velocity, there is irreversible flux of momentum. Thus the viscosity is the irreversible flow of momentum.

In order to describe such fluid motion with viscosity in the frame of thermodynamics, it is desirable to have momentum as an independent variable of entropy. If we read standard books of fluid mechanics, say, Landau-Lifshitz "Fluid Mechanics", the entropy production has the form $\frac{\eta}{T}\left(\frac{\partial v_x}{\partial y}\right)^2$. It may be interpreted as the product of flux and force. When I first read this part, I did not understand how to separate the flux and force. There should be some definitions of flux and force from a general principle. Somehow, any textbook of nonequilibrium thermodynamics did not give me any satisfactory answer. This was my first encounter with nonequilibrium thermodynamics.

External Contact

Depending on how a system contacts with environments, we can distinguish "isolated system", "system in contact with a thermal bath" and "system in contact with two different baths". In the last case, we can keep the energy flow if the two baths have different temperature. If they have different chemical potentials, mass flow is sustained in the system. If there is flow of energy, mass or momentum due to the contact with baths, we may call the system " nonequilibrium open system"[2] .

3 Kinetic energy of one-component fluids

We consider here one-component fluids. As we noted above, internal energy u is not a conserved variable. We constitute thermodynamics in terms of total energy instead of internal energy.

$$e = u + \frac{|\boldsymbol{v}|^2}{2}$$

If we put this to the Gibbs-Duhem relation, we have

$$\rho \left(e - \frac{|\boldsymbol{v}|^2}{2} \right) + P - \rho\mu = \rho s T$$

Then we differentiate both sides,

$$\rho s dT + T d(\rho s) = d(\rho e) - d\left(\rho \frac{|\boldsymbol{v}|^2}{2} \right) - \rho d\mu - \mu d\rho + dP$$

Then subtracting both sides by the Gibbs-Duhem relation $\rho s dT = dP - \rho d\mu$, we obtain

$$d(\rho s) = \frac{1}{T} d(\rho e) - \frac{\boldsymbol{v}}{T} \cdot d(\rho \boldsymbol{v}) - \frac{1}{T} \left(\mu - \frac{|\boldsymbol{v}|^2}{2} \right) d\rho$$

Certainly this is reduced to the equilibrium relation

$$d(\rho s) = \frac{1}{T} d(\rho u) - \frac{\mu}{T} d\rho$$

when there is no convective flow ($\boldsymbol{v} = 0$). In this extended Gibbs relation, we have the momentum density $\rho \boldsymbol{v}$ as an independent variable of entropy density ρs. When we write

$$d(\rho s) = \sum_j F_j da_j$$

where a_j is the density of an extensive variable, we may call F_j intensive parameter associated with the extensive variable a_j. Thus we have the following table.

extensive variable	density	intensive parameter
total energy	ρe	$1/T$
momentum	$\rho \boldsymbol{v}$	$-\boldsymbol{v}/T$
mass	ρ	$-\left(\mu - \frac{\lvert\boldsymbol{v}\rvert^2}{2} \right)/T$

Since the momentum is conserved, the force which causes the irreversible flow of momentum, namely viscosity stress, is the spatial gradient of the intensive parameter $-\boldsymbol{v}/T$. The total energy is also conserved. Thus the thermodynamic force, which causes the irreversible flow of energy, namely, heat, is the spatial gredient of $1/T$. From the extended Gibbs relation, we may discuss the viscosity phenomena in the framework of irreversible process in nonequiibrium thermodynamics.

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[2] G. Nicolis, "Introduction to Nonlinear Science" (Cambridge University Press, 1997)

4 Hydrodynamics of one-component fluids

Fluid is an idealized concept of gas and liquid. Fluid can change its shape freely as the boundary imposes. Real liquid behaves as fluid or as elastic body, depending on the speed of phenomena. For a very high speed, or a very high frequency, liquid can behave as elastic[3] . For a slow motion, liquid can change its shape freely.

Fluid is charecterized by the mass density $\rho(\boldsymbol{r},t)$ and the velocity $\boldsymbol{v}(\boldsymbol{r},t)$, which are functions of space and time. $\rho\boldsymbol{v}$ is the flux of mass, which passes through a unit area per unit time. Thus the mass conservation can be written as

$$\frac{\partial\rho}{\partial t}+\mathrm{div}(\rho\boldsymbol{v})=0$$

This can be understood by the analogy with the continuity equation in the electromagnetic theory.

$$\frac{\partial}{\partial t}\int_V\rho dV=\int_V\frac{\partial\rho}{\partial t}dV=-\int_V\mathrm{div}(\rho\boldsymbol{v})=-\int_S(\rho\boldsymbol{v})\cdot\boldsymbol{n}dS$$

Thus the growth of mass in a local region V is due to the in-flux of the mass through the surface S.

Now I explain the equation of motion of fluid. In order to obtain the equation of motion, we consider a mass element in the fluid which moves with a given velocity $\boldsymbol{v}(\boldsymbol{r},t)$ at each point of space and time. The position of the mass element at time t is denoted as $\boldsymbol{R}(t)=(X(t),Y(t),Z(t))$. The velocity of the mass element is the velocity of the fluid at the position. Namely

$$\frac{d\boldsymbol{R}(t)}{dt}=\boldsymbol{v}(\boldsymbol{R}(t),t)$$

If we write the component of the vector explicitly we have

$$\begin{cases}\dfrac{dX(t)}{dt}=v_x(X(t),Y(t),Z(t),t)\\[2ex]\dfrac{dY(t)}{dt}=v_y(X(t),Y(t),Z(t),t)\\[2ex]\dfrac{dZ(t)}{dt}=v_z(X(t),Y(t),Z(t),t)\end{cases}$$

The acceleration of the mass element is obtained by differentiating the velocity with respect

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[3] D. Forster, *Hydrodynamic Fluctuations, Broken Symmetry, and Correlation Functions* (Benjamin, Frontiers in Physics 47, 1983).

to time. For example, the x component of the acceleration is

$$\begin{aligned}
\frac{d^2X(t)}{dt^2} &= \frac{d}{dt}v_x(X(t),Y(t),Z(t),t)\\
&= \frac{\partial v_x}{\partial x}\frac{dX(t)}{dt} + \frac{\partial v_x}{\partial y}\frac{dY(t)}{dt} + \frac{\partial v_x}{\partial z}\frac{dZ(t)}{dt} + \frac{\partial v_x}{\partial t}\\
&= \frac{\partial v_x}{\partial x}v_x + \frac{\partial v_x}{\partial y}v_y + \frac{\partial v_x}{\partial z}v_z + \frac{\partial v_x}{\partial t}\\
&= (\boldsymbol{v}\cdot\boldsymbol{\nabla})v_x + \frac{\partial v_x}{\partial t}
\end{aligned}$$

For the mass element contained in a small volume $dxdydz$, the force acting from the other part of the fluid is called "stress". More precisely, we define the stress P_{ij} as follows.

Suppose a surface S_i which is perpendicular to the i-direction!J$i = x, y, z$!Kat x_{i0}. The force which is exerted from the part $x_i > x_{i0}$ on the part $x_i < x_{i0}$ is denoted by a vector

$$\boldsymbol{P}_iS_i = (P_{ix}S_i, P_{iy}S_i, P_{iz}S_i).$$

Here S_i is the area of the surface.

The the equation of motion, say, for the x-component is

$$\begin{aligned}
&\rho dxdydz\left((\boldsymbol{v}\cdot\boldsymbol{\nabla})v_x + \frac{\partial v_x}{\partial t}\right)\\
&= S_x\left[P_{xx}(x+dx,y,z) - P_{xx}(x,y,z)\right] + S_y\left[P_{yx}(x,y+dy,z) - P_{yx}(x,y,z)\right]\\
&+S_z\left[P_{zx}(x,y,z+dz) - P_{zx}(x,y,z)\right]\\
&\simeq dxS_x\frac{\partial P_{xx}}{\partial x} + dyS_y\frac{\partial P_{yx}}{\partial y} + dzS_z\frac{\partial P_{zx}}{\partial z}\\
&= dxdydz\left(\frac{\partial P_{xx}}{\partial x} + \frac{\partial P_{yx}}{\partial y} + \frac{\partial P_{zx}}{\partial z}\right).
\end{aligned}$$

Thus by deviding both sides by $dxdydz$ we obtain

$$\rho\left((\boldsymbol{v}\cdot\boldsymbol{\nabla})v_x + \frac{\partial v_x}{\partial t}\right) = \left(\frac{\partial P_{xx}}{\partial x} + \frac{\partial P_{yx}}{\partial y} + \frac{\partial P_{zx}}{\partial z}\right).$$

In general the strss tensor can be written as

$$P_{ij} = -P\delta_{ij} + \Pi_{ij}$$

The first term on the right hand side stands for hydrostatic pressure, which is negative and always perpendicular to the surface. The second term is the viscosity tensor.

$$\Pi_{ij} = \eta \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} - \frac{2}{3}\delta_{ij}\mathrm{div}\boldsymbol{v} \right) + \zeta \delta_{ij}\mathrm{div}\boldsymbol{v}$$

Especially when the fluid is incompressible, we have $\mathrm{div}\boldsymbol{v} = 0$. Thus we have

$$\Pi_{ij} = \eta \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right)$$

In this incompressible case, we have

$$\rho \left((\boldsymbol{v} \cdot \boldsymbol{\nabla}) v_x + \frac{\partial v_x}{\partial t} \right) = -\frac{\partial P}{\partial x} + \eta \nabla^2 v_x.$$

We can see that the viscosity is the diffusion of momentum.

5 Evolution equation of entropy

In the extended Gibbs relation for a one-component fluid,

$$d(\rho s) = \frac{1}{T} d(\rho e) - \frac{\boldsymbol{v}}{T} \cdot d(\rho \boldsymbol{v}) - \frac{1}{T} \left(\mu - \frac{|\boldsymbol{v}|^2}{2} \right) d\rho$$

the derivative denoted by d can be understood as time derivative.

$$\frac{\partial(\rho s)}{\partial t} = \frac{1}{T}\frac{\partial(\rho e)}{\partial t} - \frac{\boldsymbol{v}}{T} \cdot \frac{\partial(\rho \boldsymbol{v})}{\partial t} - \frac{1}{T} \left(\mu - \frac{|\boldsymbol{v}|^2}{2} \right) \frac{\partial \rho}{\partial t}$$

The time derivative is of the order of $\tau = l/v_{th}$, where l is the mean free path and v_{th} is the thermal velocity $v_{th} = \sqrt{kT/m}$. We substitute the Navier-Stokes equation and the continuity equation in the second and the third terms on the right hand side. For the time derivative of the total energy density, we substitute $\rho e = \rho u + \frac{\rho}{2}|\boldsymbol{v}|^2$. Then,

$$\frac{\partial(\rho e)}{\partial t} = \frac{\partial(\rho u)}{\partial t} + \frac{\partial}{\partial t} \left(\frac{\rho}{2} |\boldsymbol{v}|^2 \right).$$

Here for the time derivative of the internal energy density, we use

$$\frac{\partial(\rho u)}{\partial t} + \mathrm{div}(\rho u \boldsymbol{v} + \boldsymbol{Q}) = \sum_{i,j} \Pi_{ij} \frac{\partial v_i}{\partial x_j} - P \mathrm{div}\boldsymbol{v}$$

The term $\rho u \boldsymbol{v}$ is the internal energy conveyed by the convective motion of the fluid. $\boldsymbol{Q}$ is heat flow. The first term on the right hand side is the viscosity heating. The kinetic energy of the convective motion is transformed into the internal energy by the viscosity. This viscosity heating term is always positive since

$$\sum_{i,j} \Pi_{ij} \frac{\partial v_i}{\partial x_j}$$

$$= \eta \sum_{i,j} \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} - \frac{2}{3} \delta_{ij} \mathrm{div} \boldsymbol{v} \right) \frac{\partial v_i}{\partial x_j} + \zeta \sum_{i,j} \delta_{ij} \mathrm{div} \boldsymbol{v} \frac{\partial v_i}{\partial x_j}$$

$$= \eta \sum_{i,j} \left(\frac{\partial v_i}{\partial x_j} \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \frac{\partial v_i}{\partial x_j} \right) - \frac{2}{3} \eta (\mathrm{div} \boldsymbol{v})^2 + \zeta (\mathrm{div} \boldsymbol{v})^2$$

$$= \frac{\eta}{2} \sum_{i,j} \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right)^2 + \left(\zeta - \frac{2}{3} \eta \right) (\mathrm{div} \boldsymbol{v})^2$$

$$= \frac{\eta}{2} \sum_{i \neq j} \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right)^2 + \zeta (\mathrm{div} \boldsymbol{v})^2$$

$$+ \frac{2\eta}{3} \left[\left(\frac{\partial v_x}{\partial x} - \frac{\partial v_y}{\partial y} \right)^2 + \left(\frac{\partial v_y}{\partial y} - \frac{\partial v_z}{\partial z} \right)^2 + \left(\frac{\partial v_z}{\partial z} - \frac{\partial v_x}{\partial x} \right)^2 \right] > 0$$

Thus we have the energy balance equation

$$\frac{\partial (\rho e)}{\partial t} + \mathrm{div}(\rho e \boldsymbol{v} + P \boldsymbol{v} + \boldsymbol{Q} - \boldsymbol{\Pi} : \boldsymbol{v}) = 0.$$

Thus the entropy balance equation is written as

$$\frac{\partial (\rho s)}{\partial t} + \mathrm{div} \boldsymbol{J}_s = \sigma[S]$$

where $\boldsymbol{J}_S$ is the entropy flux

$$\boldsymbol{J}_s = \frac{\boldsymbol{Q}}{T} + \rho s \boldsymbol{v}$$

and $\sigma[S]$ is the entropy production rate

$$\sigma[S] = \boldsymbol{Q} \cdot \boldsymbol{\nabla} \left(\frac{1}{T} \right) + \frac{1}{T} \sum_{i,j} \Pi_{ij} \frac{\partial v_i}{\partial x_j},$$

which can be rewritten as

$$\sigma[S] = \sum_j \left(Q_j + \sum_i (-\Pi_{ij}) v_i \right) \frac{\partial}{\partial x_j} \left(\frac{1}{T} \right) + \sum_{i.j} (-\Pi_{ij}) \frac{\partial}{\partial x_j} \left(-\frac{v_i}{T} \right)$$

Note that $\frac{\partial}{\partial x_j} \left(\frac{1}{T} \right)$ is the thermodynamic force for the irreversible energy transport, which is heat, and $\frac{\partial}{\partial x_j} \left(-\frac{v_i}{T} \right)$ is the thermodynamic force for the irreversible momentum transport, which is viscosity stress. As shown in the next section, these two transports are mutually interfering.

6 Linear response

We have seen that the thermodynamic force for an irreversible transport of a conserved variable a_i is the gradient of the corresponding intensive parameter F_i. Suppose irreversible flows and thermodynamic forces are linearly related. Then we can write

$$-\Pi_{ij} = L_{ij,kl}\frac{\partial}{\partial x_k}\left(-\frac{v_l}{T}\right) + L_{ij,k}\frac{\partial}{\partial x_k}\left(\frac{1}{T}\right) = -\frac{L_{ij,kl}}{T}\frac{\partial v_l}{\partial x_k} - L_{ij,kl}v_l\frac{\partial}{\partial x_k}\left(\frac{1}{T}\right) + L_{ij,k}\frac{\partial}{\partial x_k}\left(\frac{1}{T}\right)$$

Note that the viscosity stress should be Galilei invariant. Namely, for the change of velocity $\boldsymbol{v} \to \boldsymbol{v} + \boldsymbol{u}$ where $\boldsymbol{u}$ is the constant velocity, the stress tensor should be invariant. If not, a bucket of water would experience different stress when the bucket is carried by constant velocity. Therefore $\boldsymbol{v}$ should appear in the form of $\nabla \boldsymbol{v}$. Thus we should have

$$L_{ij,kl}v_l = L_{ij,k}$$

Then we have

$$\Pi_{ij} = \frac{L_{ij,kl}}{T}\frac{\partial v_l}{\partial x_k}$$

For the irreversible energy flow we may put

$$J_{ei} = L_{ik}\frac{\partial}{\partial x_k}\left(\frac{1}{T}\right) + L_{i,kl}\frac{\partial}{\partial x_k}\left(-\frac{v_l}{T}\right) = L_{ik}\frac{\partial}{\partial x_k}\left(\frac{1}{T}\right) - L_{i,kl}v_l\frac{\partial}{\partial x_k}\left(\frac{1}{T}\right) - \frac{L_{i,kl}}{T}\frac{\partial v_l}{\partial x_k}$$

Thus for the Galilei invariance, we should have

$$L_{ik} = L_{i,kl}v_l + \lambda_{ik}$$

Then we have

$$J_{ei} = \lambda_{ik}\frac{\partial}{\partial x_k}\left(\frac{1}{T}\right) - \frac{L_{i,kl}}{T}\frac{\partial v_l}{\partial x_k}$$

As we will see soon we have the symmetry relation

$$L_{ij,kl} = L_{kl,ij}$$

Therefore we have

$$L_{ij,k}(\boldsymbol{v}) = L_{ij,kl}v_l = L_{kl,ij}v_l$$

Furthermore, we will have another symmetry relation

$$L_{ij,k}(\boldsymbol{v}) = -L_{k,ij}(-\boldsymbol{v})$$

Therefore we can put

$$L_{k,ij}(\boldsymbol{v}) = L_{kl,ij}v_l$$

Thus

$$\frac{L_{i,kl}}{T}\frac{\partial v_l}{\partial x_k} = \frac{L_{ij,kl}}{T}v_j\frac{\partial v_l}{\partial x_k} = \Pi_{ij}v_j$$

Hence we may write

$$J_{ei} = \lambda_{ik}\frac{\partial}{\partial x_k}\left(\frac{1}{T}\right) - \Pi_{ij}v_j = Q_i - \Pi_{ij}v_j$$

7 Mathematical structure of hydrodynamics

Suppose we can write the differential of entropy density ρs in terms of densities of extensive variables a_i

$$d(\rho s) = \sum_i F_i da_i$$

Then we may call F_i intensive parameters. I will show that all hydrodynamic equations can be cast into the following form

$$\frac{\partial a_i(\boldsymbol{r},t)}{\partial t} = \int d^3\boldsymbol{r}' M_{ij}(\boldsymbol{r},\boldsymbol{r}') F_j(\boldsymbol{r}') = \int d^3\boldsymbol{r}' L_{ij}(\boldsymbol{r},\boldsymbol{r}') F_j(\boldsymbol{r}')$$

with the antisymmetric relation

$$M_{ij}(\boldsymbol{r},\boldsymbol{r}') = -M_{ji}(\boldsymbol{r}',\boldsymbol{r})$$

This antisymmetry can be derived from a microscopic theory. We consider the system consists of N particles, whose coordinates and momenta are denoted as $\boldsymbol{q}_1, \cdots, \boldsymbol{q}_N$ and $\boldsymbol{p}_1, \cdots, \boldsymbol{p}_N$. The equation of motion is

$$\begin{cases} \dfrac{d\boldsymbol{q}_i}{dt} = \dfrac{\partial \mathcal{H}}{\partial \boldsymbol{p}_i} \\[2ex] \dfrac{d\boldsymbol{p}_i}{dt} = -\dfrac{\partial \mathcal{H}}{\partial \boldsymbol{q}_i} \end{cases}$$

which can be written in terms of Poisson's bracket

$$\begin{cases} \dfrac{d\boldsymbol{q}_i}{dt} = \{\boldsymbol{q}_i, \mathcal{H}\} = \mathcal{L}\boldsymbol{q}_i \\[2ex] \dfrac{d\boldsymbol{p}_i}{dt} = \{\boldsymbol{p}_i, \mathcal{H}\} = \mathcal{L}\boldsymbol{p}_i \end{cases}$$

where $\mathcal{L}$ is a linear operator defined by the Poisson's bracket

$$\mathcal{L}f = \{f, \mathcal{H}\}$$

If we introduce an abbreviated notation

$$\Gamma \equiv (\boldsymbol{q}_1, \cdots, \boldsymbol{q}_N, \boldsymbol{p}_1, \cdots, \boldsymbol{p}_N)$$

we may write the equation of motion as

$$\frac{d\Gamma}{dt} = \mathcal{L}\Gamma$$

and its solution is

$$\Gamma(t) = e^{\mathcal{L}t} = \sum_{n=0}^{\infty} \frac{t^n}{n!} \mathcal{L}^n \Gamma$$

with the initial condition

$$\Gamma(0) = \Gamma$$

Since $\mathcal{L}$ is a first-order differential operator, we have

$$e^{\mathcal{L}t} f(\Gamma) = f(e^{\mathcal{L}t}\Gamma)$$

Thus the time evolution of a physical quantity $A(\Gamma)$, which is defined in terms of microscopic variables Γ, we have

$$A(\Gamma(t)) = A(e^{\mathcal{L}t}\Gamma) = e^{\mathcal{L}t} A(\Gamma)$$

Now in the Γ-space, we may consider the probability of the initial states$f_0(\Gamma)$. Then the average of the physical variable is

$$\langle A(\Gamma(t))\rangle = \int d\Gamma f_0(\Gamma) \left(e^{\mathcal{L}t} A(\Gamma)\right) = \int d\Gamma \left(e^{-\mathcal{L}t} f_0(\Gamma)\right) A(\Gamma)$$

Here we have used the property of the Liouville operator $\mathcal{L}$,

$$\int d\Gamma A(\mathcal{L}B) = -\int d\Gamma (\mathcal{L}A) B$$

which is obtained by partial integration. Then we may introduce the time-dependent distribution function defined by

$$f(\Gamma, t) \equiv e^{-\mathcal{L}t} f_0(\Gamma)$$

Then the average is written as

$$\langle A(\Gamma(t))\rangle = \int d\Gamma f(\Gamma, t) A(\Gamma)$$

The time evolution of the distribution function is then,

$$\frac{\partial f(\Gamma, t)}{\partial t} = -\mathcal{L} f(\Gamma, t)$$

Now we introduce "local equilibrium distribution function" defined by the set of macroscopic variables $A_i(\Gamma)$ $(i = 1, \cdots, n)$.

$$f_l(\Gamma, t) \equiv \frac{1}{Z_l(t)} \exp\left(-\sum_{j=1}^{n} \lambda_j(t) A_j(\Gamma)\right)$$

Here $Z_l(t)$ is the normalization constant,

$$Z_l(t) = \int d\Gamma \exp\left(-\sum_{j=1}^{n} \lambda_j(t) A_j(\Gamma)\right)$$

The time-dependent parameters $\lambda_j(t)$ are defined as functions of the average values

$$a_i(t) = \langle A_i(\Gamma)\rangle \equiv \int d\Gamma A_i(\Gamma) f(\Gamma, t)$$

through the condition

$$a_i(t) = \int d\Gamma A_i(\Gamma) f_l(\Gamma, t) = \frac{1}{Z_l(t)} \int d\Gamma A_i(\Gamma) \exp\left(- \sum_{j=1}^{n} \lambda_j(t) A_j(\Gamma) \right) \equiv \langle A_i \rangle_l$$

Somehow, we will consider the situation in which the local equilibrium distribution is a good reference state as the first approximation. We define entropy of the system by

$$\begin{aligned} S &= -k_B \int d\Gamma f_l(\Gamma, t) \ln f_l(\Gamma, t) \\ &= k_B \ln Z_l(t) + k_B \sum_{j=1}^{n} \lambda_j(t) \langle A_j \rangle_l \\ &= k_B \ln Z_l(t) + k_B \sum_{j=1}^{n} \lambda_j(t) a_j(t) \end{aligned}$$

Then we have

$$\frac{\partial S}{\partial a_i} = k_B \frac{\partial \ln Z_l(t)}{\partial a_i} + k_B \sum_{j=1}^{n} \frac{\partial \lambda_j}{\partial a_i} a_j + k_B \lambda_i$$

Now note that

$$\begin{aligned} \frac{\partial \ln Z_l(t)}{\partial a_i} &= \frac{1}{Z_l(t)} \frac{\partial Z_l(t)}{\partial a_i} \\ &= \frac{1}{Z_l(t)} \sum_{j=1}^{n} \frac{\partial \lambda_j}{\partial a_i} \frac{\partial Z_l(t)}{\partial \lambda_j} \\ &= \sum_{j=1}^{n} \frac{\partial \lambda_j}{\partial a_i} \frac{1}{Z_l(t)} \int d\Gamma (-A_j) \exp\left(- \sum_{j=1}^{n} \lambda_j A_j \right) \\ &= - \sum_{j=1}^{n} \frac{\partial \lambda_j}{\partial a_i} a_j \end{aligned}$$

Thus we obtain

$$\frac{\partial S}{\partial a_i} = k_B \lambda_i$$

If we compare this result with the thermodynamic relation

$$dS = \sum_{j=1}^{n} F_j da_j$$

we may identify the parameter $\lambda_j(t)$ in the local equilibrium distribution function with the intensive parameter F_j

$$F_j = k_B \lambda_j$$

Now let us identify

$$\frac{da_i}{dt} = \int d\Gamma(\mathcal{L}A_i)f(\Gamma,t)$$

and putting $f(\Gamma,t) = f_l(\Gamma,t) + f'(\Gamma,t)$. Then we put

$$\left(\frac{da_i}{dt}\right)_{rev} = \int d\Gamma(\mathcal{L}A_i)f_l(\Gamma,t)$$

and

$$\left(\frac{da_i}{dt}\right)_{irr} = \int d\Gamma(\mathcal{L}A_i)f'(\Gamma,t)$$

Then we have

$$\begin{aligned}\left(\frac{da_i}{dt}\right)_{rev} &= \int d\Gamma\{A_i,\mathcal{H}\}f_l \\ &= \sum_{j=1}^{n}\langle\mathcal{H}\{A_i,A_j\}\rangle_l\lambda_j \\ &= \frac{1}{k_B}\sum_{j=1}^{n}\langle\mathcal{H}\{A_i,A_j\}\rangle_l F_j\end{aligned}$$

Thus it is clear that if we put

$$\left(\frac{da_i}{dt}\right)_{rev} = \sum_{j=1}^{n} M_{ij}F_j$$

we have the antisymmetric relation

$$M_{ij} = \frac{1}{k_B}\langle\mathcal{H}\{A_i,A_j\}\rangle_l = -M_{ji}$$

Microscopic reversibility in equilibrium

In an equilibrium state, we have detailed balance of two reversed trajectories. If there exists an orbit starting from (q,p,t) to $q',p',t')$, we have the reversed trajectory $(q',-p',t)$ to $(q,-p,t')$. Namely for the joint probability $P(q,p,t;q',p',t')$ we should have

$$P(q,p,t;q',p',t') = P(q',-p',t;q,-p,t')$$

Then for two macroscopic varibles, $A_i(q,p)$ and $A_j(q,p)$, we have

$$\begin{aligned}\langle A_i(t)A_j(t')\rangle &= \int dq\int dp\int dq'\int dp' A_i(q,p)A_j(q',p')P(q,p,t;q',p',t') \\ &= \int dq\int dp\int dq'\int dp' A_i(q,p)A_j(q',p')P(q',-p',t;q,-p,t') \\ &= \int dq\int dp\int dq'\int dp' A_i(q,-p)A_j(q',-p')P(q',p',t;q,p,t')\end{aligned}$$

If A_i and A_j have time-reversal symmetry, we have

$$A_i(q,-p) = A_i(q,p), \qquad A_j(q',-p') = A_j(q',p')$$

Then we have

$$\langle A_i(t)A_j(t')\rangle = \int dq \int dp \int dq' \int dp' A_i(q,p)A_j(q',p')P(q',p',t;q,p,t') = \langle A_j(t)A_i(t')\rangle$$

Onsager's hypothesis

Now I explain Onsager's hypothesis of linear regression. Suppose the evolution of macroscopic variables is given by

$$\frac{da_i}{dt} = \sum_j M_{ij}F_j + \sum_j L_{ij}F_j$$

This describes the approach of a macroscopic state towards the equilibrium state. So it describes the macroscopic nonequilibrium state. After arriving at the equilibrium state, the macroscopic state is stationary, but there exists fluctuation. If we collect the fluctuation data, which start from a given initial value a_0, and take the average, we will get the average evolution with a given initial data. Onsager assumed that the average evolution of fluctuation obeys the same law as the macroscpoic law. For a short time, we have

$$a_i(t) = a_i^0 + \left[\sum_j M_{ij}\frac{\partial S}{\partial a_j}(\boldsymbol{a}^0) + \sum_j L_{ij}\frac{\partial S}{\partial a_j}(\boldsymbol{a}^0)\right] t + \mathcal{O}(t^2)$$

We consider that the average of fluctuation with a given initial condition also follows the macroscopic law,

$$\langle a_i(t)\rangle_{\boldsymbol{a}^0} = a_i^0 + \left[\sum_j M_{ij}\frac{\partial S}{\partial a_j}(\boldsymbol{a}^0) + \sum_j L_{ij}\frac{\partial S}{\partial a_j}(\boldsymbol{a}^0)\right] t + \mathcal{O}(t^2)$$

Then the correlation function in equilibrium is

$$\begin{aligned}\langle a_i(t)a_j(0)\rangle &= \langle\langle a_i(t)\rangle_{\boldsymbol{a}^0} a_k^0\rangle_{eq} \\ &= \langle a_i^0 a_k^0\rangle_{eq} + \left[\sum_j \left\langle M_{ij}\frac{\partial S}{\partial a_j}(\boldsymbol{a}^0)a_k^0\right\rangle_{eq} + \sum_j L_{ij}\left\langle\frac{\partial S}{\partial a_j}(\boldsymbol{a}^0)a_k^0\right\rangle_{eq}\right] t + \mathcal{O}(t^2)\end{aligned}$$

Due to Boltzmann-Einstein principle, we have

$$P_{eq}(\boldsymbol{a}) = \exp\left[S(\boldsymbol{a})/k_B\right]$$

Thus

$$\begin{aligned}\left\langle\frac{\partial S}{\partial a_j}(\boldsymbol{a}^0)a_j^0\right\rangle_{eq} &= \int da_1^0 \cdots \int da_n^0 \frac{\partial S}{\partial a_i^0} a_j^0 \exp\left[S(\boldsymbol{a})/k_B\right] \\ &= -k_B \int da_1^0 \cdots \int da_n^0 \frac{\partial a_j^0}{\partial a_i^0} \exp\left[S(\boldsymbol{a})/k_B\right] \\ &= -k_B\delta_{ij}\end{aligned}$$

Thus we have

$$\sum_j L_{ij} \left\langle \frac{\partial S}{\partial a_i}(\boldsymbol{a}^0) a_j^0 \right\rangle_{eq} = -k_B L_{ik}$$

If a_i and a_j are time-reversal symmetric, we have

$$\langle a_i(t) a_j(0) \rangle = \langle a_j(t) a_i(0) \rangle.$$

Thus as far as the irreversible part is concerned, we have $L_{ij} = L_{ji}$. Similarly, if a_i is time-reversal symmetric and a_j is anti-symmetric, we have $L_{ij} = -L_{ji}$.

For detail, see S. R. de Groot and P. Mazur[4] .

Now how about the reversible part. We may make the following approximation

$$\begin{aligned}
\sum_j \left\langle M_{ij} \frac{\partial S}{\partial a_j}(\boldsymbol{a}^0) a_k^0 \right\rangle_{eq} &\simeq \sum_j \langle M_{ij} \rangle_{eq} \left\langle \frac{\partial S}{\partial a_j}(\boldsymbol{a}^0) a_k^0 \right\rangle_{eq} \\
&= \sum_j \frac{1}{k_B} \langle \langle \mathcal{H}\{A_i, A_j\} \rangle_l \rangle_{eq} (-k_B \delta_{jk}) \\
&\simeq -\langle \mathcal{H}\{A_i, A_k\} \rangle_{eq}
\end{aligned}$$

Thus if A_i and A_j have the same time-reversal symmetry, we have $\langle \mathcal{H}\{A_i, A_k\} \rangle_{eq} = 0$. If not,$\langle \mathcal{H}\{A_i, A_k\} \rangle_{eq} \neq 0$ but antisymmetric.

Canonical equations for an ideal fluid

The reversible part of hydrodynamic equationcan be formulated in a more analogous way to Hamilton dynamics. Let us consider irrotational flow

$$\boldsymbol{v} = \nabla \phi$$

and define the Hamiltonian by

$$\mathcal{H} = \int d^3\boldsymbol{r} \left(\frac{\rho}{2} |\boldsymbol{v}|^2 + f(\rho) \right) = \int d^3\boldsymbol{r} \left(\frac{\rho}{2} |\nabla \phi|^2 + f(\rho) \right)$$

Then

$$\delta \mathcal{H} = \int d^3\boldsymbol{r} \left(\frac{\delta \rho}{2} |\boldsymbol{v}|^2 + \rho (\nabla \phi) \nabla (\delta \phi) + f'(\rho) \delta \rho \right) = \int d^3\boldsymbol{r} \left[\delta \rho \left(\frac{|\boldsymbol{v}|^2}{2} + f'(\rho) \right) - \delta \phi \nabla (\rho \nabla \phi) \right]$$

Thus we obtain

$$\frac{\delta \mathcal{H}}{\delta \rho(\boldsymbol{r})} = \frac{|\nabla \phi|^2}{2} + f'(\rho)$$

and

$$\frac{\delta \mathcal{H}}{\delta \phi(\boldsymbol{r})} = -\nabla (\rho \nabla \phi) = -\nabla (\rho \boldsymbol{v})$$

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[4] S. R. de Groot and P. Mazur, *Nonequilibrium Thermodynamics*(Dover, paperback).

We may write the continuity equation as

$$\frac{\partial \rho}{\partial t} = \frac{\delta \mathcal{H}}{\delta \phi(\boldsymbol{r})}$$

and the Euler equation as

$$\frac{\partial \phi}{\partial t} = -\frac{\delta \mathcal{H}}{\delta \rho(\boldsymbol{r})} = -\frac{|\boldsymbol{v}|^2}{2} - f'(\rho)$$

Indeed, if we take the gradient of both sides, we obtain for x-component,

$$\frac{\partial v_x}{\partial t} = -\nabla \phi \cdot \frac{\partial}{\partial x} \nabla \phi - \frac{\partial}{\partial x} f'(\rho) = -\boldsymbol{v} \cdot \nabla v_x - \frac{1}{\rho} \frac{\partial P}{\partial x}$$

where we should have

$$df = \frac{1}{\rho} dP$$

There are more involved formulations; see Morrison[5] .

8 Multicomponent fluid

We consider mixture. Let M_k is the mass of the k-th component. Entropy is a function of internal energy U, volume V and masses M_k.

$$S = S(U, V, M_1, \cdots, M_n)$$

The Gibbs relation is

$$TdS = dU + pdV - \sum_{k=1}^{n} \mu_k dM_k$$

The extensivity of entropy requires

$$\begin{cases} U + PV - \sum_{k=1}^{n} \mu_k M_k = TS \\ \\ SdT = VdP - \sum_{k=1}^{n} M_k d\mu_k \end{cases}$$

Let $M = \sum_{k=1}^{n} M_k$ be the total mass. Then we introduce quantities per unit mass;

$$s = \frac{S}{M}, \quad u = \frac{U}{M}, \quad v = \frac{V}{M} = \frac{1}{\rho}, \quad c_k = \frac{M_k}{M}$$

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[5] D. D. Holm, J. E. Marsden, T. Ratiu and A. Weinstein, *Phys. Rep.***123**(1985) 1; J. E. Marsden, R. Montgomery, P. J. Morrison and W. B. Thompson, *Ann. Phys.* **169** (1986) 29.

Then we have

$$\begin{cases} u + Pv - \sum_{k=1}^{n} \mu_k c_k = Ts \\ \\ \rho s dT = dP - \sum_{k=1}^{n} \rho_k d\mu_k \end{cases}$$

Now we have mass flow of each component, whose velocity is $\boldsymbol{v}$. Then

$$\boldsymbol{v} = \sum_{k=1}^{n} c_k \boldsymbol{v}_k$$

is the barycentric velocity. Then kinetic energy per unit mass is

$$\sum_{k=1}^{n} \frac{c_k}{2} |\boldsymbol{v}|^2 = \frac{|\boldsymbol{v}|^2}{2} + \sum_{k=1}^{2} \frac{c_k}{2} |\boldsymbol{w}_k|^2$$

where we introduce the diffusional velocity

$$\boldsymbol{w} = \boldsymbol{v}_k - \boldsymbol{v}$$

Then the total energy per unit mass is

$$e = u + \frac{|\boldsymbol{v}|^2}{2} + \sum_{k=1}^{2} \frac{c_k}{2} |\boldsymbol{w}_k|^2$$

Then we have

$$T\rho s = \rho u - \frac{\rho |\boldsymbol{v}|^2}{2} - \sum_{k=1}^{2} \frac{\rho_k}{2} |\boldsymbol{w}_k|^2 + P - \sum_{k=1}^{2} \mu_k \rho_k$$

From this, we may derive the extended Gibbs relation,

$$\begin{aligned} d(\rho s) \ &= \frac{1}{T} d(\rho e) - \frac{\boldsymbol{v}}{T} d(\rho \boldsymbol{v}) - \sum_{k=1}^{n} \frac{\boldsymbol{w}_k}{T} \cdot d\boldsymbol{J}_k \\ &- \sum_{k=1}^{n} \left(\mu_k - \frac{|\boldsymbol{v}|^2}{2} - \frac{|\boldsymbol{w}_k|^2}{2} \right) d\rho_k \end{aligned}$$

here we put $\boldsymbol{J}_k = \rho_k \boldsymbol{w}_k$ and we should note

$$\sum_{k=1}^{n} \boldsymbol{J}_k = 0$$

Thus all $\boldsymbol{J}_k$ are not independent. Thus we should write

$$\begin{aligned} d(\rho s) \ &= \frac{1}{T} d(\rho e) - \frac{\boldsymbol{v}}{T} d(\rho \boldsymbol{v} - \sum_{k=1}^{n-1} \frac{\boldsymbol{w}_k - \boldsymbol{w}_n}{T} \cdot d\boldsymbol{J}_k \\ &- \sum_{k=1}^{n} \left(\mu_k - \frac{|\boldsymbol{v}|^2}{2} - \frac{|\boldsymbol{w}_k|^2}{2} \right) d\rho_k \end{aligned}$$

Since the diffusion flows are not conserved, the irreversible process of diffusion flows of a two-component system can be written as

$$\frac{d\boldsymbol{J}_1}{dt} = L_{11}\left(-\frac{\boldsymbol{w}_1 - \boldsymbol{w}_2}{T}\right)$$

for the solute species. Since the solvent fluid is abundant, we may put $\boldsymbol{w}_2 \simeq 0$. Thus, we have

$$\frac{d\boldsymbol{J}_1}{dt} = -L_{11}\frac{\boldsymbol{w}_1}{T} = -\frac{L_{11}}{T\rho_1}\boldsymbol{J}_1$$

Thus we may say that

$$\gamma_1 \equiv \frac{L_{11}}{T\rho_1}$$

is the friction coefficient.

Now let us construct the hydrodynamic equations. The mass conservation is

$$\frac{\partial \rho_k}{\partial t} + \nabla \cdot (\rho \boldsymbol{v}_k) = \text{chemical reaction rate}$$

The Navier-Stokes equation for multicomponent fluid is obtained by considering the motion of a mass element of the k-th component. Let $\boldsymbol{R}_k(t)$ is the position of a mass element of the k-th component at time t. Then its velocity is the velocity of the k-th component at the position

$$\frac{d\boldsymbol{R}_k(t)}{dt} = \boldsymbol{v}_k(\boldsymbol{R}_k(t), t)$$

Therefore its accerelation is

$$\frac{d^2\boldsymbol{R}_k(t)}{dt^2} = \left(\frac{d\boldsymbol{R}_k(t)}{dt} \cdot \nabla\right) \boldsymbol{v}_k(\boldsymbol{R}_k(t), t) + \frac{\partial \boldsymbol{v}_k(\boldsymbol{R}_k(t), t)}{\partial t}$$

Thus we may write

$$\rho_k \left(\frac{\partial \boldsymbol{v}_k}{\partial t} + (\boldsymbol{v}_k \cdot \nabla)\boldsymbol{v}_k\right) = \rho_k \boldsymbol{F}_k$$

The problem is to find the proper force $\boldsymbol{F}_k$ per unit mass.By using the continuity equation without chemical reactions, we have

$$\begin{aligned}
\frac{\partial(\rho_k \boldsymbol{v}_k)}{\partial t} &= \frac{\partial \rho_k}{\partial t}\boldsymbol{v}_k + \rho_k \frac{\partial \boldsymbol{v}_k}{\partial t} \\
&= -\nabla \cdot (\rho_k \boldsymbol{v}_k)\boldsymbol{v}_k + \rho_k \boldsymbol{F}_k - \rho_k(\boldsymbol{v}_k \cdot \nabla)\boldsymbol{v}_k \\
&= -\nabla \cdot (\rho_k \boldsymbol{v}_k \boldsymbol{v}_k) + \rho_k \boldsymbol{F}_k
\end{aligned}$$

Summing both sides with respect to k leads to an equation for the barycentric velocity

$$\frac{\partial(\rho \boldsymbol{v})}{\partial t} + \nabla \cdot \left(\rho \boldsymbol{v}\boldsymbol{v} + \sum_{k=1}^{n} \rho_k \boldsymbol{w}_k \boldsymbol{w}_k + P\mathbf{1} - \mathbf{\Pi}\right) = 0$$

$\boldsymbol{\Pi}$ is the irreversible part of stress. It is not at all clear whether we can assume a simple Newtonian expression for the stress tensor.In general, the stress should be a linear combination of thermodynamic forces, such as $\nabla(1/T)$, $\nabla(-\boldsymbol{v}/T)$, $-(\boldsymbol{w}_k - \boldsymbol{w}_n)/T$ and $\nabla(-(\mu_k - |\boldsymbol{v}|^2/2 - |\boldsymbol{w}_k|^2/2))$ as far as the linear law requires. Since we have $\rho_k \boldsymbol{v}_k = \rho_k \boldsymbol{v} + \boldsymbol{J}_k$, we derive an equation for the diffusional flow $\boldsymbol{J}_k$,

$$\frac{\partial \boldsymbol{J}_k}{\partial t} + (\nabla \cdot \boldsymbol{v})\boldsymbol{J}_k + (\boldsymbol{J}_k \cdot \nabla)\boldsymbol{v} + \nabla(\rho_k \boldsymbol{w}_k \boldsymbol{w}_k) - c_k \sum_{k'=1}^{n} (\rho_{k'} \boldsymbol{w}_{k'} \boldsymbol{w}_{k'})$$

$$= \left(\frac{\partial \boldsymbol{J}_k}{\partial t}\right)_{rev} + \left(\frac{\partial \boldsymbol{J}_k}{\partial t}\right)_{irr}$$

The reversible forces described in terms of thermodynamic functions should reduce to the gredient of partial pressure $-\nabla P_k$ in the limit of dilution of the k-th component. Indeed, it turns out that

$$\left(\frac{\partial \boldsymbol{J}_k}{\partial t}\right)_{rev} = \rho_k T \left[\nabla\left(-\frac{\mu_k}{T}\right) + h_k^* \nabla\left(\frac{1}{T}\right) - \sum_{k'=1}^{n} c_{k'} \left(\nabla\left(-\frac{\mu_{k'}}{T}\right) + h_{k'} \nabla\left(\frac{1}{T}\right)\right)\right]$$

Indeed, h_k^* reduces to partial enthalpy $h_k = \dfrac{\partial H}{\partial M_k} = \dfrac{5k_B T}{2m_k}$ in the dilute limit and the partial pressure is defined by

$$dP_k = \rho_k d\mu_k + \rho_k (h_k - \mu_k) \frac{dT}{T}$$

The irreversible part should be

$$\left(\frac{\partial \boldsymbol{J}_k}{\partial t}\right)_{irr} = L_{ke} \nabla\left(\frac{1}{T}\right) + \sum_{k'=1}^{n-1} L_{kk'} \left(-\frac{\boldsymbol{w}_{k'} - \boldsymbol{w}_n}{T}\right)$$

Suppose temperature is uniform $\nabla T = 0$ and there is no convective flow, $\boldsymbol{v} = 0$. We assume further that the mixture consists of two components; a solute and a solvent. The solvent is much more abundant; $c_1 \ll c_2$ and $\boldsymbol{w}_2 \simeq 0$. We also assume that the volocity of the solute $\boldsymbol{w}_1$ is so small that we may neglect the second-order terms in $\boldsymbol{w}_1$ and $\boldsymbol{w}_2$. Then we have

$$\frac{\partial \boldsymbol{J}_1}{\partial t} = -\rho_1 \nabla \mu_1 - L_{11} \frac{\boldsymbol{w}_1}{T} = -\frac{k_B T}{m_1} \nabla \rho_1 - \gamma \boldsymbol{J}_1$$

where we have introduced

$$\mu_1 = \frac{k_B T}{m_1} \ln \rho_1 + \cdots, \qquad \gamma \equiv \frac{L_{11}}{\rho_1 T}$$

When the diffusion flow becomes stationary, namely $\dfrac{\partial \boldsymbol{J}_1}{\partial t} \simeq 0$, we have Fick's law,

$$\boldsymbol{J}_1 = -D \nabla \rho_1$$

where the diffusion constant is given by

$$D = \frac{k_B T}{m_1 \gamma_1}$$

This is called !HEinstein's relation !I

9 Zubarev's method

Up to now, we have discussed irreversible processes on the phenomenological ground. There is a formulation to derive nonequilibrium thermodynamics at least formally[6] . This is different from Mori's theory, which derives the linear Brownian motion of fluctuation in equilibrium.

Let $f(\Gamma, t)$ is the distribution function in the Γ-space. $A_j(\Gamma)$ is a macroscopic variable defined in the Γ-space. The local equilibrium distribution $f_l(\Gamma, t)$ is defined by

$$f_l(\Gamma, t) \equiv \frac{1}{Z_l(t)} \exp\left(- \sum_j \lambda_j(t) A_j(\Gamma) \right)$$

The parameters $\lambda_j(t)$ are determined as functions of the ensemble average $a_j(t) = \langle A_j(\Gamma) \rangle$ through the relations

$$\int d\Gamma A_j(\Gamma) f(\Gamma, t) = \int d\Gamma A_j(\Gamma) f_l(\Gamma, t)$$

We have already seen that the reversible part of the evolution equations of thermodynamic variables are given in terms of the local equilibrium distribution function. Now we will estimate the other part of the distribution function $f'(\Gamma, t)$.

Zubarev introduced the following Liouville equation, which includes the coupling with external thermal bath. The external bath drives the system into the state, which is represented by then local equilibrium distribution function.

$$\frac{\partial f}{\partial t} = -\mathcal{L} f - \varepsilon (f - f_l)$$

We assume that at the infinite past the system was exactly in a state, which is represented by the local equilibrium distribution.

$$\lim_{t \to -\infty} (f - f_l) = 0$$

Namely,

$$\lim_{t \to -\infty} f' = 0$$

If we substitute $f = f_l + f'$ into the Liouville equation, we obtain,

$$\frac{\partial f'}{\partial t} = -(\mathcal{L} + \varepsilon) f' - \left(\frac{\partial}{\partial t} + \mathcal{L} \right) f_l$$

Now we introduce so-called!HKawasaki-Gunton !Iprojection operator. First note that the local equilibrium distribution function depends on time through the parameters $\{\lambda(t)\} =$

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[6] D. Zubarev, V. Morozov and G. Röpke, *Statistical Mechanics of Nonequilibrium Processes, vol.1* (Akademie Verlag, 1996)

$(\lambda_1(t), \cdots)$, which are again functions of $\{a(t)\} = (a_1(t), \cdots)$. The projection operator $\mathcal{P}(t)$ is defined by

$$\begin{aligned}\mathcal{P}(t)G(\Gamma) &= f_l(\Gamma, \{a(t)\}) \int d\Gamma' G(\Gamma') \\ &+ \sum_j \frac{\partial f_l(\Gamma, \{a(t)\})}{\partial a_j(t)} \left(\int d\Gamma' G(\Gamma') A_j(\Gamma') - a_j(t) \int d\Gamma' G(\Gamma') \right)\end{aligned}$$

for an arbitrary function $G(\Gamma)$. The projection operator $\mathcal{P}(t)$ is time-dependent and it has the following properties.

$$\begin{cases} \mathcal{P}(t)\mathcal{P}(t') = \mathcal{P}(t) \\ \int d\Gamma (\mathcal{P}(t)G)(\Gamma) = \int d\Gamma G(\Gamma) \\ \mathcal{P}(t) f(\Gamma, t) = f_l(\Gamma, \{a(t)\}) \\ \mathcal{P}(t) \dfrac{\partial f(\Gamma, t)}{\partial t} = \dfrac{\partial}{\partial t} f_l(\Gamma, \{a(t)\}) \end{cases}$$

Then we can derive

$$\frac{\partial f'}{\partial t} = -[\mathcal{Q}(t)\mathcal{L} + \varepsilon] f' - \mathcal{Q}(t)\mathcal{L} f_l$$

where we have introduced another projection operator

$$\mathcal{Q}(t) \equiv 1 - \mathcal{P}(t)$$

Note also

$$\mathcal{L} f_l(\Gamma, t) = -\sum_j \lambda_j (\mathcal{L} A_j) f_l(\Gamma, \{a(t)\})$$

We introduce an operator $\hat{U}(t)$ defined by

$$\frac{d}{dt} \hat{U}(t) = -[\mathcal{Q}(t)\mathcal{L} + \varepsilon] \hat{U}(t)$$

with the initial condition $\hat{U}(0) = 1$. Then the irreversible part of the distribution function is

$$f'(\Gamma, t) = \sum_j \int_{-\infty}^{t} dt' \hat{U}(t) \hat{U}^{-1}(t') \mathcal{Q}(t') f_l(\Gamma, \{a(t')\}) \lambda_j(t')$$

Therefore, the irreversible part of the evolution is

$$\left(\frac{da_i}{dt} \right)_{irr} = \int d\Gamma (\mathcal{L} A_i) f'(\Gamma, t) = \sum_j \int_{-\infty}^{t} dt' L_{ij}(t, t') \lambda_j(t')$$

where

$$L_{ij} = \int d\Gamma (\mathcal{L} A_i) \hat{U}(t) \hat{U}^{-1}(t') \mathcal{Q}(t') (\mathcal{L} A_j) f_l(\Gamma, \{a(t')\}) \lambda_j(t')$$

Namely, the irreversible part is written as the linear combination of intensive parameters $\{\lambda(t')\}$ in the past.

Suppose we are in a stationary situation in which the intensive parameters are constant, we have

$$\left(\frac{da_i}{dt}\right)_{irr} = \sum_j \int_{-\infty}^{0} dt'_{ij}(0,t')\lambda_j$$

Thus

$$L_{ij} \equiv \int_{-\infty}^{0} dt' \int d\Gamma(\mathcal{L}A_i)\hat{U}^{-1}(t')\mathcal{Q}(-\infty)(\mathcal{L}A_j)f_l(\Gamma,\{a\})$$

is the Onsager's coefficients for non-equilibrium systems. It is not yet clear for me how it is related to the traditional Green-Kubo formula.

Mori Theory

Mori considered the fluctuation of macroscopic variables in equilibrium. Let $A_i(\Gamma)$ is a macroscopic variable. Suppose the system is in equilibrium. A projection operator $\mathcal{P}$ is defined in terms of macroscopic variables.

$$\mathcal{P}G = \sum_j A_i(\Gamma)\left(\langle AA\rangle^{-1}\right)_{ij}\langle A_j G\rangle$$

where $\langle AA\rangle^{-1}$ is the inverse matrix of the matrix $\langle A_i A_j\rangle$ defined by

$$\langle A_i A_j\rangle \equiv \frac{1}{Z}\int d\Gamma e^{-\beta\mathcal{H}}A_i A_j, \qquad Z = \int d\Gamma e^{-\beta\mathcal{H}}$$

The equation of motion of the macroscopic variable A_i

$$\frac{dA_i}{dt} = \mathcal{L}A_i$$

is transformed into the form of a Brownian motion

$$\frac{dA_i}{dt} = -\sum_j \int_0^t d\tau\Gamma_{ij}(t-\tau)A_j(\tau) + R_i(t)$$

where $R_i(t)$ is interpreted as a random noise with the property

$$\sum_l \langle R_i(t)R_l(0)\rangle(\langle AA\rangle^{-1})_{lj} = \Gamma_{ij}(t)$$

which is the expression of fluctuation-dissipation theorem[7] . Note the random noise does not follow Hamilton dynamics

$$R_i(t) = e^{\mathcal{QL}t}\mathcal{L}A_i$$

where $\mathcal{Q} = 1 - \mathcal{P}$. No one has yet succeed to create computer algorithm to simulate the projected dynamics represented by the operator $\mathcal{QL}$. If we are interested in the dynamics

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[7] R. Kubo, M. Toda and N. Hashitsume, *Statistical Physics II* (Springer)

of physical quantity in the small wave number, the corresponding wave number dependent operator $\mathcal{Q}_{\boldsymbol{k}}\mathcal{L}$ becomes $\mathcal{L}$ itself. However, it is not clear whether we can take this limit first before the final expression for the transport coefficient is reached[8] .

Nosé-Hoover dynamics

In order to compute dynamics of particles in contact with a heat bath, Nosé invented the following equations,

$$\begin{cases} \dfrac{dq_i}{dt} = p_i \\ \\ \dfrac{dp_i}{dt} = F_i - \alpha p_i \end{cases}$$

where α depends on the dynamical state of all particles

$$\alpha = \sum_i p_i F_i(\{q\}) \Big/ \sum_i p_i^2$$

This choice assures that the kinetic energy of particles is conserved

$$\sum_i p_i^2 = \text{constant}$$

This Nosé-Hoover dynamics assures the convergence of transport coefficients in the representation of correlation functions. However, there is a serious problem; Nosé-Hoover dynamics does not assure local conservation of momentum.

10 Master equation and stochastic processes

When we discuss fluctuations, the probabilistic description is appropriate[9] . Suppose $X(t)$ is a fluctuating variable, called `!H`random variable `!I` The probability of having $x_1 < X(t_1) < x_1 + dx_1$ is denoted by $P_1(x_1, t_1)dx_1$. Similarly the probability of having $x_1 < X(t_1) < x_1 + dx_1$ and $x_2 < X(t_2) < x_2 + dx_2$ is denoted by $P_2(x_2, t_2; x_1, t_1)dx_1 dx_2$. We can define $P_n(x_n, t_n; \cdots; x_1, t_1)$ similarly. We define `!H`conditional probability `!I`

$$T(x_n, t_n | x_{n-1}, t_{n-1}; \cdots; x_1, t_1) = \frac{P_n(x_n, t_n; \cdots; x_1, t_1)}{P_{n-1}(x_{n-1}, t_{n-1}; \cdots; x_1, t_1)}$$

Namely, it is the probability of having $x_n < X(t_n) < x_n + dx_n$ under the condition that we had $X(t_1) = x_1, \cdots, X(t_{n-1}) = x_{n-1}$.

Markoffian process

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[8] D. J. Evans and G. P. Morris,"Statistical Mechanics of Nonequilibrium Liquids" (Academic Press, 1990).

[9] Wax, *Selected Papers on Noise and Stochastic Processes* (Dover, paperback)

The Markoffian process is defined by

$$T(x_n, t_n|x_{n-1}, t_{n-1}; \cdots; x_1, t_1) = T(x_n, t_n|x_{n-1}, t_{n-1})$$

In this case, we have Chapman-Kolmogorov equation

$$\int dx_2 T(x_3, t_3|x_2, t_2) T(x_2, t_2|x_1, t_1) = T(x_3, t_3|x_1, t_1)$$

The conditional probability for a short time interval Δt is estimated to be

$$T(x_2, t_1 + \Delta t|x_1, t_1) = A\delta(x_2 - x_1) + \Delta t W(x_1 \to x_2) + \mathcal{O}(\Delta t)^2$$

Normalization condition requires

$$1 = \int dx_2 T(x_2, t_1 + \Delta t|x_1, t_1) = A + \Delta t \int dx_2 W(x_1 \to x_2) + \cdots$$

Thus we may write

$$\begin{aligned} T(x_2, t_1 + \Delta t|x_1, t_1) &= \left(1 - \Delta t \int dx' W(x_1 \to x')\right) \delta(x_2 - x_1) \\ &\quad + \Delta t W(x_1 \to x_2) + \cdots \end{aligned}$$

$W(x_1 \to x_2)$ is called !Htransition probability !I but I prefer to call it !Htransition rate !I since it is not probability in the sense of normalization. This gives the transition rate per unit time. If we substitute this expression into Chapman-Kolmogorov equation, we obtain !Hmaster equation !I

$$\frac{\partial P(x,t)}{\partial t} = -\int dx' W(x \to x') P(x,t) + \int dx' W(x' \to x) P(x', t)$$

This can be rewritten in the form of !HKramers-Moyal expansion !I

$$\frac{\partial P(x,t)}{\partial t} = \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \left(\frac{\partial}{\partial x}\right)^n C_n(x) P(x,t)$$

where

$$C_n(x) = \int dr W(x \to x + r) r^n = \lim_{t \to 0} \frac{1}{t} \int dr T(x + r, t|x, 0)$$

The last equality comes from the definition of the transition rate in terms of the short time expansion of the conditional probability. Therefore, we may write

$$C_n(x) = \lim_{t \to 0} \frac{1}{t} \left\langle (x(t) - x)^n \right\rangle_{x(0)=x}$$

Here $\langle \cdots \rangle_{x(0)=x}$ is the average with a fixed initial value $(0) = x$. This interpretation is used when we derive a master equation from a mechanical equation of fluctuation. For example, we consider the Langevin eqaution

$$\frac{dx}{dt} = F(x) + R(t)$$

Then we have

$$\begin{aligned} x(t) - x &= \int_0^t dt_1 F(x(t_1)) + \int_0^t dt_1 R(t_1) \\ &= \int_0^t dt_1 F\left(x + \int_0^{t_1} dt_2 F(x(t_2)) + \int_0^{t_1} dt_2 R(t_2)\right) + \int_0^t dt_1 R(t_1) \end{aligned}$$

Therefore

$$\begin{aligned} &\langle x(t) - x \rangle \\ &= F(x)t + F'(x) \int_0^t dt_1 \int_0^{t_1} dt_2 \langle F(x(t_2)) \rangle + F'(x) \int_0^t dt_1 \int_0^{t_1} dt_2 \langle R(t_2) \rangle \end{aligned}$$

Thus we have

$$C_1(x) = F(x)$$

and from the second moment, we obtain

$$C_2(x) = 2D$$

where we put

$$\langle R(t_1) R(t_2) \rangle = 2D\delta(t_1 - t_2)$$

Brownian motion

Let u be the velocity of a solute particle in a solvent.

$$m\frac{du}{dt} = -\gamma m u + R(t)$$

with $\langle R(t_1)R(t_2)\rangle = 2D_u \delta(t_1 - t_2)$. The master equation becomes!HFokker-Planck !Iequation,

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial u}\left(\gamma u + \frac{D_u}{m^2}\frac{\partial}{\partial u}\right) P$$

The steady state solution with the boundary condition $\lim_{|u|\to\infty} P(u,t) = 0$ should be Maxwellian

$$P_{eq}(u) \propto \exp\left(-\frac{mu^2}{2k_B T}\right)$$

Therefore we have to put

$$D_u = \gamma m k_B T$$

This is called!HFluctuation-dissipation theorem !I The diffusion constant is also estimated from this model by noting

$$D = \lim_{t\to\infty} \frac{\langle (x(t) - x(0))^2 \rangle}{2t}$$

and

$$x(t) - x(0) = \int_0^t d\tau u(\tau)$$

The result is

$$D = \frac{k_B T}{m\gamma}$$

which is called !HEinstein's relation !I

The idea of the Fokker-Planck equation can be extended to thermodynamical variables, whose non-equilibrium evolution is described by

$$\frac{da_i}{dt} = \sum_j M_{ij} F_j + \sum_j L_{ij} F_j$$

Then the fluctuation in nonequilibrium is assumed to obey the Langevin equation

$$\frac{da_i}{dt} = \sum_j M_{ij} F_j + \sum_j L_{ij} F_j + R_i(t), \quad \langle R_i(t) R_j(t') \rangle = 2D_{ij}\delta(t-t')$$

Then the Fokker-Planck equation reads

$$\frac{\partial P}{\partial t} = -\sum_i \sum_j \frac{\partial}{\partial a_i}\left(M_{ij} F_j P + \sum_j L_{ij} F_j P \right) + \sum_i \sum_j D_{ij} \frac{\partial^2 P}{\partial a_i \partial a_j}$$

Suppose k_B is a small parameter to give the smallness of fluctuations and note that the equilibrium probability distribution is given in terms of entropy

$$P_{eq} = \exp\left(S/k_B\right)$$

Then for small k_B, we have

$$\sum_i \sum_j \frac{\partial S}{\partial a_i}(M_{ij} + L_{ij}) F_j = \sum_i \sum_j D_{ij} \frac{\partial S}{\partial a_i} \frac{\partial S}{\partial a_j} \frac{1}{k_B}$$

Due to the property of the reversible part $M_{ij} = -M_{ji}$, we have

$$\sum_i \sum_j F_i L_{ij} F_j = \frac{1}{k_B} \sum_i \sum_j D_{ij} F_i F_j$$

Thus we may put

$$D_{ij} = k_B L_{ij}$$

This is called !HFluctuation-dissipation theorem !I Actually, we need not the condition of small k_B. In the case of hydrodynamics, we can check that

$$\sum_i \sum_j M_{ij} F_j = 0$$

by using functional derivative method; see my book (Kodansha) or Saarloos, Bedeaux and Mazur[10] .

The fluctuation-dissipation theorem implies that the transport coefficients which describe non-equilibrium ralaxation process towards equilibrium can be obtained in terms of fluctuations in equilibrium.

$$L_{ij} = \frac{1}{k_B} \int_0^\infty dt \langle R_i(t) R_j(0) \rangle_{eq}$$

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[10] W. van Saarloos, D. Bedeaux and P.Mazur, *Physica* **107A** (1981), 109, 147; K. Kitahara and Y. Toshikawa,*Hiheikoukei no kagaku I*(Kodansha Scientific, 1994).

11 Nonequilibrium fluctuations of macroscopic variables

We consider a macroscopic system, described by a variable X, which is extensive in that it is proportional to the size of the system Ω. When the variable changes, $X \to X + r$, r is microscopic. X may be the population of a town. r is the number of new-born babies. The town consisits of many subregions, each of which can give birth to some babies. Thus the size of the town increases, the probability of finite increment r per unit time increases in proportionality to the size of the system Ω and may be dependent on the density of population X/Ω. Thus the transition rate should have the form

$$W(X \to X + r) = \Omega w\left(\frac{X}{\Omega}; r\right)$$

Then we have for the scaled probability distribution function $P(x, t)$,

$$\frac{\partial P}{\partial t} = -\Omega \sum_r \left(1 - e^{-(r\partial/\partial x)/\Omega}\right) x(x; r) P(x, t)$$

which may be rewritten in a familiar form

$$\frac{1}{\Omega}\frac{\partial P}{\partial t} = -\mathcal{H}\left(x, \frac{1}{\Omega}\frac{\partial}{\partial x}\right) P(x, t)$$

where the `!H`Hamiltonian `!I`is defined by

$$\mathcal{H}(x, p) = \sum_r \left(1 - e^{-rp}\right) w(x; r)$$

In analogy with quantum mechanics, we use `!H`WKB approximation `!I`

$$P(x, t) = A(x, t) e^{\Omega\phi(x,t)}$$

Then we have `!H`Hamilton-Jacobi equation `!I`

$$\frac{\partial \phi}{\partial t} + H\left(x, \frac{\partial \phi}{\partial x}\right) = 0$$

If we make further a Gaussian approximation

$$\phi(x, t) = -\frac{1}{2\sigma(t)}(x - y(t))^2 + \cdots$$

we obtain a closed set of equations,

$$\begin{cases} \dfrac{dy}{dt} = C_1(y) \\[2ex] \dfrac{d\sigma}{dt} = 2C_1'(y)\sigma + C_2(y) \end{cases}$$

Ehrenfest !s model of random walk

Let us consider a one-dimensional lattice consisting of $2N+1$ sites. Suppose a particle is at site M. The transition rate for $M \to M \pm 1$ is given by

$$\begin{cases} W(M \to M+1) = \dfrac{1}{\tau}(N-M) \\ \\ W(M \to M-1) = \dfrac{1}{\tau}(N+M) \end{cases}$$

Suppose we have a large lattice, $N \to \infty$, and put $x = M/N$. Then we may write

$$\begin{cases} W(M \to M+1) = \dfrac{N}{2\tau}(1-x) = Nw(x,+1) \\ \\ W(M \to M-1) = \dfrac{N}{2\tau}(1+x) = Nw(x,-1) \end{cases}$$

Then we have

$$\begin{cases} C_1(x) = -\dfrac{x}{\tau} \\ \\ C_2(x) = \dfrac{1}{\tau} \end{cases}$$

The equations for $y(t)$ and $\sigma(t)$ are easily obtained,

$$\begin{cases} \dfrac{dy}{dt} = -\dfrac{y}{\tau} \\ \\ \dfrac{d\sigma}{dt} = -\dfrac{2}{\tau}(\sigma - 1) \end{cases}$$

Namely, the model converges to a Gaussian distribution. We may apply a general method of Hamilton - Jacobi equation; solve the caconical equations

$$\begin{cases} \dfrac{dx}{dt} = \dfrac{\partial\mathcal{H}}{p} \\ \\ \dfrac{dp}{dt} = -\dfrac{\partial\mathcal{H}}{x} \end{cases}$$

.with the Hamiltonian

$$\mathcal{H}(x,p) = \frac{1}{2\tau}\left[\left(1-e^{-p}\right)(1-x) + \left(1-e^{p}\right)(1+x)\right]$$

The phase flows look like the figure below.

Models of chemical reactions

Suppose there is a reaction of the scheme,

$$A \to X, \quad X \to A$$

Let X be the number of X molecules. Then the transition rates are

$$\begin{cases} W(X \to X+1) = kA \\ W(X \to X-1) = k'X \end{cases}$$

Let Ω be the size of the reactor and xX/Ω and $a = A/\Omega$ are the concentrations. Then we may put

$$\begin{cases} W(X \to X+1) = \Omega ka = \Omega w(x;+1) \\ W(X \to X-1) = \Omega k'x = \Omega w(x;-1) \end{cases}$$

If the system is closed, one should be careful since A also changes with $A + X = N$(total number of molecules). Then we have a different transition rate

$$\begin{cases} W(X, A \to X+1, A-1) = kA \\ W(X, A \to X-1, A+1) = k'X \end{cases}$$

Multivariate master equation

If the master equation as the following transition rate

$$W(\{X\} \to \{X + r\}) = \Omega w(\{x\}; \{r\})$$

with $X_i = x_i$, we have

$$\begin{cases} C_{1k}(\{x\}) = \sum_{\{r\}} r_k w(\{x\}; \{r\}) \\ C_{2kl}(\{x\}) = \sum_{\{r\}} r_k r_l w(\{x\}; \{r\}) \end{cases}$$

The evolution equations are

$$\begin{cases} \dfrac{dy_k}{dt} = C_{1k}(\{y\}) \\ \dfrac{d\sigma_{kl}}{dt} = \sum_m (K_{km\sigma_{ml}} + \sigma_{km} K_{lm}) + C_{2kl}(\{x\}) \end{cases}$$

with

$$K_{km} = \frac{\partial C_{1k}}{\partial x_m}$$

12 Boltzmann equation

We denote by $f(\boldsymbol{c}, \boldsymbol{r}, t) d^3\boldsymbol{c} d^3\boldsymbol{r}$ the number of particles with velocity and position within a small region $d^3\boldsymbol{c} d^3\boldsymbol{r}$ in the μ-space. By this definition, we have

$$\int\int f(\boldsymbol{c}, \boldsymbol{r}, t) d^3\boldsymbol{c} d^3\boldsymbol{r} = N$$

where N is the total number of particles.

$$n(\boldsymbol{r},t) \equiv \int f(\boldsymbol{c},\boldsymbol{r},t) d^3\boldsymbol{c}$$

in the number density. If there is no collision, we have

$$f(\boldsymbol{c},\boldsymbol{r},0) = f(\boldsymbol{c},\boldsymbol{r}+\boldsymbol{c}t,t)$$

Thus if we take time-derivative, we obtain,

$$\frac{\partial f}{\partial t} + \boldsymbol{c}\cdot\frac{\partial f}{\partial \boldsymbol{r}} = 0$$

If we take the collision effect into account, we should get

$$\frac{\partial f}{\partial t} + (\boldsymbol{c}\cdot\nabla)f = \left(\frac{\partial f}{\partial t}\right)_{coll}$$

The collision term

$$\begin{aligned}\left(\frac{\partial f}{\partial t}\right)_{coll} &= \int d^3\boldsymbol{c}' \int d^3\boldsymbol{c}_1 \int d^3\boldsymbol{c}'_1 \sigma(\boldsymbol{c}\boldsymbol{c}_1|\boldsymbol{c}'\boldsymbol{c}'_1) f(\boldsymbol{c}',\boldsymbol{r},t) f(\boldsymbol{c}'_1,\boldsymbol{r},t) \\ &= -\int d^3\boldsymbol{c}' \int d^3\boldsymbol{c}_1 \int d^3\boldsymbol{c}'_1 \sigma(\boldsymbol{c}'\boldsymbol{c}'_1|\boldsymbol{c}\boldsymbol{c}_1) f(\boldsymbol{c},\boldsymbol{r},t) f(\boldsymbol{c}_1,\boldsymbol{r},t)\end{aligned}$$

The scattering rate has the following symmetry due to the time-reversal symmetry of collision process

$$\sigma(\boldsymbol{c}'\boldsymbol{c}'_1|\boldsymbol{c}\boldsymbol{c}_1) = \sigma(-\boldsymbol{c}-\boldsymbol{c}_1|-\boldsymbol{c}'-\boldsymbol{c}'_1)$$

Furthermore due to the space-reversal symmetry we have

$$\sigma(-\boldsymbol{c}-\boldsymbol{c}_1|-\boldsymbol{c}'-\boldsymbol{c}'_1) = \sigma(\boldsymbol{c}\boldsymbol{c}_1|\boldsymbol{c}'\boldsymbol{c}'_1)$$

Therefore we have

$$\sigma(\boldsymbol{c}'\boldsymbol{c}'_1|\boldsymbol{c}\boldsymbol{c}_1) = \sigma(\boldsymbol{c}\boldsymbol{c}_1|\boldsymbol{c}'\boldsymbol{c}'_1)$$

We introduce the following abbreviated notations

$$f = f(\boldsymbol{c},\boldsymbol{r},t), \quad f_1 = f(\boldsymbol{c}_1,\boldsymbol{r},t), \quad f' = f(\boldsymbol{c}',\boldsymbol{r},t), \quad f'_1 = f(\boldsymbol{c}_1,\boldsymbol{r},t)$$

Then the collision term becomes

$$\left(\frac{\partial f}{\partial t}\right)_{coll} = \int d^3\boldsymbol{c}' \int d^3\boldsymbol{c}_1 \int d^3\boldsymbol{c}'_1 \sigma(\boldsymbol{c}\boldsymbol{c}_1|\boldsymbol{c}'\boldsymbol{c}'_1)(f'f'_1 - ff_1)$$

Now we introduce "H function" defined by

$$H(\boldsymbol{r},t) = \int d^3\boldsymbol{c} f \ln f$$

Then we have

$$\begin{aligned}\frac{\partial H}{\partial t} &= \int d^3\boldsymbol{c}\frac{\partial f}{\partial t}(\ln f+1)\\ &= \int d^3\boldsymbol{c}\left[-(\boldsymbol{c}\cdot\nabla)f+\left(\frac{\partial f}{\partial t}\right)_{coll}\right](\ln f+1)\\ &= -\nabla\cdot\int d^3\boldsymbol{c}(\boldsymbol{c}f\ln f)+\int d^3\boldsymbol{c}\left(\frac{\partial f}{\partial t}\right)_{coll}(\ln f+1)\end{aligned}$$

We may call

$$\boldsymbol{J}_H\equiv\int d^3\boldsymbol{c}(\boldsymbol{c}f\ln f)$$

"H flow". Then we have We may call

$$\frac{\partial H}{\partial t}+\mathrm{div}\boldsymbol{J}_H=\int d^3\boldsymbol{c}\left(\frac{\partial f}{\partial t}\right)_{coll}(\ln f+1)$$

Note

$$\int d^3\boldsymbol{c}\left(\frac{\partial f}{\partial t}\right)_{coll}=0$$

Therefore

$$\begin{aligned}\int d^3\boldsymbol{c}\left(\frac{\partial f}{\partial t}\right)_{coll}\ln f &= \frac{1}{4}\int d^3\boldsymbol{c}\int d^3\boldsymbol{c}_1\int d^3\boldsymbol{c}'\int d^3\boldsymbol{c}_1'\sigma(\boldsymbol{c}'\boldsymbol{c}_1'|\boldsymbol{c}\boldsymbol{c}_1)\\ &\times(f'f_1'-ff_1)\ln\left(\frac{ff_1}{f'f_1'}\right)\leq 0\end{aligned}$$

The last inequality comes from the fact that for $\forall a,\forall b>0$, we have

$$(a-b)\ln\left(\frac{b}{a}\right)<0$$

The equality holds only if $f'f_1'=ff_1$.

Especially when f is independent of $\boldsymbol{r}$, namely the system is homogeneous, we can prove the system will be in an equilibrium state. Let the equilibrium distribution function be

$$f_{eq}=n\left(\frac{m}{2\pi k_BT}\right)^{3/2}\exp\left(-\frac{m|\boldsymbol{v}|^2}{2k_BT}\right)$$

Then we can show that the H function, defined by

$$H(t)=\int d^3\boldsymbol{c}f\ln\left(\frac{f}{f_{eq}}\right)$$

has the following properties

1. $H \geq 0$ and the equality holds only when $f = f_{eq}$.
2. $\dfrac{dH}{dt} \leq 0$ and the equality holds only when $f = f_{eq}$.

Thus f_{eq} is the asymptotic limit of f for $t \to \infty$.

Let us go back to the inhomogeneous situation. The H function takes a stationary value when we have $f' f_1' = f f_1$. Since the consition of $\sigma(\boldsymbol{c}'\boldsymbol{c}_1'|\boldsymbol{c}\boldsymbol{c}_1)$ requires

1. $|\boldsymbol{c}|^2 + |\boldsymbol{c}_1|^2 = |\boldsymbol{c}'|^2 + |\boldsymbol{c}_1'|^2$
2. $\boldsymbol{c} + \boldsymbol{c}_1 = \boldsymbol{c}' + \boldsymbol{c}_1'$

the function f which satisfies $f' f_1' = f f_1$ should be of the following form,

$$f^{(0)}(\boldsymbol{c}, \boldsymbol{r}, t) = \exp\left(A|\boldsymbol{c}|^2 + \boldsymbol{B} \cdot \boldsymbol{c} + C\right)$$

If we choose the parameters A, $\boldsymbol{B}$ and C, we may write

$$f^{(0)}(\boldsymbol{c}, \boldsymbol{r}, t) = n(\boldsymbol{r}, t) \left(\frac{m}{2\pi k_B T(\boldsymbol{r}, t)}\right)^{3/2} \exp\left(-\frac{m|\boldsymbol{c} - \boldsymbol{v}(\boldsymbol{r}, t)|^2}{2k_B T(\boldsymbol{r}, t)}\right)$$

This is called local equilibrium distribution function.

To see $f' f_1' = f f_1$ implies the local equilibrium, we assume first that $f^{(0)}$ is of the form,

$$f^{(0)} = F(|\boldsymbol{c}|^2) G(\boldsymbol{c})$$

Then we have

$$F(|\boldsymbol{c}|^2) G(\boldsymbol{c}) F(|\boldsymbol{c}_1|^2) G(\boldsymbol{c}_1) = F(|\boldsymbol{c}'|^2) G(\boldsymbol{c}') F(|\boldsymbol{c}_1'|^2) G(\boldsymbol{c}_1')$$

Thus we may assume

$$G(\boldsymbol{c}) G(\boldsymbol{c}_1) = G(\boldsymbol{c}') G(\boldsymbol{c}_1')$$
$$F(|\boldsymbol{c}|^2) F(|\boldsymbol{c}_1|^2) = F(|\boldsymbol{c}'|^2) F(|\boldsymbol{c}_1'|^2)$$

Then the task is to determine the function $f(x)$, which satisfies $f(x)f(y) = f(z)f(x+y-z)$. If we differentiate both sides with respect to x, we have $f'(x)f(y) = f(z)f'(x+y-z)$. Then we put $x = z = 0$. We obtain $f'(0)f(y) = f(0)f'(y)$. This implies $f(x)$ is an exponential function.

The parameters $n(\boldsymbol{r}, t)$, $T(\boldsymbol{r}, t)$ and $\boldsymbol{v}(\boldsymbol{r}, t)$ are defined by the distribution functions

$$\begin{cases} \displaystyle\int d^3c f = n \\[2ex] \displaystyle\int d^3c f \boldsymbol{c} = n\boldsymbol{v} \\[2ex] \displaystyle\int d^3c f \frac{m}{2} |\boldsymbol{c} - \boldsymbol{v}|^2 = \frac{3nk_B T}{2} \end{cases}$$

and we have the following relations

$$\begin{cases} \int d^3\boldsymbol{c} f^{(0)} = n \\ \int d^3\boldsymbol{c} f^{(0)}\boldsymbol{c} = n\boldsymbol{v} \\ \int d^3\boldsymbol{c} f^{(0)}\frac{m}{2}|\boldsymbol{c}-\boldsymbol{v}|^2 = \frac{3nk_BT}{2} \end{cases}$$

Collision invariants

A function $\varphi(\boldsymbol{c})$ is called "collision invariant" if it satisfies

$$\int d^3\boldsymbol{c}\varphi\left(\frac{\partial f}{\partial t}\right)_{coll} = 0$$

In fact, we can prove the following relation by using the symmetry of σ,

$$\int d^3\boldsymbol{c}\varphi(\boldsymbol{c})\left(\frac{\partial f}{\partial t}\right)_{coll}$$

$$= \frac{1}{4}\int d^3\boldsymbol{c}\int d^3\boldsymbol{c}_1\int d^3\boldsymbol{c}'\int d^3\boldsymbol{c}_1'\sigma(f'f_1' - ff_1)$$

$$\times[\varphi(\boldsymbol{c}) + \varphi(\boldsymbol{c}_1) - \varphi(\boldsymbol{c}') - \varphi(\boldsymbol{c}_1')]$$

Thus the collision invariant implies

$$\varphi(\boldsymbol{c}) + \varphi(\boldsymbol{c}_1) = \varphi(\boldsymbol{c}') + \varphi(\boldsymbol{c}_1')$$

Therefore there are five collision invariants

$$\varphi(\boldsymbol{c}) = \begin{cases} 1 \\ \boldsymbol{c} \\ |\boldsymbol{c}|^2 \end{cases}$$

The collision invariants are closely related to hydrodynamics[11] We may write

$$\int d^3\boldsymbol{c}\varphi(\boldsymbol{c}f) = n(\boldsymbol{r},t)\langle\varphi\rangle$$

Then we have

$$\frac{\partial}{\partial t}(n\langle\varphi\rangle) + \nabla\cdot(n\langle\varphi\boldsymbol{c}\rangle) = 0$$

Namely the collision term does not appear explicitly and the resulting equation takes the form of a conservation law.

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[11] P. Résibois and M. DeLeener,*Classical Kinetic Theory of Fluids* (John-Wiley, 1977).

For example, if we choose $\varphi 1$,we have

$$\frac{\partial n}{\partial t} + \nabla \cdot (n\boldsymbol{v}) = 0$$

If we put $\rho = mn$ we oftain the mass conservation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \boldsymbol{v}) = 0$$

If we choose $\varphi = \boldsymbol{c}$ we obtain

$$\frac{\partial}{\partial t}(nv_i) + \frac{\partial}{\partial x_j}(n\langle c_j c_i\rangle) = 0$$

If we put

$$c_i = v_i + (c_i - v_i)$$

and $\rho = mn$, we obtain

$$\frac{\partial}{\partial t}(\rho v_i) + \frac{\partial}{\partial x_j}\rho(v_i v_j + \langle (c_j - v_j)(c_i - v_i)\rangle) = 0$$

If we compare it with the hydrodynamic equation, we can conclude

$$P\delta_{ij} - \Pi_{ji} = \rho\langle (c_j - v_j)(c_i - v_i)\rangle$$

Suppose the distribution function f, which is the solution of the Boltzmann equation, can be written as

$$f = f^{(0)} + f'$$

we can write

$$\langle (c_j - v_j)(c_i - v_i)\rangle = \rho\langle (c_j - v_j)(c_i - v_i)\rangle^{(0)} + \langle (c_j - v_j)(c_i - v_i)\rangle'$$

The local equilibrium is a Gaussian distribution around the average velocity, we can easily calculate the local equilibrium average

$$\langle (c_j - v_j)(c_i - v_i)\rangle^{(0)} = \delta_{ij}\frac{k_B T}{m}$$

Thus

$$\rho\langle (c_j - v_j)(c_i - v_i)\rangle^{(0)} = \delta_{ij}\frac{\rho k_B T}{m} = \delta_{ij} n k_B T = P\delta_{ij}$$

This is hydrostatic pressure. Therefore we can identify the viscosity tensor

$$\Pi_{ij} = -\rho\langle (c_j - v_j)(c_i - v_i)\rangle'$$

If we choose $\varphi = |\boldsymbol{c}|^2$, we have

$$\frac{\partial}{\partial t}(n\langle |\boldsymbol{c}|^2\rangle) + \nabla \cdot (n\langle |\boldsymbol{c}|^2 \boldsymbol{c}\rangle) = 0$$

We put again

$$\boldsymbol{c} = \boldsymbol{v} + (\boldsymbol{c} - \boldsymbol{v})$$

we have

$$\langle |\boldsymbol{c}|^2 \rangle = \langle |\boldsymbol{v}|^2 \rangle + \langle |\boldsymbol{c} - \boldsymbol{v}|^2 \rangle$$

Thus if we identify

$$\rho e = \frac{\rho}{2} \langle |\boldsymbol{c}|^2 \rangle$$

we have

$$\rho u = \frac{\rho}{2} \langle |\boldsymbol{c} - \boldsymbol{v}|^2 \rangle = \frac{3}{2} n k_B T$$

Next we note

$$\begin{aligned} \langle |\boldsymbol{c}|^2 \boldsymbol{c} \rangle &= |\boldsymbol{v}|^2 \boldsymbol{v} + \langle |\boldsymbol{c} - \boldsymbol{v}|^2 \rangle \boldsymbol{v} \\ &+ 2\boldsymbol{v} \cdot \langle (\boldsymbol{c} - \boldsymbol{v})(\boldsymbol{c} - \boldsymbol{v}) \rangle + \langle |\boldsymbol{c} - \boldsymbol{v}|^2 (\boldsymbol{c} - \boldsymbol{v}) \rangle \end{aligned}$$

Then we will get

$$\frac{\partial(\rho e)}{\partial t} + \nabla \cdot \left(\rho e \boldsymbol{v} + \rho \boldsymbol{v} \cdot \langle (\boldsymbol{c} - \boldsymbol{v})(\boldsymbol{c} - \boldsymbol{v}) \rangle + \frac{\rho}{2} \langle |\boldsymbol{c} - \boldsymbol{v}|^2 (\boldsymbol{c} - \boldsymbol{v}) \rangle \right) = 0$$

Therefore if we identify this with the energy balance equation, we can put

$$\boldsymbol{Q} = \frac{\rho}{2} \langle |\boldsymbol{c} - \boldsymbol{v}|^2 (\boldsymbol{c} - \boldsymbol{v}) \rangle$$

This is heat current.