TOPICS ON THE THEORY OF POLYMER DYNAMICS AND ON THE KINETIC THEORIES OF TRANSPORT PHENOMENA IN DILUTE POLYMER SOLUTIONS

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Chapter 1

General Concepts on Statistical Mechanics

1.1 Hamiltonian Dynamics

Statistical mechanics is generally concerned with the systematic study of large assemblies of simple systems,varying in size from monatomic molecules in a gas up to stars in a galaxy or even people forming communities.What is of primary interest is to get a closer view to the behavior of the system in terms of the behavior of its constituents.Just because of the interactions between the particles of the system one does not expect that the system behaves as a superposition of the individual constituents' behaviors.The laws that govern the behavior of the individual particles are well known from classical and quantum mechanics.

A class of systems that occupy the center of attention of statistical mechanics are those that are governed by the laws of Hamiltonian dynamics.The structure that characterizes Hamiltonian dynamics is common in classical and quantum systems and is one of the reasons that make Hamiltonian dynamics especially tempting.

Given a fixed instant of time,a system in Hamiltonian dynamics is characterized by a set of $2N$ variables which are, $q_1, ...q_N$ known as generalized coordinates and $p_1, ..., p_N$ being the generalized momenta conjugate to the $q_i's$ .Although the $q_i's$ and $p_i's$ may represent the physical space coordinates and momenta respectively,they may also represent more abstract quantities (for instance the $q_i's$ may be numbers characterizing the internal degrees of freedom e.t.c).So the dynamical system is characterized by a point $(q_1, ...q_N, p_1, ...p_N)$ or (q, p) abbreviated (where $q \equiv (q_1, ...q_N)$, $p \equiv (p_1, ..., p_N)$) in the $2N-$ dimensional Cartesian space.This space bears the name phase-space and is the framework of dynamics and statistical mechanics.

Functions of the phase space variables (q,p) ,play an important role and will be called dynamical functions denoted by $b(q,p)$ .Physical quantities that can be realized as functions of (q,p) are for instance the energy, the momentum and so on. Certain types of dynamical functions are for example analytical functions of q,p ,formally expressed by

$$b(q,p) = \sum_{n_1,\dots,n_N,m_1,\dots,m_N=0}^{\infty} \bar{\beta}_{n_1,\dots,m_N} q_1^{n_1} \dots q_N^{n_N} p_1^{m_1} \dots p_N^{m_N} \tag{1.1}$$

where $\bar{\beta}_{n_1,\dots,m_N}$ are real constants.In case $b(q,p)$ obeys other smoothness criteria, it can be represented as Fourier series or integrals, e.g

For the study of the evolution in time of the dynamical system use is made of a specific dynamical function called the Hamiltonian $H(q,p)$ of the system. In most cases the Hamiltonian represents the total energy of a physical system. The trajectory of the motion of the system in phase space described by the $2N$ time dependent variables $(q(t),p(t))$ is determined by the $2N$ Hamilton's equations:

$$\dot{q}_i = \frac{\partial H(q,p)}{\partial p_i} \tag{1.2}$$

$$\dot{p}_i = -\frac{\partial H(q,p)}{\partial q_i} \tag{1.3}$$

together with the initial conditions $q_i(0) = q_i^0, p_i(0) = p_i^0$

Thus the rate of change of a dynamical variable $b(q,p)$ with respect to time is

$$\begin{aligned} \dot{b}(q,p) &= \sum_{n=1}^{N} \left(\frac{\partial b}{\partial q_n} \cdot \dot{q}_n + \frac{\partial b}{\partial p_n} \cdot \dot{p}_n\right) = \\ &= \sum_{n=1}^{N} \left(\frac{\partial b}{\partial q_n} \cdot \frac{\partial H}{\partial p_n} - \frac{\partial b}{\partial p_n} \cdot \frac{\partial H}{\partial q_n}\right) \end{aligned} \tag{1.4}$$

Some elementary algebra may be introduced for the study of several concepts on Hamiltonian dynamics. We introduce an operation between two dynamical function b,c that is called Poisson bracket and is defined by

$$[b,c]_P = \sum_{n=1}^{N} \left(\frac{\partial b}{\partial q_n} \cdot \frac{\partial c}{\partial p_n} - \frac{\partial b}{\partial p_n} \cdot \frac{\partial c}{\partial q_n}\right) \tag{1.5}$$

so that equation **??** can be written in form $\dot{b} = [b,H]_P$.

It is easily seen that the Poisson bracket is a closed algebraic operation on dynamical functions and obeys the rules that characterize a Lie bracket, which are:

$$[b,c]_P = -[c,b]_P \tag{1.6}$$

the Jacobi relation

$$[b,[c,d]_P]_P+[c,[d,b]_P]_P+[d,[b,c]_P]_P=0 \tag{1.7}$$

and for a scalar α

$$[b,\alpha]_P=0 \tag{1.8}$$

Other properties of the Poisson bracket are:

$$[(b+c),d]_P=[b,d]_P+[c,d]_P \tag{1.9}$$

for a scalar α

$$[\alpha b,c]_P=\alpha[b,c]_P \tag{1.10}$$

and

$$[bc,d]_P=b[c,d]_P+[b,d]_P c \tag{1.11}$$

Finally, the Poisson bracket of any two dynamical functions b, c can be obtained by the "bracket multiplication table" of the fundamental elements q_r, p_r. This table is

$$[q_r,q_s]_P=0 \tag{1.12}$$

$$[p_r,p_s]_P=0 \tag{1.13}$$

$$[q_r,p_s]_P=\delta_{rs} \tag{1.14}$$

We are defining a dynamical algebra D as the set of all dynamical functions and note that the operations of addition,multiplication and the Poisson bracket are closed in D .Such a set adopts the special name of a Lie algebra.

Let α be an element of D. An operator $[\alpha]$ acting on an element b of the algebra D is defined through

$$[\alpha]b\equiv[b,\alpha]_P \tag{1.15}$$

We wish to express the evolution in time of a dynamical function $b(q,p;t)$ by means of the aforementioned idea. Till now we know that for "good" $b(q,p;t)$ we can write

$$b(q,p;t)=\sum_{n_1,\ldots,n_N,m_1,\ldots,m_N=0}^{\infty}\bar{\beta}_{n_1,\ldots,n_N,m_1,\ldots,m_N}q_1^{n_1}(t)\ldots q_N^{n_N}(t)p_1^{m_1}(t)\ldots p_N^{m_N}(t) \tag{1.16}$$

or using the Hamilton's equations we get an expression of $b(q,p;t)$ as a function of the initial conditions q^i, p^i, that is

$$b(q,p;t)=\sum_{n_1,\ldots,n_N,m_1,\ldots,m_N=0}^{\infty}\bar{\beta}_{n_1,\ldots,n_N,m_1,\ldots,m_N}(t)q^{1n_1}\ldots q^{Nn_N}p^{1m_1}\ldots p^{Nm_N} \tag{1.17}$$

where in the aforementioned cases

$$\bar{\beta}_{n_1,\ldots,n_N,m_1,\ldots,m_N}(t) \neq \bar{\beta}_{n_1,\ldots,n_N,m_1,\ldots,m_N} \tag{1.18}$$

with the second point of view being more close to statistical mechanics.

Now let $b(q,p)$ be a dynamical function at time $t=0$ and $b(q,p;t)$ its value at time t. We expand in Taylor series and get

$$b(t) = \sum_{r=0}^{\infty} \frac{1}{r!} t^r b^{(r)}(0) \tag{1.19}$$

Taking in consideration the fact that

$$\dot{b} = [b, H]_P = [H]b \tag{1.20}$$

we can easily find by induction that $b^{(r)}(t) = [H]^r b(0)$ and hence get

$$b(t) = \sum_{r=0}^{\infty} \frac{1}{r!} t^r [H]^r b(0) = e^{t[H]} b(0) \equiv \bar{U}(t) b(0) \tag{1.21}$$

where $\bar{U}(t) = \exp\{t[H]\}$ is the Green operator or propagator and has the properties of a group. Indeed, performing successively the operations $\bar{U}(t_1)$ and $\bar{U}(t_2)$ is the same as if we performed the operation $\bar{U}(t_1 + t_2)$ e.t.c.

1.2 Classical Ensembles;The introduction of the Distribution Function;The Liouville Equation

Macroscopic properties of the surrounding objects can be represented by functions of the physical space x and of time t: $B(x,t)$. Such continuous or even piecewise-continuous (for certain classes of phenomena) functions are called fields and their behavior is governed by partial differential and integrodifferantial equations (e.g Navier-Stokes equations e.t.c).

The revolutionary advent of the atomistic theory gave a strike to our illusion that matter is a continuum. When we move to magnitudes of length down to 10^{-7} cm what we observe is a collection of interacting particles and so the natural framework of microscopic physics is that of the dynamics of the many body problem. Statistical mechanics is the bridge between these two levels of description. One has to keep in mind that statistical mechanics not only provides the tools needed to overcome the extreme difficulties that are involved in computations of the dynamics of many bodies problem, but also provides the answers that have a qualitative and quantitative significance.

Let's examine closer the aforementioned correspondence rule between physical space-time fields: $B(x,t)$ and microscopic dynamical quantities that are functions of the phase-space coordinates (q,p) and probably x: $b(q,p;x;t)$. The correspondence rule in a more abstract language tells us that for any microscopic dynamical function $b(q,p;x;t)$ there corresponds a unique macroscopic function :

$$b(q,p;x;t) \rightarrow B(x,t) \tag{1.22}$$

This mapping is a functional and is denoted by $\langle ... \rangle$. That is

$$B(x;t) = \langle b(q,p;x;t) \rangle \equiv \langle b \rangle \tag{1.23}$$

and is required to have special properties, which are
linearity : $\langle \beta b + \gamma c \rangle = \beta \langle b \rangle + \gamma \langle c \rangle$
where β, γ are real numbers and b, c are dynamical functions
the unit may not be affected by the mapping: $\langle 1 \rangle = 1$

If we define $B(x,t) = \int\int \; dqdpb(q,p;x;t)F(q,p)$ then this operation will satisfy the above two properties if we pose the extra requirement that
$\int\int \; dqdpF(q,p) = 1$ holds.

Any function F that is normalized to unity is called a phase-space distribution function and is of great significance as it specifies the state of the system at a given instant of time.

We may now add the extra condition $F(q,p) \geq 0$, so that $F(q,p)$ could be interpreted as the probability density that the system is located at (q,p) . Although the formalism resembles the one used in probability theory ,it is only an extramechanical "statistical" assumption entering the theory. The system obeys the rules of classical or quantum mechanics.

Going back to our problem , let $F(q,p)$ be the distribution function describing the state of our system at time $t = 0$. Also ,let $b(q,p;x;t=0) = b(q,p;x)$ .Then $B(x,0) = \int\int \; dqdpb(q,p;x)F(q,p)$ .In order to determine how the observable $B(x,t)$ changes with respect to time one needs to consider the Hamiltonian character of the system. We then define

$$B(x,t) = \int\int \; dqdp[e^{[H]t}b(q,p;x)]F(q,p) \tag{1.24}$$

and in virtue of lemma...(see appendix)

$$\begin{aligned} B(x,t) &= \int\int \; dqdp[e^{-[H]t}e^{[H]t}b(q,p;x)][e^{-[H]t}F(q,p)] \\ &= \int\int \; dqdpb(q,p;x)[e^{-[H]t}F(q,p)] \end{aligned} \tag{1.25}$$

What we have managed to do is to transfer the time dependence from the dynamical function to the distribution function and now we only need to solve an initial value problem for a partial differential equation and the average value of several quantities can be obtained.

The introduction of the time-dependent distribution function $F(q, p; t)$ follows naturally by the last equality and is given by

$$F(q, p; t) = e^{-[H]t} F(q, p) \tag{1.26}$$

Then the observable at time t is expressed as

$$B(x, t) = \int \int \, dqdpb(q, p; x) F(q, p; t) \tag{1.27}$$

and the main problem of statistical mechanics reduces to the study of the differential equation that governs the evolution of $F(q, p; t)$. Indeed, differentiating with respect to time 1.26 we get

$$\partial_t F(q, p; t) = -[e^{-[H]t} F(q, p), H]_P \tag{1.28}$$

or

$$\partial_t F(q, p; t) = [H(q, p), F(q, p; t)]_P = -[H]F \tag{1.29}$$

an equation playing a central role in statistical mechanics that bears the name Liouville equation, an analog of the Schrodinger equation for quantum mechanics.

We finally introduce the Liouville operator to be

$$\text{Ł}F \equiv [H, F]_P = \sum_{n=1}^{N} \{ \frac{\partial H}{\partial q_n} \cdot \frac{\partial F}{\partial p_n} - \frac{\partial H}{\partial p_n} \cdot \frac{\partial F}{\partial q_n} \} \tag{1.30}$$

Remark:A formal derivation of the Liouville equation through the measure preserving property of the Canonical transformation is given in the appendix.

1.3 Reduced Distribution Functions;The BBGKY Hierarchy

1.3.1 Reduced Distribution Functions

Let M be the phase space of the ensemble of N identical particles (dim $M = 6N$) with coordinates $x_i = (q_i, p_i)$ $i = 1, ..., N$.Individual and collective measures are: $d\mu_i = dx_i = dq_i dp_i$, $\mu = \prod_{i=1}^{N} \mu_i$
The N particle distribution function

$$F_N(q_1, p_1, ..., q_N, p_N, t) \equiv F(q, p, t) \tag{1.31}$$

satisfies the Liouville equation

$$\frac{\partial F_N}{\partial t} = [H, F_N]_P \tag{1.32}$$

where F_N is normalized to unity

$$\int F_N(q_1, p_1, ..., q_N, p_N, t) d\mu = 1 \tag{1.33}$$

Considering Hamiltonians of the form

$$H = \sum_{i=1}^{N} (\frac{p_i^2}{2m} + V_i(q)) + \sum_{1 \leq i < j \leq N} V_{ij}(q_i, q_j) \tag{1.34}$$

where $V_i(q)$ is the potential due to an external field and $V_{ij}(q_i, q_j)$ is the mutual potential of particles i and j
A similar decomposition can be presented for the Liouville operator.Thus

$$Ł = \sum_{j=1}^{N} (\frac{p_j}{m} \frac{\partial}{\partial q_j} - \frac{\partial V_j}{\partial q} \frac{\partial}{\partial p_j}) - \sum_{1 \leq i < j \leq N} Ł_{ij} \tag{1.35}$$

where

$$Ł_{ij} = \frac{\partial V_{ij}}{\partial q_i} \frac{\partial}{\partial p_i} + \frac{\partial V_{ij}}{\partial q_j} \frac{\partial}{\partial p_j} \tag{1.36}$$

We are now in position to define the reduced s-particle distribution function writing

$$f_s(x_1, ..., x_s) = \frac{N!}{(N-s)!} \int dx_{s+1} ... dx_N F(x_1, ..., x_s, x_{s+1}, ..., x_N) \tag{1.37}$$

for $s \leq N - 1$
and $f_N \equiv F(q, p, t)$ for $s = N$
The reduced s-particle distribution function is thus normalized by

$$\int dx_1 ... dx_s f_s = \frac{N!}{(N-s)!} \tag{1.38}$$

The next step will be to write down a hierarchy for the distribution vector

$$f \equiv \{f_0, f_1, ..., f_N\} \tag{1.39}$$

1.3.2 The BBGKY Hierarchy

The Liouville equation of a system of N particles can be written according to the aforementioned format as

$$\partial_t F = \sum_{i=1}^{n} \text{Ł}_i F + \sum \sum_{1\leq i<j\leq N} \text{Ł}_{ij} F \tag{1.40}$$

Since the number of particles in the system is conserved this implies that

$$\int dx_1 ... dx_N F(x_1, ..., x_N, t) = const \forall t \tag{1.41}$$

so

$$\int dx_1 ... dx_N \partial_t F(x_1, ..., x_N, t) = 0 \tag{1.42}$$

or

$$\int dx_1 ... dx_N \{ \sum_{i=1}^{N} \text{Ł}_i + \sum \sum_{1\leq i<j\leq N} \text{Ł}_{ij} \} F = 0 \tag{1.43}$$

We can go on and write down relations that hold and will eventually be the building tool for our hierarchy.Assuming that F falls sufficiently when $p_j \rightarrow \infty$ and vanishes in the physical boundaries one can obtain from Gauss' theorem that

$$\int dq_j \frac{\partial F}{\partial q_j} = 0 \tag{1.44}$$

and

$$\int dp_j \frac{\partial F}{\partial p_j} = 0 \tag{1.45}$$

so it is easily implied that

$$\int dx_j L_j F(x_1, ..., x_N) = 0 \tag{1.46}$$

and

$$\int dx_j dx_n L_{jn} F(x_1, ..., x_N) = 0 \tag{1.47}$$

The equation of evolution for the reduced distribution function f_s is thus

$$\begin{aligned} \partial_t f_s(x_1, ..., x_n) &= \partial_t \frac{N!}{(N-s)!} \int dx_{s+1} ... dx_N F(x_1, ..., x_N) \\ &= \frac{N!}{(N-s)!} \int dx_{s+1} ... dx_N (\sum_{j=1}^{N} L_j F + \sum_{1\leq i<j\leq N} \sum L_{ij} F) \end{aligned} \tag{1.48}$$

The term $\sum_{j=1}^{N} L_j F$ may be treated independently in the upcoming manner. We write

$$\sum_{j=1}^{N} L_j F = \sum_{j=1}^{s} L_j F + \sum_{j=s+1}^{N} L_j F \tag{1.49}$$

and remark that when $j \in \{1, ..., s\}$ then L_j since it is not affected by the integration can be brought outside the integral and if $j \in \{s+1, ..., N\}$ then it vanishes. So

$$\frac{N!}{(N-s)!} \int dx_{s+1}...dx_N \sum_{j=1}^{N} L_j F = \sum_{j=1}^{s} L_j \frac{N!}{(N-s)!} \int dx_{s+1}...dx_N F \tag{1.50}$$

the second term is treated taking in consideration three cases:
• If both j and n belong to $\{1, ..., s\}$ then the operator L_{jn} can again be written in front of the integral.
• If both j and n belong to $\{s+1, ..., N\}$ then we have already shown that it vanishes.
• If j belongs to $\{1, ..., s\}$ and n to the group $\{s+1, ..., N\}$ then

$$\begin{aligned} &\frac{N!}{(N-s)!} \int dx_{s+1}...dx_N \sum_{j=1}^{s} \sum_{n=s+1}^{N} L_{jn} F(x_1, ..., x_N) \\ &= ... = \sum_{j=1}^{s} \int dx_{s+1} L_{js+1} f_{s+1}(x_1, ..., x_{s+1}) \end{aligned} \tag{1.51}$$

The final equation we get after collecting the various terms is

$$\begin{aligned} \partial_t f_s(x_1, ..., x_s) = \sum_{j=1}^{s} L_j f_s(x_1, ..., x_s) + \sum \sum_{j<n=1}^{s} L_{jn} f_s(x_1, ..., x_s) \\ \sum_{j=1}^{s} \int dx_{s+1} L_{js+1} f_{s+1}(x_1, ..., x_{s+1}) \end{aligned} \tag{1.52}$$

1.4 Microcanonical and Canonical Ensembles

1.4.1 Microcanonical Ensemble

The system we are considering is an N particle system in a volume V whose total energy is constrained to a narrow range above a reference energy E.

$$E \leq energy \leq E + \Delta \tag{1.53}$$

with $\Delta << E$.
Thus we are keeping fixed 3 macroscopic quantities E, N and V as well as others which will not be carried in our development.Our aim is to impose a probability density on the phase space of the many particle system, such that information of the system will be contained in the probability density.

The choice we are going to make is known as the "postulate of equal a priori probabilities" which is contained in the fact that we assign to the probability density a constant value for all the accessible states of the system.The accessible states are those consistent with the constraint $(E, N, V, ...)$

So in the classical case:

$$f(\{p, q\}) = \begin{cases} \frac{1}{\Omega}, & \text{when } E < H(p,q) \leq E + \Delta \\ 0, & \text{elsewhwere} \end{cases} \tag{1.54}$$

and

$$\Omega \equiv \int_{accessible} dp, dq = \Omega(E, V, N) \tag{1.55}$$

We may go on and obtain information for the state X, of a system which is

$$\begin{aligned} f(X) &= \int_{except\{p,q\}} f(\{p, q\})\{dp, dq\} \\ &= \frac{1}{\Omega} \int_{except\{p,q\}} \{dp, dq\} \\ &= \frac{\Omega'(consistentwithX)}{\Omega} \end{aligned} \tag{1.56}$$

1.4.2 Canonical Ensembles;The method of the most probable distribution

We are about to present the traditional derivation of the Canonical Ensemble based on 'the method of the most probable distribution'

We consider a 'Universe' having energy E that is isolated (interchanges no energy with its outside) and that consists of N sub-systems $S_i (i = 1, ..., N)$ which are allowed to interchange energy but only weakly.We are thus in position to disregard this correlation (due to energy exchange)

Let's assume that the energy of S_i is E_i then the energy of the whole universe is $E = \sum_{i=1}^{N} E_i$.Each system S_i possesses a different spectrum of eigenvalues ε_l.The number of systems in the energy level ε_l is ν_l and thus a given a given configuration can be realized in $P = \frac{N!}{\nu_1!\nu_2!...\nu_l!...}$ ways.

What the 'method of the most probable distribution' asserts is that the canonical Ensemble will be gained by maximizing P (or equivalently $\log(P)$) under the only so far imposed constraints

$$\sum_l \nu_l = N \tag{1.57}$$

$$\sum_l \nu_l \varepsilon_l = E \tag{1.58}$$

We will use Lagrange's method to optimize $\log(P)$.Thus we are determining the extremum of

$$\log(P) - \alpha \sum_l \nu_l - \beta \sum_l \nu_l \varepsilon_l \tag{1.59}$$

(for α, β being the Lagrange multipliers).

Substituting 1.57,1.58 into 1.59and using the asymptotic approximation

$$\log(n!) \approx n \log(n) - 1 \tag{1.60}$$

We are thus led to the result

$$\nu_l = e^{-\alpha - \beta \varepsilon_l} \tag{1.61}$$

The first parameter to be eliminated is α.Thus, by 1.57

$$\nu_l = \frac{N}{\sum_m e^{-\beta \varepsilon_m}} e^{-\beta \varepsilon_l} \tag{1.62}$$

And the probability p_l of finding the system in state l is

$$p_l = \frac{\nu_l}{N} = \frac{e^{-\beta \varepsilon_l}}{\sum_l e^{-\beta \varepsilon_m}} \tag{1.63}$$

1.5 The Boltzmann Equation of Non-Equilibrium Statistical Mechanics

The Boltzmann equation is the most fundamental kinetic equation of non-equilibrium statistical mechanics. It was derived by Boltzmann in 1872 and describes the evolution of the single-particle distribution function.

Consider a gas of N identical particles. Then the single-particle distribution function $f(x, v, t)$ is defined in such a way that $f(x, v, t) dx dv$ is the number of particles located at time t in the $(x, v) - space$ element $dx dv$ around (x, v), normalized by

$$\int dx dv f(x, v, t) = N \tag{1.64}$$

For the derivation of the Boltzmann equation, we follow the motion of a volume element in $(x, v) - space$ during the time interval $[t, t + dt]$. The deformation of a volume element in $(x, v) - space$ is assumed to have a unit Jacobian. So if $dx^{'}dv^{'}$ is the deformed $(x, v) - space$ element then $dxdv = dx^{'}dv^{'}$.

The number of particles at time t in $dxdv$ is $f(x, v, t)dxdv$ and the number of particles in the volume element $dx^{'}dv^{'}$ which develops after the time interval dt is $f(x + vdt, v + \frac{1}{m}Fdt, t + dt)dx^{'}dv^{'}$. If the gas particles were assumed collision free then these two numbers would be the same. A change in these particle numbers can only occur through collisions. We thus obtain:

$$[f(x + vdt, v + \frac{1}{m}Fdt, t + dt) - f(x, v, t)]dxdv = \frac{\partial f}{\partial t}|_{coll}dtdxdv \tag{1.65}$$

i.e the change in the particle number is equal to the change due to collisions. The expansion of the balance equation yields

$$[\frac{\partial}{\partial t} + v\nabla_x + \frac{1}{m}F(x)\nabla_v]f(x, v, t) = \frac{\partial f}{\partial t}|_{coll} \tag{1.66}$$

The collision term in the right side of this equation can be represented as the difference of gain and loss processes.

$$\frac{\partial f}{\partial t}|_{coll} = G - L \tag{1.67}$$

Thus $Gdxdv$ is the number of particles scattered during the time interval dt into the volume $dxdv$ by collisions and $Ldxdv$ is the number of particles scattered out of the volume $dxdv$ during the same time interval.

The following expression is the celebrated Stosszahlansatz (assumption regarding the number of collisions)

$$\frac{\partial f}{\partial t}|_{coll} = \int dv_2dv_3dv_4W(v, v_2; v_3, v_4)[f(x, v_3, t)f(x, v_4, t) - f(x, v, t)f(x, v_2, t)] \tag{1.68}$$

$W(v, v_2; v_3, v_4)$is the transition probability $v, v_2 \rightarrow v_3, v_4$,i.e the probability that in a collision of two particles with the velocities v, v_2 the velocities of those two particles will be v_3, v_4 afterwards.

The Stosszahlansatz together with the balance equation, yields the Boltzmann equation

$$\begin{gathered}[\frac{\partial}{\partial t} + v\nabla_x + \frac{1}{m}F(x)\nabla_v]f(x, v, t) = \\ \int dv_2 \int dv_3 \int dv_4W(v, v_2; v_3, v_4)[f(x, v_3, t)f(x, v_4, t) - f(x, v, t)f(x, v_2, t)]\end{gathered} \tag{1.69}$$

The transition probability $W(v, v_2; v_3, v_4)$ has many symmetry properties

- Invariance under particle exchange:

$W(v, v_2; v_3, v_4) = W(v_2, v; v_4, v_3)$

- Rotational and reflection invariance:

$W(Dv, Dv_2; Dv_3, Dv_4) = W(v, v_2; v_3, v_4)$ for an orthogonal matrix D

The inversion symmetry is contained in this relation:

$W(-v, -v_2; -v_3, -v_4) = W(v, v_2; v_3, v_4)$

- Time-inverse invariance:

$W(v, v_2; v_3, v_4) = W(-v_3, -v_4; -v, -v_2)$ The combination inversion and time reversal yields the relation which we have already used $W(v_3, v_4; v, v_2) = W(v, v_2; v_3, v_4)$

1.6 The Boltzmann's H-Theorem

We are now in position to answer the question, why Boltzmann's equation shows irreversible behavior. We will actually derive the second law of thermodynamics following the steps of the famous H theorem that was derived by Boltzmann in 1872.

As is well known the second law claims the existence of a state function, that bears the name entropy, that is not conserved. Rather it can only increase in time during the evolution of an isolated system. When the system reaches equilibrium this increase stops and at that point the entropy attains its maximum value.

Firstly, we introduce the quantity H which is related to the negative of the entropy :

$$H(x,t) = \int d^3v f(x,v,t) \log f(x,v,t) \tag{1.70}$$

We take the time derivative of H and make use of the Boltzmann equation

$$\begin{aligned} \dot{H}(x,t) &= \int d^3v (1 + \log f) \dot{f} \\ &= -\int d^3v (1 + \log f)(v\nabla_x + \frac{1}{m} F \nabla_v) f - I \\ &= -\nabla_x \int d^3v (f \log f) v - I \end{aligned} \tag{1.71}$$

The second term in the large brackets in the last line is proportional to $\int d^3v \nabla_v (f \log f)$ and vanishes, since there are no particles with infinite velocities, i.e $f \to 0$ for $v \to \infty$.

The collision term is

$$I = \int d^3v_1 d^3v_2 d^3v_3 d^3v_4 W(v_1, v_2; v_3, v_4)(f_1 f_2 - f_3 f_4)(1 + \log f_1) \tag{1.72}$$

and becomes by making use of the invariance of W with respect to the exchanges $1,3 \leftrightarrow 2,4$ and $1,2 \leftrightarrow 3,4$

$$I = \frac{1}{4}\int d^3v_1 d^3v_2 d^3v_3 d^3v_4 W(v_1, v_2; v_3, v_4)(f_1f_2 - f_3f_4)\log\frac{f_1f_2}{f_3f_4} \tag{1.73}$$

We note that $(x-y)\log\frac{x}{y} \geq 0$ for $x \geq y$ so it follows that $I \geq 0$.
The time derivative of the H can be written in the form

$$\dot{H}(x,t) = -\nabla_x j_H(x,t) - I \tag{1.74}$$

where $j_H = \int d^3v f \log f v$ is the current density.

The first term on the right hand side of 1.74 gives the change in H due to the entropy flow and the second gives the change in H due to entropy production.

Discussion:
a)If no external forces are present, $F(x) = 0$, then the simplified situation may occur that $f(x,v,t) = f(v,t)$ is independent of x. Thus 1.74 becomes (since $\nabla_x j_H(x,t) = 0$) $\dot{H} = -I \leq 0$
The quantity H decreases and tends towards a minimum which is finite since $f\log f$ has a lower bound and the integral over v exists (see appendix).
b)If $F(x) \neq 0$ and we are dealing with a closed system of volume V, then
$\int_V d^3x \nabla_x j_H(x,t) = \int_{O(V)} dO j_H(x,t) = 0$ holds
The flux of H through the surface of this volume vanishes if the surface is an ideal reflector;then for each contribution $-vdO$ there is a corresponding contribution vdO and it follows that.

$$\frac{d}{dt}H_{tot} \equiv \frac{d}{dt}\int_V d^3x H(x,t) = -\int_V d^3x I \leq 0 \tag{1.75}$$

H_{tot} decreases and we have irreversibility.The fact that irreversibility follows from an equation derived from Newtonian mechanics, which itself is time-reversal invariant, was met at first with skepticism.However, the Stosszahlansatz contains a probabilistic element that makes the difference.

1.7 Topics on Irreversibility

1.7.1 Poincare Recurrence Theorem

Theorem:The system trajectory of a bounded isolated system of finite energy will, after sufficient time, return arbitrarily close to its initial location in Γ-space
Proof:Let $z \equiv (q_0, p_0)$ be the initial state in the phase space Γ, which is contained in a set Ω_0 of measure $m(\Omega_0) > 0$ ($z \in \Omega_0$. Let also $\hat{T}$ denote an operator of the

displacement/unit time.
Due to Liouville's theorem

$$m(\Omega_0) = m(\hat{T}\Omega_0) = m(\hat{T}(\hat{T}\Omega_0)) \equiv m(\hat{T}^2\Omega_0) \tag{1.76}$$

and if those sets $(\Omega_0, \hat{T}\Omega_0, \hat{T}^2\Omega_0, ...)$ do not intersect then the space on which they move would have to be of infinite measure. This contradicts our assumption, so

$$\exists k, n \in N : \hat{T}^k\Omega_0 \cap \hat{T}^n\Omega_0 \neq \emptyset \tag{1.77}$$

Since $\hat{T}$ is a one-to-one mapping due to uniqueness of trajectories we have

$$\hat{T}(A \cap B) = \hat{T}(A) \cap \hat{T}(B) \forall A, B \in \Gamma \tag{1.78}$$

so applying $\hat{T}^{-n}$ to 1.77 we get

$$\hat{T}^{-n}(\hat{T}^k\Omega_0 \cap \hat{T}^n\Omega_0) \neq \emptyset \tag{1.79}$$

or

$$\hat{T}^{k-n}\Omega_0 \cap \Omega_0 \neq \emptyset \tag{1.80}$$

and letting $m(\Omega_0)$ be arbitrarily small establishes the theorem.

1.7.2 Recurrence Time

Zermelo (1896) based his criticism of the Boltzmann equation on Poincare's recurrence-time theorem. It states that a closed finite conservative system will return arbitrarily closely to its initial configuration within a finite time, called the recurrence time τ_p. According to Zermelo's paradox, $H(t)$ could not decrease monotonically, but instead must finally again increase and regain its value $H(0)$.

We are now going to estimate the recurrence time with the aid of a model to adjudge this objection. The system we are going to use is the one of classical harmonic oscillators with displacements q_n, moment p_n and the Hamiltonian

$$H = \sum_{n=1}^{N} \{ \frac{1}{2m} p_n^2 + \frac{m\Omega^2}{2}(q_n - q_{n-1})^2 \} \tag{1.81}$$

The equations of motion are then obtained:

$$\dot{p}_n = m\ddot{q}_n = m\Omega^2(q_{n+1} + q_{n-1} - 2q_n) \tag{1.82}$$

Assuming periodic boundary conditions $q_0 = q_N$, we are dealing with a translationally invariant problem, which is diagonalized by the Fourier transformation

$$q_n = \frac{1}{(mN)^{1/2}} \sum_s e^{isn} Q_s, p_n = (\frac{m}{N})^{1/2} \sum_s e^{-isn} P_s \tag{1.83}$$

Q_s and P_s are called the normal coordinates (and momenta). The periodic boundary conditions require that $1 = e^{isN}$ i.e $s = \frac{2\pi l}{N}$ with integral l. A possible choice of the values l, e.g for odd N would be: $l = 0, \pm 1, ..., \pm(N-1)/2$. Since q_n and p_n are real, it follows that
$Q_s^* = Q_{-s}$ and $P_s^* = P_{-s}$

The Fourier coefficients obey the orthogonality relations

$$\frac{1}{N}\sum_{n=1}^{N} e^{isn}e^{-is^{'}n} = \Delta(s - s^{'}) \tag{1.84}$$

and the completeness relation

$$\frac{1}{N}\sum_{s} e^{-isn}e^{isn^{'}} = \delta_{nn^{'}} \tag{1.85}$$

Insertion of the transformation to normal coordinates yields

$$H = \frac{1}{2}\sum_{s}(P_sP_s^* + \omega_s^2 Q_sQ_s^*) \tag{1.86}$$

with dispersion relation

$$\omega_s = 2\Omega(\sin\frac{1}{2}) \tag{1.87}$$

The motion of normal coordinates can be represented most intuitively by introducing complex vectors

$$Z_s = P_s + i\omega_s Q_s \tag{1.88}$$

which move on a unit circle according to

$$Z_s = a_s e^{i\omega t} \tag{1.89}$$

with complex amplitude a_s

Assuming that the frequencies ω_s of $N-1$ such normal coordinates are incommensurate, i.e their ratios are not natural numbers. Then the phase vectors Z_s rotate independently of one another, without coincidences. We now want to calculate how much time passes until all N vectors lie within an interval $\Delta\phi$ around their initial positions. The probability that Z_s lies within $\Delta\phi$ is given by $\frac{\Delta\phi}{2\pi}$ and the probability that all $N-1$ vectors lie within this interval is $(\frac{\Delta\phi}{2\pi})^{N-1}$. The number of rotations required for this recurrence is therefore $(\frac{2\pi}{\Delta\phi})^{N-1}$. The recurrence time can now be easily found by multiplying by the typical rotational period $\frac{1}{\omega}$:
Thus, $\tau_p \simeq (\frac{2\pi}{\Delta\phi})^{N-1}\frac{1}{\omega}$
Taking $\Delta\phi = \frac{2\pi}{100}, N = 10$ and $\omega = 10Hz$, we obtain $\tau_p \simeq 10^{12}$ years, i.e more than the age of the Universe. These times of course becomes much longer if we consider a macroscopic system with $N \simeq 10^{20}$. Thus, the recurrence time in practice plays no role. We have thereby eliminated Zermelo's paradox.

Chapter 2

Statistical Mechanics of Transport Phenomena(Kirkwood's paper)

2.1 Abstract

We are following closely the lines of Kirkwoods IV (STM IV)publication in the area of Statistical mechanics that bears the name "The equations of Hydrodynamics".In the first section we are presenting the equations of hydrodynamics (namely the continuity equation and the momentum and heat transport equations) derived in the phenomenological theory and go on with basic definitions in Statistical mechanics that are essential for the development.In the next three sections we are concerned with the derivation of these hydrodynamic equations by means of classical Statistical mechanics and derive expressions for the stress tensor and heat current density in terms of molecular variables.Finally,in the last section a compilation of the results is performed.

2.2 Preliminaries

From continuum mechanics assumptions, letting $\rho(r,t)$ and $u(r,t)$ be the mass density and local velocity at the point r at time t respectively, then the equations of hydrodynamics take the form:

$$\frac{\partial}{\partial t}\rho(r,t) = -\nabla_r \cdot [\rho(r,t)u(r,t)] \tag{2.1}$$

$$\frac{\partial}{\partial t}[\rho u] + \nabla_r \cdot (\rho u u) = X + \nabla_r \cdot \sigma \tag{2.2}$$

$$\frac{\partial}{\partial t}E + \nabla_r \cdot [Eu + q - u \cdot \sigma] = 0 \tag{2.3}$$

where $X(r,t)$ is the force/unit volume due to external sources, $\sigma(r,t)$ the stress tensor, $E(r,t)$ the total internal energy density consisting of three parts, the interaction potential energy density $E_v(r,t)$; the kinetic energy density $E_k(r,t)$; and the potential energy density $E_\psi(r,t)$ due to external sources assumed to be conservative. Thus $E = E_v + E_k + E_\psi$. Moreover, Eu is the convective energy current and q is the conductive heat current...

For a phenomenological derivation of hydrodynamics equations see [...]. A more abstract and mathematically speaking 'formal' derivation is presented in [...]

Now let's shift to the statistical mechanical theory and consider a system consisting of N molecules. The instantaneous state of the system may be represented by a point in the $6N$-dimensional Gibb's phase space, representing the $3N$ coordinates and $3N$ momenta of the system. The probability distribution function is $f(R_1, R_2, ..., R_N; p_1, p_2, ..., p_N; t)$ properly normalized by

$$\int ... \int_{6N-fold} f(R_1, ..., R_N; p_1, ..., p_N; t) dR_1 ... dR_N dp_1 ... dp_N = 1 \tag{2.4}$$

where R_i and p_i are the position and momentum of the i'th molecule. The evolution of f is characterized by the Liouville equation

$$\frac{\partial f}{\partial t} = \sum_{k=1}^{N} [-\frac{p_k}{m_k} \cdot \nabla_{R_k} f + \nabla_{R_k} U \cdot \nabla_{p_k} f] \tag{2.5}$$

(We note here that $\dot{R}_k = \frac{1}{m_k} p_k$ and $\dot{p}_k = -\nabla_{R_k} U$ where U is the potential energy of the system.)

If $\alpha(R_1, ...R_N; p_1, ..., p_N)$ is any time independent dynamical variable then its expectation value is

$$\langle \alpha; f \rangle = \int ... \int_{6N-fold} \alpha(R_1, ..., R_N; p_1, ...p_N) f(R_1, ..., R_N; p_1, ..., p_N; t) dR_1 ... dR_N dp_1 ... dp_N \tag{2.6}$$

The rate of change of the expectation value of α is

$$\begin{aligned} \frac{\partial}{\partial t}\langle \alpha; f \rangle = \langle \alpha; \frac{\partial}{\partial t} f \rangle &= \sum_{k=1}^{N} [\langle \alpha; -\frac{p_k}{m_k} \cdot \nabla_{R_k} f \rangle + \langle \alpha; \nabla_{R_k} U \cdot \nabla_{p_k} f \rangle] \\ &= \langle \sum_{k=1}^{N} [\frac{p_k}{m_k} \cdot \nabla_{R_k} \alpha - \nabla_{R_k} U \cdot \nabla_{p_k} \alpha]; f \rangle \end{aligned} \tag{2.7}$$

Finally,

$$\frac{\partial}{\partial t}\langle\alpha; f\rangle = \sum_{k=1}^{N}\langle\frac{p_k}{m_k}\cdot\nabla_{R_k}\alpha - \nabla_{R_k}U\cdot\nabla_{p_k}\alpha; f\rangle \tag{2.8}$$

is the general equation of change needed for the derivation of the equations of hydrodynamics.

We will focus in expressing the mass,momentum and energy density as the expectation values of certain dynamical variables over an ensemble having distribution function f.

The probability/unit volume that the kth molecule be at R_k is

$$\int\ldots\int_{6N-3fold} f(R_1,...,R_N;p_1,...,p_N;t)dR_1...dR_{k-1}dR_{k+1}...dR_N dp_1...dp_N \tag{2.9}$$

similarly the probability/unit volume that the kth molecule be at r is

$$\langle\delta(R_k-r);f\rangle = \int\ldots\int_{6N-fold}\delta(R_k-r)f(R_1,...,R_N,;p_1,...,p_N;t)dR_1...dR_N dp_1...dp_N \tag{2.10}$$

Next we give the expressions of the densities as expectation values.

$$\rho(r,t) = \sum_{k=1}^{N} m_k\langle\delta(R_k-r);f\rangle \tag{2.11}$$

$$\rho(r,t)u(r,t) = \sum_{k=1}^{N}\langle p_k\delta(R_k-r);f\rangle \tag{2.12}$$

$$E_k(r,t) = \sum_{k=1}^{N}\langle\frac{p_k^2}{2m_k}\delta(R_k-r);f\rangle \tag{2.13}$$

If we recall the fact that the probability /unit volume that the kth molecule be at r at time t is $\langle\delta(R_k-r);f\rangle$ then particle k contributes to the total mass density at point r and time t,only if it is located at point r at time t and thus the first equation establishes itself.

The mean momentum of the kth molecule,providing it is at r and the location of the others are unspecified,is given by the ratio

$$\frac{\langle p_k\delta(R_k-r);f\rangle}{\langle\delta(R_k-r);f\rangle} \tag{2.14}$$

so as $\langle p_k\delta(R_k-r);f\rangle$ is the product of the mean momentum of the k'th molecule by the probability/unit volume that the k'th molecule be at r and the second equation is derived.The last one is obtained along the same lines of reasoning. The potential energy of the system can be written as

$$U = \sum_{k=1}^{N} \psi_k(R_k) + \frac{1}{2}\sum\sum_{j \neq k} V_{jk} \tag{2.15}$$

where $\psi_k(R_k)$ is the potential energy of the kth molecule due to an external field of force and V_{jk} is the mutual potential between the jth and kth molecules. The potential energy density at r is

$$E_\psi(r;t) = \sum_{k=1}^{N} \langle [\psi_k(R_k)]\delta(R_k - r); f\rangle = \sum_{k=1}^{N} \psi_k(r)\langle \delta(R_k - r); f\rangle \tag{2.16}$$

and the external force/unit volume at r is

$$X(r;t) = -\sum_{k=1}^{N} \langle [\nabla_{R_k}\psi_k(R_k)\delta(R_k - r); f\rangle = -\sum_{k=1}^{N} [\nabla_r \psi_k(r)]\langle \delta(R_k - r); f\rangle \tag{2.17}$$

If we assume the V_{jk} such that the total interaction potential energy residing in the kth molecule is $\frac{1}{2}\sum_{j=1,j\neq k}^{N} V_{jk}$ then the total interaction potential energy at r is

$$E_V(r;t) = \frac{1}{2}\sum\sum_{j \neq k} \langle V_{jk}\delta(R_k - r); f\rangle. \tag{2.18}$$

Finally, we define the pair density $\rho^{(2)}(r;r^{'};t)$ as the probability/unit volume that any molecule be at r and another at r'. So

$$\rho^{(2)}(r;r^{'};t) = \sum\sum_{j \neq k} \langle \delta(R_j - r)\delta(R_k - r^{'}); f\rangle \tag{2.19}$$

and the particle current density in pair space as

$$j^{(2)}(r;r^{'};t) = \sum\sum_{k \neq i} \langle \frac{p_k}{m_k} \oplus \frac{p_i}{m_i})\delta(R_k - r)\delta(R_i - r^{'}); f\rangle, \tag{2.20}$$

namely a six-component vector and its projection onto the space of its first argument as

$$j_1^{(2)}(r;r^{'};t) = \sum\sum_{k \neq i} \langle \frac{p_k}{m_k}\delta(R_k - r)\delta(R_i - r^{'}); f\rangle \tag{2.21}$$

We now set forth to give the formal expressions of the various parts of the stress tensor and heat current by means of statistical mechanics.

2.3 The Equation of Continuity

Taking $\alpha = \sum_{j=1}^{N} m_j \delta(R_j - r)$
We calculate

$$\frac{p_k}{m_k} \cdot \nabla_{R_k} \alpha - \nabla_{R_k} U \cdot \nabla_{p_k} \alpha = -\nabla_r \cdot [p_k \delta(R_k - r)] \tag{2.22}$$

and indeed get

$$\frac{\partial}{\partial t} \rho(r;t) = \frac{\partial}{\partial t} \langle \alpha; f \rangle = -\nabla_r \cdot [\rho(r;t) u(r;t)] \tag{2.23}$$

2.4 The Momentum Transport Equation and the Stress Tensor

This time taking $\alpha = \sum_{j=1}^{N} p_j \delta(R_j - r)$ we have

$$\frac{p_k}{m_k} \cdot \nabla_{R_k} \alpha - \nabla_{R_k} U \cdot \nabla_{p_k} \alpha = -\nabla_r \cdot [\frac{p_k p_k}{m_k} \delta(R_k - r)] - (\nabla_{R_k} U) \delta(R_k - r) \tag{2.24}$$

We recall that $U = \sum_{k=1}^{N} \psi_k(R_k) + \frac{1}{2} \sum_{j \neq k} \sum V_{jk}$ so

$$(\nabla_{R_k} U = \nabla_{R_k} \psi_k(R_k) + \sum_{j=1, j \neq k}^{N} \nabla_{R_k} V_{jk}) \tag{2.25}$$

and

$$\begin{aligned} \frac{\partial}{\partial t} [\rho(r;t) u(r;t)] = -\nabla_r \cdot \sum_{k=1}^{N} \langle \frac{p_k p_k}{m_k} \delta(R_k - r); f \rangle + X(r;t) \\ - \sum \sum_{j \neq k} \langle (\nabla_{R_k} V_{jk}) \delta(R_k - r); f \rangle \end{aligned} \tag{2.26}$$

We note that

$$\begin{aligned} \sum_{k=1}^{N} m_k \langle (\frac{p_k}{m_k} - u)(\frac{p_k}{m_k} - u) \delta(R_k - r); f \rangle = \\ ... = \sum_{k=1}^{N} \langle \frac{p_k p_k}{m_k} \delta(R_k - r); f \rangle - \rho u u \end{aligned} \tag{2.27}$$

The last term of 2.26 is

$$- \sum \sum_{j \neq k} \langle (\nabla_{R_k} V_{jk}) \delta(R_k - r); f \rangle =$$

$$... = \nabla_r \cdot [\frac{1}{2}\sum\sum_{j\neq k}\langle(\nabla_{R_k}V_{jk})R_{jk}\{1-\frac{1}{2}R_{jk}\cdot\nabla_r+...+\frac{1}{n!}(-R_{jk}\cdot\nabla_r)^{n-1}+...\}\delta(R_j-r);f\rangle] \tag{2.28}$$

Finally we get

$$\frac{\partial}{\partial t}[\rho u]+[\nabla_r\cdot\rho uu] = X+\nabla_r\cdot[-\sum_{k=1}^{N}m_k\langle(\frac{p_k}{m_k}-u)(\frac{p_k}{m_k}-u)\delta(R_k-r);f\rangle$$

$$+\frac{1}{2}\sum\sum_{j\neq k}\langle(\nabla_{R_k}V_{jk})R_{jk}\{1-\frac{1}{2}R_{jk}\cdot\nabla_r+...+\frac{1}{n!}(-R_{jk}\cdot\nabla_r)^{n-1}+...\}\delta(R_j-r);f\rangle] \tag{2.29}$$

Now we restrict ourselves to identical particles of mass m and use the assumption that $V_{jk}=V(R_{jk})$ and

$$\nabla_{R_k}V_{jk}=\frac{R_{jk}}{|R_{jk}|}V^{'}(|R_{jk}|) \tag{2.30}$$

The kinetic and intermolecular parts of the stress tensor are:

$$\sigma_k(r;t) = -\sum_{k=1}^{N}m\langle(\frac{p_k}{m_k}-u)(\frac{p_k}{m_k}-u)\delta(R_k-r);f\rangle \tag{2.31}$$

$$\sigma_v(r;t)=\frac{1}{2}\sum\sum_{j\neq k}\langle\frac{R_{jk}R_{jk}}{|R_{jk}|}V^{'}(|R_{jk}|)\{1-\frac{1}{2}R_{jk}\cdot\nabla_r+...+\frac{1}{n!}(-R_{jk}\cdot\nabla_r)^{n-1}+...\}\delta(R_j-r);f\rangle \tag{2.32}$$

the last one may be contracted in

$$\sigma_v(r;t)=\frac{1}{2}\int_{3-fold}\frac{RR}{|R|}V^{'}(|R|)\{1-\frac{1}{2}R\cdot\nabla_r+...+\frac{1}{n!}(R\cdot\nabla_r)^{n-1}+...\}\rho^{(2)}(r,r+R;t)dR \tag{2.33}$$

It is now the appropriate time to comment on the interpretation of σ_k and σ_v from a phenomenological approach.
At first σ_k is the kinetic contribution to the stress tensor and $\sigma_k\cdot dS$ is the force acting across dS due to the spread of the fluid velocities about the mean fluid velocity u.On the other hand σ_v is the contribution of intermolecular forces to the stress tensor and $\sigma_v\cdot dS$ is the force acting across dS due to interactions of molecules on opposite sides of dS.The σ_k term is dominant in gases and the σ_v one in liquids.
The pair density can be expressed by means of the correlation function, namely $g^{(2)}$ for a liquid with identical particles. Thus

$$\rho^{(2)}(r,r+R;t)=\frac{1}{m^2}\rho(r;t)\rho(r+R;t)g^{(2)}(r,R;t) \tag{2.34}$$

Taking into account the fact that the function $\rho(r;t)$ is slowly varying with respect to R then the last equation takes the form (when we neglect all but the first term of the Taylor series)

$$\sigma_v(r;t) = \frac{[\rho(r;t)]^2}{2m} \int \frac{RR}{|R|} V'(|R|) g^{(2)}(r;R;t) dR \tag{2.35}$$

The pressure is obtained by taking the diagonal sum of the stress tensor

$$P = -\frac{1}{3} Trace\sigma \tag{2.36}$$

and taking in consideration the formulas

$$-\frac{1}{3} Trace\sigma_k = \frac{2}{3} \sum_{k=1}^{N} \langle \frac{m}{2} |\frac{p_k}{m} - u|^2 \delta(R_k - r); f\rangle \tag{2.37}$$

$$-\frac{1}{3} Trace\sigma_v = -\frac{[\rho(r;t)]^2}{6m^2} \int_{fold} |R| V'(|R|)(|R|) g^{(2)}(r;R;t) dR \tag{2.38}$$

The equilibrium pressure obtained is

$$P_{eq} = \frac{\rho}{m} KT - \frac{2\pi}{3} (\frac{\rho}{m})^2 \int R^3 V'(|R|) g^{(2)}(R) dR \tag{2.39}$$

2.5 The Energy Transport Equation and the Heat Current Density(Heat Flux Vector)

For $\alpha = \sum_{j=1}^{N} \frac{p_j^2}{2m_j} \delta(R_j - r)$ then $E_k(r;t) = \langle \alpha; f\rangle$

$$\frac{p_k}{m_k} \cdot \nabla_{R_k} \alpha - \nabla_{R_k} U \cdot \nabla_{p_k} \alpha = \dots = -\nabla_r \cdot [\frac{p_k^2}{2m_k} \frac{p_k}{m_k} \delta(R_k - r)]$$

$$-[\nabla_{R_k} \psi_k(R_k) + \sum_{j=1, j\neq k}^{N} \nabla_{R_k} V_{jk}] \cdot \frac{p_k}{m_k} \delta(R_k - r) \tag{2.40}$$

So

$$\frac{\partial}{\partial t} E_k(r;t) = -\nabla_r \cdot \sum_{k=1}^{N} \langle \frac{p_k^2}{2m_k} \frac{p_k}{m_k} \delta(R_k - r); f\rangle - \sum_{k=1}^{N} [\nabla_r \psi_k(r)] \cdot \langle \frac{p_k}{m_k} \delta(R_k - r); f\rangle$$

$$-\sum \sum_{j\neq k} \langle (\nabla_{R_k} V_{jk}) \cdot \frac{p_k}{m_k} \delta(R_k - r); f\rangle \tag{2.41}$$

For $\alpha = \sum_{j=1}^{N} \psi_j(r)\delta(R_j - r)$

$$\frac{p_k}{m_k} \cdot \nabla_{R_k}\alpha - \nabla_{R_k}U \cdot \nabla_{p_k}\alpha = -\psi_k(r)\nabla_r \cdot [(\frac{p_k}{m_k})\delta(R_k - r)] \tag{2.42}$$

and

$$\frac{\partial}{\partial t}E_\psi(r;t) = -\sum_{k=1}^{N} \psi_k(r)\nabla_r \cdot \langle \frac{p_k}{m_k}\delta(R_k - r); f\rangle \tag{2.43}$$

Finally for $\alpha = \frac{1}{2}\sum\sum_{i\neq j} V_{ij}\delta(R_j - r)$ then $E_v(r;t) = \langle \alpha; f\rangle$ and

$$\frac{p_k}{m_k} \cdot \nabla_{R_k}\alpha - \nabla_{R_k}U \cdot \nabla_{p_k}\alpha$$

$$= \frac{p_k}{2m_k} \cdot \sum_{j=1\neq k}^{N} (\nabla_{R_k}V_{jk})[\delta(R_j - r) + \delta(R_k - r)] - \frac{1}{2}\nabla_r \cdot [\sum_{j=1\neq k}^{N} V_{jk}\frac{p_k}{m_k}\delta(R_k - r)]$$

$$\frac{\partial}{\partial t}E_v(r;t) = \frac{1}{2}\sum\sum_{j\neq k}\langle (\nabla_{R_k}V_{jk}) \cdot \frac{p_k}{m_k}[\delta(R_j - r) + \delta(R_k - r)]; f\rangle$$

$$-\frac{1}{2}\nabla_r \cdot [\sum\sum_{j\neq k}\langle V_{jk}\frac{p_k}{m_k}\delta(R_k - r); f\rangle] \tag{2.44}$$

Adding the expressions for the various types of energies and the term $\nabla_r \cdot (Eu)$ we get

$$\begin{aligned}\frac{\partial}{\partial t}R(r,t) + \nabla_r \cdot (Eu) = -\nabla_r \cdot [&\sum_{k=1}^{N}\langle \frac{p_k^2}{2m_k}(\frac{p_k}{m_k} - u)\delta(R_k - r); f\rangle \\ &+\sum_{k=1}^{N}\psi_k(r)\langle (\frac{p_k}{m_k} - u)\delta(R_k - r); f\rangle \\ &+\frac{1}{2}\sum\sum_{j\neq k}\langle V_{jk}(\frac{p_k}{m_k} - u)\delta(R_k - r); f\rangle] \\ +\frac{1}{2}\sum\sum_{j\neq k}\langle (\nabla_{R_k}V_{jk}) \cdot \frac{p_k}{m_k}&[\delta(R_j - r) - \delta(R_k - r)]; f\rangle\end{aligned} \tag{2.45}$$

The time has come to go on with the development under the assumption of a single component,single phase system.Another assumption used is that of the central intermolecular forces depending range.

Under the above assumption the second term on the right of the above equation vanishes and to reveal the form of the hydrodynamic equation of energy we need a definition of the heat current density ($q(r,t)$) which must satisfy:

$$\begin{aligned}\nabla_r\cdot(q-u\cdot\sigma)=\nabla_r\cdot[&\sum_{k=1}^{N}\langle\frac{p_k^2}{2m}(\frac{p_k}{m}-u)\delta(R_k-r);f\rangle\\ &+\frac{1}{2}\sum_{j\neq k}\sum\langle V(R_{kj})(\frac{p_k}{m}-u)\delta(R_k-r);f\rangle]\\ \frac{1}{2}\sum_{j\neq k}\sum\langle\frac{V^{'}(R_{kj})}{R_{kj}}R_{kj}\cdot\frac{p_k}{m}&[\delta(R_j-r)-\delta(R_k-r)];f\rangle\end{aligned}\tag{2.46}$$

In the last equation ,use has been made of the relations:
$V_{jk}=V(|R_{jk}|)$ and

$$\nabla_{R_k}V_{jk}=\frac{R_{jk}}{|R_{jk}|}V^{'}(|R_{jk}|)=-\frac{R_{kj}}{|R_{kj}|}V^{'}(|R_{jk}|)\tag{2.47}$$

Expressions for the heat current density finally obtained are

$$\begin{aligned}q_k(r;t)&=\sum_{k=1}^{N}\langle\frac{m}{2}|\frac{p_k}{m_k}-u|^2(\frac{p_k}{m_k}-u)\delta(R_k-r);f\rangle\\ q_V(r,t)&=u\cdot[\sigma_V-\frac{1}{2}\sum_{j\neq k}\sum\langle V(|R_{kj}|)1\delta(R_k-r);f\rangle]\\ &+\frac{1}{2}\sum_{j\neq k}\sum\langle[V(|R_{kj}|)1-\frac{V^{'}(|R_{kj}|)}{|R_{kj}|}R_{kj}R_{kj}\{1+...\\ &+\frac{1}{n!}(-R_{kj}\cdot\nabla_r)^{n-1}+...\}]\cdot\frac{p_k}{m}\delta(R_k-r);f\rangle\end{aligned}\tag{2.48}$$

We will go on writing various equivalent relations for the last term in order to involve the pair density and particle current density in pair space.So

$$\begin{aligned}q_V(r,t)=u\cdot[\sigma_V-\frac{1}{2}\sum_{j\neq k}\sum\langle\int_{3-fold}\delta(R_{kj}-r)\\ \times V(|R|)1\delta(R_k-r)dR;f\rangle]+\frac{1}{2}\sum_{j\neq k}\sum\langle\int_{3-fold}\delta(R_{kj}-R)\\ \times[V(|R|)1-\frac{V^{'}(|R|)}{|R|}RR\{1+...\\ \frac{1}{n!}(-R\cdot\nabla_r)^{n-1}+...\}]\cdot\frac{p_k}{m}\delta(R_k-r)dR;f\rangle\end{aligned}$$

$$
\begin{aligned}
&= u \cdot [\sigma_V - \frac{1}{2}\int_{3-fold} V(|R|)1 \sum_{j\neq k}\sum \langle \delta(R_{kj} - R) \\
&\times \delta(R_{kj} - r); f\rangle dR] + \frac{1}{2}\int_{3-fold}[V(|R|)1 - \frac{RR}{|R|}V^{'}(|R|) \\
&\times\{1 - \frac{1}{2}R\cdot\nabla_r + ... + \frac{1}{n!}(-R\cdot\nabla_r)^{n-1} + ...\}] \\
&\cdot[\sum_{j\neq k}\sum \frac{p_k}{m}\delta(R_{kj} - R)\delta(R_k - R); f\rangle]dR \\
&= -\frac{1}{2}u(r,t)\cdot\int_{3-fold}[V(|R|)1 - \frac{RR}{|R|}V^{'}(|R|)\{1 - \frac{1}{2}R\cdot\nabla_r \\
&+ ... + \frac{1}{n!}(-R\cdot\nabla_r)^{n-1} + ...\}]\rho^{(2)}(r, r+R, t)dR \\
&+\frac{1}{2}\int_{3-fold}[V(|R|)1 - \frac{RR}{|R|}V^{'}(|R|)\{1 - \frac{1}{2}R\cdot\nabla_r + ... \\
&+\frac{1}{n!}(-R\cdot\nabla_r)^{n-1} + ...\}]\cdot j_1^{(2)}(r, r+R, t)dR
\end{aligned} \tag{2.49}
$$

Finally,taking in consideration the fact that $\rho^{(2)}$ and $j_1^{(2)}$ are slow functions of r,we may neglect all but the first order's terms and get the expression

$$
q_v(r;t) = \frac{1}{2}\int_{3-fold}[V(|R|)1 - \frac{RR}{|R|}V^{'}(|R|)]\cdot[j^{(2)}(r, r+R; t) - u(r;t)\rho^{(2)}(r, r+R; t)]dR \tag{2.50}
$$

2.6 Compilation of Results

The various quantities that appear in the hydrodynamic equations and that have been defined or obtained are:

- The mass density at r

$$
\rho(r,t) = \sum_{k=1}^{N} m_k\langle\delta(R_k - r); f\rangle \tag{2.51}
$$

- The fluid velocity at r

$$
u(r,t) = \frac{1}{\rho(r,t)}\sum_{k=1}^{N}\langle p_k\delta(R_k - r); f\rangle \tag{2.52}
$$

- Body force/unit volume due to external fields at r

$$
X(r,t) = -\sum_{k=1}^{N}[\nabla_r\psi_k(r)]\langle\delta(R_k - r); f\rangle \tag{2.53}
$$

- Energy density at r

$$E(r,t) = E_k + E_\psi + E_V \tag{2.54}$$

- Kinetic Energy density

$$E_k(r,t) = \sum_{k=1}^{N} \langle \frac{p_k^2}{2m_k} \delta(R_k - r); f \rangle \tag{2.55}$$

- Potential Energy density due to external fields

$$E_\psi(r,t) = \sum_{k=1}^{N} \psi_k(r) \langle \delta(R_k - r); f \rangle \tag{2.56}$$

- Potential Energy density due to molecular interaction

$$E_V(r,t) = \frac{1}{2} \sum \sum_{j \neq k} \langle V_{jk} \delta(R_k - r); f \rangle \tag{2.57}$$

Now comes the time to write down definitions for the single component,single phase system in which the intermolecular force depends on range only.Thus we define:

- The stress tensor at r

$$\sigma(r,t) = \sigma_k(r,t) + \sigma_V(r,t) \tag{2.58}$$

- The kinetic contribution to the stress tensor

$$\sigma_k = -\sum_{k=1}^{N} m \langle (\frac{p_k}{m} - u)(\frac{p_k}{m} - u) \delta(R_k - r); f \rangle \tag{2.59}$$

- The intermolecular contribution to the stress tensor

$$\sigma_V(r,t) = \frac{1}{2} \int_{3-fold} \frac{RR}{|R|} V^{'}(|R|) \{1 - \frac{1}{2} R \cdot \nabla_r + ... + \frac{1}{n!} (-R \cdot \nabla_r)^{n-1} + ...\} \rho^{(2)}(r, r+R, t) dR \tag{2.60}$$

- The heat current density at r

$$q(r,t) = q_k(r,t) + q_V(r,t) \tag{2.61}$$

- The heat current due to transport of thermal kinetic energy

$$q_k(r,t) = \sum_{k=1}^{N} \langle \frac{m}{2} |\frac{p_k}{m} - u|^2 (\frac{p_k}{m} - u) \delta(R_k - r); f \rangle \tag{2.62}$$

- The contribution to heat current density due to molecular interactions

$$\begin{aligned} q_V(r,t) = -\frac{1}{2}u(r,t)\cdot \int_{3-fold}[V(|R|)1 - \frac{RR}{|R|}V^{'}(|R|) \\ \times\{1-\frac{1}{2}R\cdot\nabla_r + ... + \frac{1}{n!}(-R\cdot\nabla_r)^{n-1} + ...\}] \\ \times\rho^{(2)}(r,r+R,t)dR + \frac{1}{2}\int_{3-fold}[V(|R|)1 - \frac{RR}{|R|}V^{'}(|R|) \\ \times\{1-\frac{1}{2}R\cdot\nabla_r + ... + \frac{1}{n!}(-R\cdot\nabla_r)^{n-1} + ...\}]\cdot j_1^{(2)}(r,r+R,t)dR \end{aligned} \tag{2.63}$$

Keeping in consideration the fact that $\rho^{(2)}$ and $j_1^{(2)}$ are slow functions of r (since R is fixed) then we can truncate higher than first order terms in the expressions for σ_V, q_V.The simplified expressions are thus

$$q_V(r,t) = \frac{1}{2}\int_{3-fold}[V(|R|)1 - \frac{RR}{|R|}V^{'}(|R|)]\cdot[j_1^{(2)}(r,r+R,t) - u(r,t)\rho^{(2)}(r,r+R,t)]dR$$

$$\sigma_V(r,t) = \frac{1}{2m^2}[\rho(r,t)]^2\int_{3-fold}\frac{RR}{|R|}V^{'}(|R|)g^{(2)}(r,r+R,t)dR \tag{2.64}$$

The definition of the correlation function $g^{(2)}$ is in

$$\rho^{(2)}(r,r+R,t) = \frac{1}{m^2}\rho(r,t)\rho(r+R,t)g^{(2)}(r,R,t) \tag{2.65}$$

Chapter 3

Static Mechanical Models and Equilibrium Properties of Polymer Molecules

3.1 Abstract

What makes the study of polymer molecular solutions so intense during the last decades is not only the blooming industrial interest for macromolecule properties but also the several ways by which they differ from small molecules treated in traditional kinetic theories of gases and liquids.
These are:
a)Great diversity in structure:Organic chemists have synthesized straight chain polymers, branched, closed-ring polymers e.t.c. Nowadays, research has primarily been focused in linear flexible polymers.
b)Molecular weight distribution: Polymer molecules have varying length and this "polydispersity" has enormous effect on the properties of their solutions.
c)Large number of internal degrees of freedom: Each polymer molecule is capable of existing in a huge number of configurations. Forces transmitted along the chain backbones are of specific interest in obtaining an expression for the stress tensor.

What must be kept in mind is that in the equilibrium state the calculations of the properties of polymer solutions are much easier and can involve more complex mechanical models, although nonequilibrium calculations which are of great rheological interest have been available only for extremely simple models (elastic dumbbells e.t.c)

3.2 The Freely Jointed Bead-Rod Chain Model(Kramer's Chain Model or Pearl Necklace Model)

We consider a freely jointed chain of N beads of mass m and friction coefficient ζ connected by $N-1$ rigid, massless rods of length α.

By means of equilibrium statistical mechanics one can obtain the configurational distribution function that the $i'th$ link is found to be within the range $d\theta_i d\phi_i$ about θ_i, ϕ_i. That is $\psi_{i,eq}(\theta_i, \phi_i)d\theta_i d\phi_i = \frac{1}{4\pi}\sin\theta_i d\theta_i d\phi_i$. This is done by assuming that the distribution function behaves as a 'random walk' distribution which is a quite good approximation.

Since each link can be taken to move independently of all the others, we can obtain the configurational distribution function:

$$\psi_{eq}(\theta^{N-1}, \phi^{N-1}) = \prod_{i=1}^{N-1} \psi_{i,eq} = (\frac{1}{4\pi})^{N-1} \prod_{i=1}^{N-1} \sin\theta_i \tag{3.1}$$

and the average value of a property $B(\theta^{N-1}, \phi^{N-1})$ that is a function of the internal degrees of freedom is

$$\langle B \rangle_{eq} = \int\int B\psi_{eq} d\theta^{N-1} d\phi^{N-1} \tag{3.2}$$

Example :Mean-Square End-to-End distance

First of all,an expression for the end-to-end vector is essential.So our expression will be

$$r = \sum_{i=1}^{N-1} a u_i \tag{3.3}$$

where the u_i is the unit vector in the direction of the $i'th$ link.The square end-to-end distance is

$$r^2 = (r \cdot r) = a^2 \sum_{i=1}^{N-1}\sum_{j=1}^{N-1}(u_i \cdot u_j) \tag{3.4}$$

So the average value of this mean end-to-end distance is

$$\langle r^2 \rangle_{eq} = a^2 \sum_i \sum_j \int\int (u_i \cdot u_j)\psi_{eq} d\theta^{N-1} d\phi^{N-1} \tag{3.5}$$

which after simple manipulation gives

$$\langle r^2 \rangle_{eq} = a^2 \sum_i \sum_j \delta_{ij} = a^2(N-1) \tag{3.6}$$

It has to be quoted,nevertheless that the excluded volume effect was not taken in consideration and if it is accounted the mean-square end-to-end distance will be increased.

3.3 The Freely Jointed Bead Spring Model

The main difference between a freely jointed bead-rod chain model and the freely jointed bead-spring one, is that rods have been replaced by springs and so there are no internal constraints. This is the most general linear mechanical model.

Each bead experiences a hydrodynamic drag force as it moves through the solvent and this force is customarily described by Stokes law. If the springs are taken to be Hookean it bears the special name Rouse chain or Rouse-Zimm chain model. This specific model although exhibits orientability and stretchability suffers from the disadvantage that the dumbbell can be practically extended to infinity. If one wishes to overcome this difficulty then he has to include finitely extensible springs (Warner, or "FENE" springs) where the lengths of the connector vectors cannot stretch to infinity.

The equilibrium configurational distribution function for the Rouse chain is shown in the sequel to be

$$\begin{aligned}\psi_{eq} &= (\frac{H}{2\pi KT})^{3(N-1)/2}\exp(-(\frac{H}{2KT})\sum_i(Q_i\cdot Q_i)) \\ &= \prod_{j=1}^{N-1}(\frac{H}{2\pi KT})^{3/2}\exp(-(\frac{H}{2KT})Q_j^2) \qquad (3.7)\end{aligned}$$

The mean square end-to-end distance can be found for the Rouse chain to be

$$\begin{aligned}\langle r^2\rangle_{eq} &= \int\sum_i\sum_j(Q_i\cdot Q_j)\psi_{eq}(Q_1,...,Q_{N-1})dQ^{N-1} \\ &= \sum_i\int Q_i^2\prod_{j=1}^{N-1}(\frac{H}{2\pi KT})^{\frac{3}{2}}e^{-(H/2KT)Q_j^2}dQ^{N-1} \\ &= \sum_i(\frac{H}{2\pi KT})^{\frac{3}{2}}4\pi\int_0^\infty Q_i^2e^{-(H/2KT)Q_i^2}Q_i^2dQ_i \\ &= \frac{3(N-1)KT}{H} \qquad (3.8)\end{aligned}$$

3.4 Geometric Properties of Chainlike Molecules

We have to introduce some notation for the study of the general bead-rod or bead-spring chains that consist of N identical beads joined together linearly by $N-1$ connectors. No specific constraints will be used for this kind of development.

Starting we specify location of bead ν by means of the position vector r_ν with respect to a fixed coordinate system. We denote by

$$R_\nu \equiv r_\nu - r_c \tag{3.9}$$

the position vectors w.r.t the center of mass of the chain.
The "Connector vector" Q_k is defined by

$$Q_k = r_{k+1} - r_k, k = 1, ..., N-1 \tag{3.10}$$

and the center of mass of the chain is

$$r_c = \frac{1}{N}\sum_\nu r_\nu. \tag{3.11}$$

We relate position and "connector" vectors by

$$Q_k = \sum_\nu \bar{B}_{k\nu} r_\nu \tag{3.12}$$

and

$$r_\nu - r_c = \sum_k B_{\nu k} Q_k \tag{3.13}$$

where

$$\bar{B}_{k\nu} = \delta_{k+1,\nu} - \delta_{k,\nu} \tag{3.14}$$

and

$$B_{\nu k} = \begin{cases} \frac{k}{N}, & \text{when } k < \nu \\ \frac{k}{N} - 1, & \text{when } k \geq N \end{cases} \tag{3.15}$$

We also define two symmetric nonsingular matrices (C_{ij}), (A_{ij}) namely the Kramers and Rouse matrices respectively by

$$A_{ij} = \sum_\nu \bar{B}_{i\nu}\bar{B}_{j\nu} \tag{3.16}$$

and

$$C_{ij} = \sum_\nu B_{\nu i} B_{\nu j} \tag{3.17}$$

Let a_j, c_j be the eigenvalues of $A_{ij} and C_{ij}$ respectively then

$$a_j = \frac{1}{c_j} = 4\sin^2(\frac{j\pi}{2N}) \tag{3.18}$$

Polar Angles

Other ways of specifying the chain configuration is by the use of polar angles. That is, we specify the center of mass r_c of the chain, the lengths of the connectors Q_k and polar angles θ_i, ϕ_i. Alternatively, we use the unit vectors u_k in lieu of the polar angles which is particularly useful for a freely jointed bead-rod chain with equal connector lengths. One can also associate with each connector in the chain a triad of unit vectors, s_k, t_k, u_k :the first two in the positive θ and ϕ directions and the third in the direction from bead k to $k+1$.For the use of included angles see [18]

Equlibrium Properties of Polymer Molecules

We set forth with the definitions of generalized coordinates and momenta for bead-rod-spring models. We then go on giving the various types of the phase-space and configurational-space equilibrium distribution functions. We will then be in position to calculate average values of properties in the equilibrium state, as we have already done.

Generalized Coordinates and Momenta:

Let's consider a macromolecular model consisting of N beads of mass $m_\nu(\nu = 1, ..., N)$ connected in an arbitrary manner by springs and/or rigid rods. The total mass m_p of the molecule is

$$m_p = \sum_\nu m_\nu \tag{3.19}$$

The location of bead ν is given by the position vector $r_\nu(\nu = 1, ..., N)$ with respect to an arbitrary origin of coordinates. The velocity of bead ν is

$$\dot{r}_\nu = \frac{dr_\nu}{dt} \tag{3.20}$$

We define the center of mass of the chain and denote it by r_c and its velocity $\dot{r}_c$:

$$r_c = \frac{1}{m_p} \sum_\nu m_\nu r_\nu \tag{3.21}$$

and

$$\dot{r}_c = \frac{1}{m_p} \sum_\nu m_\nu \dot{r}_\nu \tag{3.22}$$

and we also define $R_\nu = r_\nu - r_c$, being the position of bead ν with respect to the of mass r_c. Then $\dot{R}_\nu = \dot{r}_\nu - \dot{c}_\nu$

We can easily note that the $R_\nu, \dot{R}_\nu$ are linearly dependent since

$$\sum_\nu m_\nu r_\nu = 0 \tag{3.23}$$

and

$$\sum_{\nu} m_{\nu}\dot{r}_{\nu} = 0 \tag{3.24}$$

We have thus reached a critical point in the development. The Hamiltonian of the system is generally (in most physical cases) expressed as the total energy of the system. We have already seen that it is a function of the generalized coordinates and its conjugate generalized momenta. In our case of a system with N particles and no constraints it can be written as

$$H = \sum_{\nu} \frac{1}{2m_{\nu}} p_{\nu}^2 + \phi(r^N) \tag{3.25}$$

, which is the sum of the total kinetic energy plus the potential energy of the system that depends on the coordinates of the particles.

The evolution of the system is characterized by the well known Hamilton's equations which are:

$$\frac{\partial H}{\partial p_{\nu}} = \dot{r}_{\nu} \tag{3.26}$$

$$\frac{\partial H}{\partial r_{\nu}} = -\dot{p}_{\nu} \tag{3.27}$$

if we substitute the expression of the Hamiltonian into the equations 3.26,3.27 we get the second law of motion for particle ν.

$$F_{\nu} = m_{\nu}\ddot{r}_{\nu} \tag{3.28}$$

For systems with constraints the Hamiltonian becomes

$$H = \frac{1}{2m_p} p_c^2 + \frac{1}{2}\sum_{s}\sum_{t} G_{st} P_s P_t + \phi(r_c, Q_1, Q_2, ..., Q_d) \tag{3.29}$$

and Hamilton's equations of motion are:
$\frac{\partial H}{\partial r_c} = -\dot{p}_c$ and $\frac{\partial H}{\partial p_c} = \dot{r}_c$ for center of mass
$\frac{\partial H}{\partial Q_s} = -\dot{P}_s$ and $\frac{\partial H}{\partial P_s} = \dot{Q}_s$ for internal coordinates

3.5 The Distribution Function in the Equilibrium State of the System

For the study of equilibrium properties we take as the object of our study a dilute solution of polymer molecules. The molecules being represented by bead-rod-spring models. The solution is at temperature T and is contained in a volume

V; there are n polymer molecules /unit volume and the solvent acts as in a 'temperature bath'. We want to know the phase-space distribution function in this equilibrium state.

We firstly introduce the single-molecule-phase-space distribution function $f_{eq}(r_c, Q, p_c, P)$. That is $f_{eq}(r_c, Q, p_c, P)dr_c dQ dp_c dP$ reveals the number of polymer molecules having configuration in the range $dr_c dQ$ around r_c, Q and momentum in the range $dp_c dP$ around p_c, P.

The distribution function f_{eq} is given by the product of the number of polymer molecules in the system and the probability density that can be obtained by equilibrium statistical mechanics and is proportional to $\exp(-H/KT)$ where H is the Hamiltonian of a single polymer molecule in the temperature bath. The only thing left is that f_{eq} has to be properly normalized over the entire phase-space,so

$$\begin{aligned} f_{eq}(r_c, Q, p_c, P) &= \frac{nV e^{(-H/KT)}}{\int\int\int\int \ e^{(-H/KT)} dr_c dQ dp_c dP} \\ &= \frac{n e^{(-H/KT)}}{\int\int\int \ e^{(-H/KT)} dQ dp_c dP} \end{aligned} \tag{3.30}$$

(The second form only in the case where $H = K + \phi$, where ϕ is independent of r_c)

The configurational distribution function is denoted by $\Psi_{eq}(r_c, Q)$ and multiplied by $dr_c dQ$ gives the number of polymer molecules in the configurational range $dr_c dQ$ about r_c, Q. It is obtained by

$$\begin{aligned} \Psi_{eq}(r_c, Q) &= \int\int \ f_{eq}(r_c, Q, p_c, P) dp_c dP \\ &= \frac{n \int\int e^{(-H/KT)} dp_c dP}{\int\int\int \ e^{(-H/KT)} dQ dp_c dP} = n\psi_{eq}(Q) \end{aligned} \tag{3.31}$$

Thus

$$\psi_{eq}(Q) = \frac{\int \ \exp(-\sum_s \sum_t G_{st} P_s P_t / 2KT) dP e^{(-\phi(Q)/KT)}}{\int\int \ \exp(-\sum_s \sum_t G_{st} P_s P_t / 2KT) e^{(-\phi(Q)/KT)} dP dQ} \tag{3.32}$$

When the integration over the $P's$ is performed, it gives $(2\pi KT)^{d/2}/\sqrt{det(G_{st})}$ and setting $g(Q) = det(g_{st}) = \frac{1}{det(G_{st})}$ then

$$\psi_{eq}(Q) = \frac{\sqrt{g(Q)} \exp(-\phi(Q)/KT)}{\int \ \sqrt{g(Q)} \exp(-\phi(Q)/KT) dQ} \tag{3.33}$$

and since $\psi_{eq}(Q)$ is normalized ($\int \ \psi_{eq}(Q) dQ = 1$) therefore $\psi_{eq}(Q)dQ$ is the probability that the internal configuration is in the range dQ about Q

3.6 Average Values

Quantities that are experimentally accessible are the results of measurements that contain an enormous ensemble of molecules. Therefore, in order to be in position to bridged the gap between experimental properties and the theory, one needs to define average values of physical quantities.

We define the average value of a function $B(r_c, Q, p_c, P)$ in the phase space of a single polymer molecule

$$\langle B\rangle_{eq} = \frac{\int\int\int\int\ Bf_{eq}dr_c dQ dp_c dP}{\int\int\int\int\ f_{eq}dr_c dQ dp_c dP} = \frac{1}{nV}\int\int\int\int\ Bf_{eq}dr_c dQ dp_c dP \quad (3.34)$$

One can also define averages in the momentum space (denoted by double brackets), thus

$$[[B]]_{eq} = \frac{\int\int\ Bf_{eq}dp_c dP}{\int\int\ f_{eq}dp_c dP} = \frac{1}{\Psi_{eq}}\int\int\ Bf_{eq}dp_c dP \quad (3.35)$$

and the phase space average can be written in form

$$\langle B\rangle_{eq} = \frac{1}{nV}\int\int\ [[B]]_{eq}\Psi_{eq}dr_c dQ \quad (3.36)$$

If the quantity B is only a function of r_c, Q then

$$[[B]]_{eq} = B \quad (3.37)$$

($[[B]]_{eq}$ is generally a function of r_c, Q)
and $\langle B\rangle_{eq} = \frac{1}{nV}\int\int\ B\Psi_{eq}dr_c dQ$.
Then if B, ϕ are only functions of Q the phase-space average of B becomes

$$\langle B\rangle_{eq} = \int\ B\Psi_{eq}dQ \quad (3.38)$$

which leads to

$$\langle B\rangle_{eq} = \frac{\int\ B\sqrt{g}e^{-\phi/KT}dQ}{\int\ \sqrt{g}e^{-\phi/KT}dQ} \quad (3.39)$$

We must however keep in mind that the last equation holds for B, ϕ being functions only of the internal coordinates and the evaluation of the quantity $\sqrt{g}$ requires in general a difficult computation.

3.7 Contracted Distribution Functions

We define

$$\psi_{1,eq}(Q) = \langle \delta(Q_1 - Q) \rangle_{eq} \tag{3.40}$$

therefore $\psi_{1,eq}(Q)dQ$ is the probability that the macromolecule chain has the connector vector Q_1 of the first spring in the range dQ_1 about Q_1 in the equilibrium state. Let's take the special case of the Rouse chain. Then after some calculations we obtain

$$\begin{aligned}
\psi_{1,eq}(Q) &= \langle \delta(Q_1 - Q) \rangle \\
&= \int \delta(Q_1 - Q)\psi_{eq}(Q^{N-1})dQ^{N-1} \\
&= \int \delta(Q_1 - Q)(\frac{H}{2\pi KT})^{3/2} \exp((-H/2KT)Q_1^2)dQ \\
&= \int_{N-2fold} ... \int [\prod_{k=2}^{N-1} (\frac{H}{2\pi KT})^{3/2} \exp(-(H/2KT)Q_k^2)]dQ_2dQ_3...dQ_{N-1} \\
&= (\frac{H}{2\pi KT})^{3/2} \exp((-H/2KT)Q^2)
\end{aligned} \tag{3.41}$$

Another interesting point is when we switch from a Cartesian coordinates framework to a polar angle coordinate one. Then $\psi_{1,eq}(Q,\theta,\phi)dQd\theta d\phi$ is the probability that the first link be located within the range $d\theta d\phi$ about θ, ϕ and has length within the range dQ about Q

Finally

$$\begin{aligned}
\psi_{1,eq}(Q) &= \int\int \psi_{1,eq}(Q,\theta,\phi)d\theta d\phi \\
&= 4\pi Q^2(\frac{H}{2\pi KT})^{3/2} \exp((-H/2KT)Q^2)
\end{aligned} \tag{3.42}$$

where we have used the fact that

$$\psi_{1,eq}(Q,\theta,\phi) = \psi_{1,eq}(Q_x,Q_y,Q_z)Q^2\sin(\theta) \tag{3.43}$$

Chapter 4

Brownian Motion and Stochastic Modelling in Polymeric Liquids

4.1 Markov Processes the Master and Fokker Planck equations

The defining property of Markov processes is that they have no memory. We go on to present a mathematically rigorous definition.

Definition:For a Markov process, we have for all n and all $t_1 < t_2 < ... < t_n$

$$P(X_n = x_n, t_n | X_{n-1} = x_{n-1}, t_{n-1}, ..., X_1 = x_1, t_1) = P(X_n = x_n, t_n | X_{n-1} = x_{n-1}, t_{n-1}) \tag{4.1}$$

In other words one has to know only the actual state of the system (x_{n-1}, t_{n-1}) in order to calculate the probability of the occurrence of (x_n, t_n). The n point joint probability may be easily calculated by iteratively applying the Markovian equation so

$$\begin{aligned} &P(X_n = x_n, t_n; X_{n-1} = x_{n-1}, t_{n-1}; ...; X_1 = x_1, t_1) = \\ &\quad \prod_{l=2}^{n} P(X_l = x_l, t_l | X_{l-1} = x_{l-1}, t_{l-1}) P(X_1 = x_1, t_1) \end{aligned} \tag{4.2}$$

Remember that Markov processes are very common in nature in the sense that systems that obey the rules of Hamiltonian dynamics lack memory and the complete knowledge of the state of the system at a given instant of time determines its future behavior.

Now passing to the $3 - \textit{point}$ joint probability we have

$$\begin{aligned} &P(X_1 = x_1, t_1; X_2 = x_2, t_2; X_3 = x_3, t_3) = \\ &P(X_3 = x_3, t_3 | X_2 = x_2, t_2) P(X_2 = x_2, t_2 | X_1 = x_1, t_1) P(X_1 = x_1, t_1) \end{aligned} \tag{4.3}$$

Next integrating over x_2 we get

$$P(X_1 = x_1, t_1; X_3 = x_3, t_3) =$$
$$P(X_1 = x_1, t_1) \int P(X_3 = x_3, t_3|X_2 = x_2, t_2)P(X_2 = x_2, t_2|X_1 = x_1, t_1)dx_2 \quad (4.4)$$

or

$$P(X_3 = x_3, t_3|X_1 = x_1, t_1) = \int dx_2 P(X_3 = x_3, t_3|X_2 = x_2, t_2)P(X_2 = x_2, t_2|X_1 = x_1, t_1) \quad (4.5)$$

for $t_3 \geq t_2 \geq t_1$ which is the Chapman-Kolmogorov equation. We are now ready to give the definition of a stationary Markov process and derive the Master equation.

A stationary Markov process exhibits the properties

$$P(X = x, t) = p_{eq} \quad (4.6)$$
$$P(X_2 = x_2, t_2|X_1 = x_1, t_1) = p_t(x_2|x_1) \quad (4.7)$$

for $t = t_2 - t_1$ where p_t is the transition probability within the time interval t from state x to state x_2 :Using the Chapman-Kolmogorov equation for p_t we get

$$p_{t+t'}(x_3|x_1) = \int dx_2 p_{t'}(x_3|x_2)p_t(x_2|x_1) \quad (4.8)$$

In order to derive the differential form of the Chapman-Kolmogorov equation for stationary Markov processes we consider the case of small time intervals $t^{'}$ and write the transition probability in the following way.

$$p_{t'}(x_3|x_2) = (1 - w_{tot}(x_2)t^{'})\delta(x_3 - x_2) + t^{'}w(x_3|x_2) + O(t^{'}) \quad (4.9)$$

where $w(x_3|x_2)$ is the transition rate(transition probability/unit time) from x_2 to x_3 and $(1 - w_{tot}(x_2)t^{'})$ is the probability to remain in state x_2 up to time $t^{'}$, that is

$$w_{tot}(x_2) = \int dx_3 w(x_3|x_2) \quad (4.10)$$

With the use of 4.40 and the Chapman-Kolmogorov equation one gets

$$p_{t+t'}(x_3|x_1) = (1 - w_{tot}(x_3)t^{'})p_t(x_3|x_1) + t^{'} \int dx_2 w(x_3|x_2)p_t(x_2|x_1) \quad (4.11)$$

or

$$\frac{p_{t+t'}(x_3|x_1) - p_t(x_3|x_1)}{t'} = \int dx_2 w(x_3|x_2)p_t(x_2|x_1) - \int dx_2 w(x_2|x_3)p_t(x_3|x_1) \quad (4.12)$$

Taking the limit $t^{'} \rightarrow 0$ we arrive at the master equation which is the differential version of the Chapman-Kolmogorov equation.
Thus

$$\frac{\partial}{\partial t}p_t(x_3|x_1) = \int \; dx_2 w(x_3|x_2)p_t(x_2|x_1) - \int \; dx_2 w(x_2|x_3)p_t(x_3|x_1) \tag{4.13}$$

When we do not assume stationarity but keep the assumption of time-homogeneity, then multiplying the last equation by $p_1(x_1,t)$ and integrating over x_1, we get

$$\frac{\partial}{\partial t}p_1(x_3,t) = \int \; dx_2 w(x_3|x_2)p_1(x_2,t) - \int \; dx_2 w(x_2|x_3)p_1(x_3,t) \tag{4.14}$$

or simplifying the expression

$$\frac{\partial}{\partial t}p(x,t) = \int \; dx^{'} w(x|x^{'})p(x^{'},t) - \int \; dx^{'} w(x^{'}|x)p(x,t) \tag{4.15}$$

Let us now set forth for further approximations of the master equation and make the following assumptions
- We write $w(x|x^{'}) = w(x-r;r)$ with $r := x - x^{'}$
- There are small 'jumps' i.e w(x-r;r) as a function of r is a sharply peaked function around $r = 0$

$\exists \delta > 0$ with $w(x-r;r) \simeq 0$ for $|r| > \delta$
- $w(x-r;r)$ is a slowly varying function of its first argument

$\exists \delta^{'} > 0$ with $w(x-r;r) \simeq w(x^{'};r)$ $|r| < \delta^{'}$
- The last holds true for $p(x,t)$ also.
- w and p are sufficiently smooth functions of both arguments

So we can rewrite the last expression

$$\frac{\partial}{\partial t}p(x,t) = \int \; dr w(x-r;r)p(x-r,t) - p(x,t)\int \; dr w(x;-r) \tag{4.16}$$

Performing a Taylor expansion in $x - r$ around $r = 0$
we obtain

$$\frac{\partial}{\partial t}p(x,t) = p(x,t)\int \; dr w(x;r) - p(x,t)\int \; dr w(x;-r)$$
$$-\int \; dr r\frac{\partial}{\partial x}[w(x;r)p(x,t)] + \frac{1}{2}\int \; dr r^2\frac{\partial^2}{\partial x^2}[w(x;r)p(x,t)] \mp ... \tag{4.17}$$

yielding

$$\frac{\partial}{\partial t}p(x,t) = \sum_{n=1}^{\infty}\frac{(-1)^n}{n!}\frac{\partial^n}{\partial x^n}[\alpha_n(x)p(x,t)] \tag{4.18}$$

$$\alpha_n(x) = \int_{-\infty}^{+\infty} \; dr r^n w(x;r) \tag{4.19}$$

which is the celebrated Kramers-Moyal expansion of the master equation. Truncating all but the first two terms of the Kramers-Moyal expansion we get the Fokker-Planck equation.

$$\frac{\partial}{\partial t}p(x,t) = -\frac{\partial}{\partial x}[\alpha_1(x)p(x,t)] + \frac{1}{2}\frac{\partial^2}{\partial x^2}[\alpha_2(x)p(x,t)] \tag{4.20}$$

4.2 The Smoluchowski Equation

In order to derive the Smoluchowski equation we will consider a phenomenological approach originated by Einstein. We will firstly consider the one-dimensional case and the generalization to higher dimensions will follow naturally.

If $c(x,t)$ is the concentration at point x and time t and $j(x,t)$ is the flux then the process of diffusion is macroscopically defined by Fick's law that states

$$j(x,t) = -D\frac{\partial c}{\partial x} \tag{4.21}$$

where D is the diffusion constant.

Combining the aforementioned equation with the Continuity equation

$$\frac{\partial c}{\partial t} = -\frac{\partial c}{\partial x} \tag{4.22}$$

we obtain the diffusion equation

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{4.23}$$

Some modifications have to be made if we allow an external potential $U(x)$ which will exert a force

$$F = -\frac{\partial U}{\partial x} \tag{4.24}$$

on the particle and in the usual condition of weak force this will be linear in F

$$v = -\frac{1}{\zeta}\frac{\partial U}{\partial x} \tag{4.25}$$

where ζ is the friction constant and its inverse $\frac{1}{\zeta}$ is called the mobility.

Modifying Fick's law by adding an additional term we get the total flux

$$j = -D\frac{\partial c}{\partial x} - \frac{c}{\zeta}\frac{\partial U}{\partial x} \tag{4.26}$$

If we substitute in the above relation the concentration in the equilibrium state which is given by the Boltzmann distribution

$$c_{eq}(x) \propto \exp(-U(x)/K_B T) \tag{4.27}$$

for which the flux must vanish, we obtain the Einstein relation

$$D = \frac{K_B T}{\zeta} \tag{4.28}$$

Using the Einstein relation and the general flux formula we get

$$j(x,t) = -\frac{1}{\zeta}(K_B T \frac{\partial c}{\partial x} + c\frac{\partial U}{\partial x}) \tag{4.29}$$

The diffusion equation is thus

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\frac{1}{\zeta}(K_B T \frac{\partial c}{\partial x} + c\frac{\partial U}{\partial x}) \tag{4.30}$$

which is the Smoluchowski equation in the one-dimensional case.

If we are to express the flux as the gradient of a quantity then

$$j = -\frac{1}{\zeta}c\frac{\partial}{\partial x}(K_B T \ln c + U) \tag{4.31}$$

The quantity $U(x) + K_B T \ln c$ is the chemical potential of noninteracting particles of concentration c

4.3 The Langevin Equation

A classical problem of nonequilibrium statistical mechanics is the Brownian motion. Brownian motion was studied by Albert Einstein in his celebrated 1905 paper and independently by Myrian Smoluchowski. It refers to the motion of a heavy colloidal particle immersed in a fluid made up of light particles and was first observed by the Scottish botanist R.Brown back in 1827. We will depart from the exact mechanical description by adding a probabilistic element in our description of the phenomenon.

Thus a macroscopic treatment reveals that the Brownian particle during its motion undergoes a friction force proportional to its velocity v
$\dot{v} = -\zeta v$ (macroscopic)

If on the other hand we want to undergo to a microscopic description we must add a random force that the Brownian particle experiences, so Newton's second

law becomes
$\dot{v} = -\zeta v + f(t)$ (microscopic)

Alternatively the Langevin equation may be written in the form $\zeta \frac{dx}{dt} = -\frac{\partial U}{\partial x} + f(t)$ where U is the potential energy.

Although we cannot specify the force $f(t)$, however, we can make various assumptions about the average effect of collisions over a large number of identical macroscopic situations. That's why equations like the one above carry the name 'stochastic equations'.

The assumptions we use are the following:
1) The average of $f(t)$ over an ensemble of Brownian particles at an instant of time is $\langle f(t)\rangle = 0$

This assumption shows the equivalence with the macroscopic behavior when taking ensemble averages.
2)We may also make the assumption that collisions well separated in time are not correlated. Hence for times t_1, t_2

$$\langle f(t_1) f(t_2)\rangle = \phi(t_1 - t_2) \tag{4.32}$$

where $\phi(t)$ is a sharply peaked at $t = 0$ function, vanishing for $|t| > \tau_c$
where τ_c is the duration of a collision

The distribution of $f(t)$ can be easily taken to be Gaussian and after taking

$$\langle f(t)\rangle = 0 \tag{4.33}$$

$$\langle f(t) f(t^{'})\rangle = 2\zeta K_B \delta(t - t^{'}) \tag{4.34}$$

then the probability distribution of $f(t)$ assumes the form

$$P[f(t)] \propto \ \exp(-\frac{1}{4\zeta K_B T}\int \ dt f(t)^2) \tag{4.35}$$

Considering now a free particle ($U = 0$) the Langevin equation reads

$$\zeta \frac{dx}{dt} = f(t) \tag{4.36}$$

If the particle is at x' at time $t = 0$, its position at time t is given by

$$x(t) = x^{'} + \frac{1}{\zeta}\int_0^t \ dt^{'} f(t^{'}) \tag{4.37}$$

It can be shown that the distribution function of $x(t)$ is also Gaussian. Hence

$$P(x(t), t) = (2\pi B)^{-1/2} \exp{(-\frac{(x - A)^2}{2B})} \tag{4.38}$$

where $A = \langle x(t) \rangle$ and $B = \langle (x(t) - A)^2 \rangle$
so

$$A = \langle x(t) \rangle = x^{'} + \frac{1}{\zeta} \int_0^t \, dt^{'} \langle f(t^{'}) \rangle = x^{'} \tag{4.39}$$

and

$$\begin{aligned} B &= \langle (\frac{1}{\zeta} \int_0^t \, dt^{'} f(t^{'}))(\frac{1}{\zeta} \int_0^t \, dt^{''} f(t^{''})) \rangle \\ &= \frac{1}{\zeta^2} \int_0^t \, dt^{'} \int_0^t \, dt^{''} \langle f(t^{'}) f(t^{''}) \rangle \\ &= \frac{2K_BT}{\zeta} \int_0^t \, dt^{'} \int_0^t \, dt^{''} \delta(t^{'} - t^{''}) = \frac{2K_BT}{\zeta} t \end{aligned} \tag{4.40}$$

and using Einstein's relation we obtain

$$B = 2Dt \tag{4.41}$$

Thus

$$P(x(t), t) = (4\pi Dt)^{-1/2} \exp{(-\frac{(x - x^{'})^2}{4Dt})} \tag{4.42}$$

If the diffusion constant D is time-dependent then the Langevin has to be modified and assumes the form

$$\zeta \frac{dx}{dt} = -\frac{\partial U}{\partial x} + f(t) + \frac{\zeta}{2} \frac{\partial D}{\partial x} \tag{4.43}$$

The Langevin equation corresponding to the Smoluchowski equation in multidimensional phase-space is

$$\frac{d}{dt} x_n = \sum_m L_{nm} (-\frac{\partial U}{\partial x_m} + f_m(t)) + \frac{1}{2} K_BT \sum_m \frac{\partial}{\partial x_m} L_{nm} \tag{4.44}$$

And the distribution of the random force is characterized by the moments

$$\langle f_n(t) \rangle = 0 \tag{4.45}$$

$$\langle f_n(t) f_m(t^{'}) \rangle = 2(L^{-1})_{nm} K_BT \delta(t - t^{'}) \tag{4.46}$$

4.4 The Irreversibility of the Smoluchowski Equation

Provided that the potential $U(\{x\})$ is independent of time and that there is no flux at the boundary Ψ approaches Ψ_{eq} where

$$\Psi_{eq} = \exp(-U(x)/K_BT) / \int \, dx \exp(-U(x)/K_BT) \tag{4.47}$$

Consider the functional

$$A[\Psi] \equiv \int dx\Psi(K_B T \ln(\Psi) + U) \tag{4.48}$$

and taking the time derivative of A we have

$$\frac{d}{dt}A = \int dx[\frac{\partial\Psi}{\partial t}(K_B T \ln(\Psi) + U) + K_B T\frac{\partial\Psi}{\partial t}] \tag{4.49}$$

Using the fact that

$$\frac{\partial\Psi}{\partial t} = \sum_{n,m}\frac{\partial}{\partial x_n}L_{n,m}(K_B T\frac{\partial\Psi}{\partial x_m} + \frac{\partial U}{\partial x_m}\Psi) \tag{4.50}$$

and after integration by parts

$$\begin{aligned}\frac{dA}{dt} &= -\int dx\Psi\sum_{n,m}L_{n,m}[\frac{\partial}{\partial x_n}(K_B T\ln(\Psi) + U)][\frac{\partial}{\partial x_m}(K_B T\ln(\Psi) + U)] \\ &= -\int dx\Psi\sum_{n,m}L_{n,m}[K_B T\frac{\partial}{\partial x_n}\ln(\Psi/\Psi_{eq})][K_B T\frac{\partial}{\partial x_m}\ln(\Psi/\Psi_{eq})]\end{aligned} \tag{4.51}$$

which is negative unless Ψ is identical to Ψ_{eq}.So Ψ will eventually reach Ψ_{eq} after a sufficiently long time.

4.5 Hydrodynamic Interaction and the Oseen Burgers Tensor

4.5.1 Hydrodynamic Interaction

In this section we are taking in account the fact that any force acting on a particle creates a velocity field that contributes to the motion of other particles.

The purpose of this chapter is to obtain a Smoluchowski equation after the calculation of the mobility matrix.Let $\{R\} = \{R_1, ..., R_N\}$ be the position of the spheres and $F_1, ..., F_N$ the forces acting on them.The velocities of the particles can be written in the form

$$V_n = \sum_m H_{nm} \cdot F_m \tag{4.52}$$

which defines the mobility matrix H_{nm} $n, m \in \{1, ..., N\}$.

The mobility matrix is assumed diagonal in very dilute solutions and takes the form $H_{nm} = \frac{I\delta_{nm}}{\zeta}$ where $\zeta = 6\pi\eta_s\alpha$ is the friction constant of the particle.In more general cases it is a non-diagonal tensor describing the resolution of the velocities due to the forces acting on the particles.

The calculation of the particle velocities V_n follows after the calculation of the velocity field $v(r)$.This can be done easily following continuum mechanics arguments for the incompressible solvent.Thus

$$\frac{\partial}{\partial r_\alpha} v_\alpha = 0 \tag{4.53}$$

Neglecting the inertia term and letting $\sigma_{\alpha\beta}(r)$ and $g_\alpha(r)$ be respectively the stress tensor and the external force acting on a unit volume of the fluid we have for the incompressible solvent

$$\sigma_{\alpha\beta} = \eta_s(\frac{\partial v_\beta}{\partial r_\alpha} + \frac{\partial v_\alpha}{\partial r_\beta}) + P\delta_{\alpha\beta} \tag{4.54}$$

an easy calculation including 4.53,4.54 and the fact that

$$\frac{\partial}{\partial r_\beta}\sigma_{\alpha\beta} = -g_\alpha(r) \tag{4.55}$$

reveals

$$\eta_s \frac{\partial^2}{\partial r_\beta} v_\alpha + \frac{\partial}{\partial r_\alpha} P = -g_\alpha \tag{4.56}$$

the so called Stokes approximation.

Regarding the particles as points then

$$g(r) = \sum_n F_n \delta(r - R_N) \tag{4.57}$$

and equation 4.56 reads

$$\eta_s \nabla^2 v + \nabla P = -\sum_n F_n \delta(r - R_n) \tag{4.58}$$

The solution of this equation is

$$v(r) = \sum_n H(r - R_n) \cdot F_n \tag{4.59}$$

with $H(r) = \frac{1}{8\pi\eta_s r}(I + \hat{r}\hat{r})$ the Oseen tensor and $\hat{r}$ being the unit vector parallel to $\hat{r}$.

The velocities V_n are then $V_n = v(R_n) = \sum_m H(R_n - R_m) \cdot F_m$ and $H(R_n - R_m) = H_{nm}$ for $n \neq m$ and since $H_{nn} = H(0)$ is not defined approximations for H_{nn} are to be used.One common approximation is that $H_{nn} = \frac{I}{\zeta}$ and $H_{nm} = H(R_n - R_m)$ for $n \neq m$
Finally the Smoluchowski equation takes the form

$$\frac{\partial \psi}{\partial t} = \sum_{n,m} \frac{\partial}{\partial R_n} \cdot H_{nm} \cdot (K_B T \frac{\partial \psi}{\partial R_m} + \frac{\partial U}{\partial R_m} \psi) \tag{4.60}$$

.

4.5.2 Calculation of the Oseen Tensor

The Oseen tensor will be calculated by means of the Fourier transform

$$v_k = \frac{1}{V} \int dr v(r) e^{ik \cdot r} \tag{4.61}$$

Equations 4.53,4.56,4.57 and 4.61 can be written in form

$$-\eta_s k^2 v_k - ikP_k = -g_k, k \cdot v_k = 0 \tag{4.62}$$

which will give us

$$v_k = \frac{1}{\eta_s k^2} (I - \hat{k}\hat{k}) \cdot g_k \tag{4.63}$$

Hence, by means of the inverse Fourier transform we have

$$v(r) = \int d\acute{r} H(r - \acute{r}) \cdot g(\acute{r}) \tag{4.64}$$

and

$$H(r) = \frac{1}{(2\pi)^3} \int dk \frac{1}{\eta_s k^2} (I - \hat{k}\hat{k}) exp(ik \cdot r) \tag{4.65}$$

We will assume that

$$H_{\alpha\beta}(r) = A\delta_{\alpha\beta} + B\hat{r}_\alpha \hat{r}_\beta \tag{4.66}$$

So

$$H_{\alpha\alpha} = 3A + B \tag{4.67}$$
$$H_{\alpha\beta}\hat{r}_\alpha \hat{r}_\beta = A + B \tag{4.68}$$

or

$$3A + B = \frac{1}{(2\pi)^3} \int dk \frac{2}{\eta_s k^2} exp(-ik \cdot r) \tag{4.69}$$

and

$$A + B = \frac{1}{(2\pi)^3} \int dk \frac{1 - (\hat{k} \cdot \hat{r})^2}{\eta_s k^2} exp(-ik \cdot r) \tag{4.70}$$

In order to calculate the above integral we introduce a change of variables $t = \hat{k}\hat{r}$ and $\xi = |k||r|$ and thus get

$$\begin{aligned} 3A + B &= \frac{2}{(2\pi)^2} \int_0^\infty d\xi \frac{2\pi}{\eta_s r} \int_{-1}^1 dt exp(-i\xi t) \\ &= \frac{1}{\pi^2 \eta_s r} \int_0^\infty d\xi \frac{sin\xi}{\xi} = \frac{1}{2\pi\eta_s r} \end{aligned} \tag{4.71}$$

and

$$\begin{aligned} A + B &= \frac{1}{(2\pi)^3} \int_0^\infty d\xi \frac{2\pi}{\eta_s r} \int_{-1}^1 dt(1 - t^2) exp(-i\xi t) \\ &= \frac{1}{2\pi^2 \eta_s r} \int_0^\infty d\xi (1 + \frac{\partial^2}{\partial \xi^2}) \frac{sin\xi}{\xi} = \frac{1}{4\pi\eta_s r} \end{aligned} \tag{4.72}$$

Finally, we get the values

$$A = B = \frac{1}{8\pi\eta_s r} \tag{4.73}$$

and

$$H(r) = \frac{1}{8\pi\eta_s r}(I + \hat{r}\hat{r}) \tag{4.74}$$

4.6 The Rouse Model

In the Rouse model the excluded volume effect and hydrodynamic interactions are being disregarded. The mobility tensor is taken to be $H_{nm} = \frac{I}{\zeta}\delta_{nm}$, and the interaction potential

$$U = \frac{k}{2} \sum_{n=2}^{N} (R_n - R_{n-1})^2 \tag{4.75}$$

where $K = \frac{3K_BT}{b^2}$.

Let $(R_1, R_2, ..., R_N) \equiv \{R_n\}$ be the position of the beads. Beads motion is supposed to be governed by the Brownian phenomenon.

The Smoluchowski equation of motion reads:

$$\frac{\partial \Psi}{\partial t} = \sum_n \frac{\partial}{\partial R_n} \cdot H_{nm} \cdot [K_BT \frac{\partial \Psi}{\partial R_m} + \frac{\partial U}{\partial R_m} \Psi] \tag{4.76}$$

(remember that $\Psi(R_1, ..., R_N, t)$ is normalized to unity)
and the Langevin equation

$$\frac{\partial}{\partial t}R_n(t) = \sum_m H_{nm} \cdot (-\frac{\partial U}{\partial R_m} + f_m(t)) + \frac{1}{2}K_B T \sum_m \frac{\partial}{\partial R_m} \cdot H_{nm} \tag{4.77}$$

or after substitution of the above values (the second term on the right in 4.77 vanishes) the equation of motion for beads is

$$\zeta \frac{\partial R_n}{\partial t} = -K(2R_n - R_{n+1} - R_{n-1}) + f_n \tag{4.78}$$

and for beads 1 and N

$$\zeta \frac{\partial R_1}{\partial t} = -K(R_1 - R_2) + f_1 \tag{4.79}$$

$$\zeta \frac{\partial R_N}{\partial t} = -K(R_N - R_{N-1}) + f_N \tag{4.80}$$

The distribution of f_n is Gaussian and characterized by the moments

$$\langle f_n(t) \rangle = 0 \tag{4.81}$$

and

$$\langle f_{n\alpha}(t) f_{m\beta}(t^{'}) \rangle = 2\zeta K_B T \delta_{nm} \delta_{\alpha\beta} \delta(t - t^{'}) \tag{4.82}$$

where the second subscripts α, β are the α'th and β'th component of vectors f_n and f_m respectively.

Regarding n a continuous variable the continuous limit of 4.78 reads

$$\zeta \frac{\partial R_n}{\partial t} = K \frac{\partial^2 R_n}{\partial n^2} + f_n \tag{4.83}$$

The above differential equation is the continuous analog of 4.78 which in difference form. Care needs to be taken to include the special form of the equations for beads $n = 1$ and $n = N$. The proper way is to introduce two artificial variables R_0, R_{N+1} such that $R_0 = R_1$ and $R_N = R_{N+1}$ so that the last two equations in the continuous limit become:

$$\frac{\partial R_n}{\partial n}|_{n=0} = 0 \tag{4.84}$$

$$\frac{\partial R_n}{\partial n}|_{n=N} = 0 \tag{4.85}$$

The moments for f_n are now

$$\langle f_n(t) \rangle = 0 \tag{4.86}$$

$$\langle f_{n\alpha}(t) f_{m\beta}(t^{'}) \rangle = 2\zeta K_B T \delta(n - m) \delta_{\alpha\beta} \delta(t - t^{'}) \tag{4.87}$$

One has to keep in mind that the discrete and continuous models agree for properties on a long time scale, but not for short times.What makes the Rouse model of particular importance is that a linear Langevin equation with localized interactions shows the behavior of the Rouse model in the long time scale
Let's consider the general form of the linearized Langevin equation

$$\frac{\partial R_n}{\partial t} = \sum_m A_{nm} R_m + g_n \tag{4.88}$$

The system is homogeneous and A_{nm} can be replaced by A_{n-m} so the Langevin equation can be written as

$$\frac{\partial R_n}{\partial t} = \sum_m A_m R_{n+m} + g_m \tag{4.89}$$

In the long time scale R_n varies slowly with n and so R_{n+m} can be expanded with respect to m.

$$\begin{aligned}\sum_m A_m R_{n+m} = \sum_m A_m (R_n + m\frac{\partial}{\partial n} R_n + \frac{1}{2} m^2 \frac{\partial^2}{\partial n^2} R_n + ...)\\ = a_0 R_n + a_1 \frac{\partial}{\partial n} R_n + a_2 \frac{\partial^2}{\partial n^2} R_n + ... \end{aligned}\tag{4.90}$$

where $a_0 = \sum_{m=-\infty}^{\infty} A_m$, $a_1 = \sum_{m=-\infty}^{\infty} m A_m$,$a_2 = \frac{1}{2}\sum_{m=-\infty}^{\infty} m^2 A_m$

The coefficient a_0 must vanish since the Langevin equation must be invariant under the spacial translation $((R_n \to R_n + r))$ and a_1 must also vanish since A_m is an even function of m. Therefore the asymptotic behavior of the Langevin equation is

$$\frac{\partial}{\partial t} R_n = a_2 \frac{\partial^2}{\partial n^2} R_n + g_n(t) \tag{4.91}$$

which is the continuous limit of 4.88.

Therefore the Rouse model displays the general features of a model that assumes local interactions.

4.7 The Zimm Model

The dynamics of polymers in dilute solutions may be better described by taking into account the hydrodynamic interaction. Thus the mobility matrix is
$H_{nn} = \frac{I}{\zeta}$ and
$H_{nm} = \frac{1}{8\pi\eta_s |r_{nm}|}[\hat{r}_{nm}\hat{r}_{nm} + I]$ for $n \neq m$
where $r_{nm} \equiv R_n - R_m$ and $\hat{r}_{nm}$ is the unit vector in the direction of r_{nm}.

The Langevin equation then becomes

$$\frac{\partial}{\partial t}R_n = \sum_m H_{nm} \cdot (-\frac{\partial U}{\partial R_m} + f_m(t)) \tag{4.92}$$

because it can be easily shown that $\frac{\partial}{\partial R_m} \cdot H_{nm} = 0$ or in the continuous limit we have

$$\frac{\partial}{\partial t}R_n = \sum_m H_{nm} \cdot (K\frac{\partial^2}{\partial m^2}R_m + f_m(t)) \tag{4.93}$$

which bears the name "Zimm's Model"
In order that we handle better H_{nm} we introduce a preaveraging approximation and we get

$$\langle H_{nm}\rangle = \int d\{R_n\}H_{nm}\Psi(\{R_n\},t) \tag{4.94}$$

or considering problems near equilibrium

$$\langle H_{nm}\rangle_{eq} \equiv \int d\{R_n\}H_{nm}\Psi_{eq}(\{R_n\}) \tag{4.95}$$

we can go on writing

$$\langle H_{nm}\rangle_{eq} = \frac{1}{8\pi\eta_s}\langle\frac{1}{|r_{nm}|_{eq}}\rangle\langle\hat{r}_{nm}\hat{r}_{nm} + I\rangle_{eq} \tag{4.96}$$

Using $\langle\hat{r}_{nm}\hat{r}_{nm}\rangle_{eq} = \frac{1}{3}$ we have

$$\langle H_{nm}\rangle_{eq} = \frac{I}{6\pi\eta_s}\langle\frac{1}{|R_n - R_m|}\rangle_{eq} \tag{4.97}$$

In the Θ condition we obtain

$$\begin{aligned}\langle H_{nm}\rangle_{eq} &= \int_0^\infty dr 4\pi r^2(\frac{3}{2\pi|n-m|b^2})^{3/2}\exp{(-\frac{3r^2}{2|n-m|b^2})}\frac{I}{6\pi\eta_s r} \\ &= \frac{I}{(6\pi^3|n-m|)^{1/2}\eta_s b} \equiv h(n-m)I\end{aligned} \tag{4.98}$$

by the preaveraging approximation the Langevin equation becomes

$$\frac{\partial}{\partial t}R_n(t) = \sum_m h(n-m)(K\frac{\partial^2}{\partial m^2}K_m(t) + f_m(t)) \tag{4.99}$$

Although the approximation may appear quite crude the results are not very different than more sophisticated calculations. One can also mention that in the Zimm model the interaction among the segments is not localized and that constitutes a major difference with the Rouse model.

To analyze the last equation we rewrite it in terms of the Rouse normal coordinates X_p defined by

$$\frac{\partial}{\partial t}X_p(t) = \sum_q h_{pq}(-K_q X_q + f_q) \tag{4.100}$$

where k_p has already been defined and

$$h_{pq} = \frac{1}{N^2}\int_0^N dn \int_0^N dm \cos(\frac{p\pi n}{N})\cos(\frac{q\pi m}{N})h(n+m) \tag{4.101}$$

using the definition of $h(n-m)$ we have

$$\begin{aligned} h_{pq} &= \frac{1}{N^2}\int_0^N dn \int_0^{N-n} dm \cos(\frac{p\pi n}{N})\cos(\frac{q\pi(n+m)}{N}) \\ = \frac{1}{N^2}&\int_0^N dn[\cos(\frac{p\pi n}{N})\cos(\frac{q\pi n}{N})\int_{-n}^{N-n} dm h(m)\cos(\frac{q\pi m}{N}) \\ &- \cos(\frac{p\pi n}{N})\sin(\frac{q\pi n}{N})\int_{-n}^{N-n} dm h(m)\sin(\frac{q\pi m}{N})] \end{aligned} \tag{4.102}$$

For large q the asymptotic values of the underlined integrals are

$$\int_{-\infty}^{\infty} dm h(m)\cos(\frac{q\pi m}{N}) = \frac{\sqrt{N}}{(3\pi^3 q)^{1/2}\eta_s b} \tag{4.103}$$

and

$$\int_{-\infty}^{\infty} dm h(m)\sin(\frac{q\pi m}{N}) = 0 \tag{4.104}$$

So ,

$$h_{qp} \simeq \frac{\sqrt{N}}{(3\pi^3 q)^{1/2}\eta_s b}\frac{1}{N^2}\int_0^N du \cos(\frac{p\pi n}{N})\cos(\frac{q\pi n}{N}) \tag{4.105}$$

or approximatelly

$$\frac{\sqrt{N}}{(3\pi^3 p)^{1/2}\eta_s b}\frac{1}{2N}\delta_{pq}. \tag{4.106}$$

Neglecting the off diagonal elements we get an equation that has the same structure as that of the Rouse model:

$$\zeta_p \frac{\partial}{\partial t}X_p(t) = -K_p X_p + f_p(t) \tag{4.107}$$

where $\zeta_p = (h_{pp})^{-1} = (12\pi^3)^{1/2}\eta_s(Nb^2p)^{1/2}$ $p = 1, 2, ...$ not correct for $p = 0$
and $k_p = \frac{6\pi^2 K_B T}{Nb^2}p^2$ $p = 0, 1, 2, ...$
Nevertheless, $\zeta_0 = (h_{00})^{-1} = \frac{1}{N^2}[\int_0^N \ dn \int_0^N \ dmh(|n-m|)]^{-1} = \frac{3}{8}(6\pi^3)^{1/2}\eta_s b\sqrt{N}$
Finally the D_G diffusion constant and τ_p relaxation time are

$$D_G = \frac{K_B T}{\zeta_0} = \frac{8K_B T}{3(6\pi^3)^{1/2}\eta_s b\sqrt{N}} = 0.196\frac{K_B T}{\eta_s \bar{R}} \tag{4.108}$$

and $\tau_p = \frac{\zeta_p}{k_p} = \tau_1 p^{-3/2}$
with $\tau_1 = \tau_r = \frac{\eta_s(\sqrt{N}b)^3}{\sqrt{3\pi}K_B T} = 0.325\frac{\eta_s \bar{R}_3}{K_B T}$
where $R = \sqrt{N}b$
so $D_G \propto M^{-1/2}, \tau_r \propto M^{3/2}$ which is in agreement with experimental results.

Chapter 5

Elastic Dumbbell Models

5.1 Preliminaries for the Elastic Dumbbells

We are now concerned with a dilute solution of a polymer, with n polymer molecules/unit volume. The solvent is a Newtonian fluid with viscosity η_s. Polymer molecules do not interact with one another. The polymer molecule is assumed to be an elastic dumbbell, that is two beads each having mass m, joined by a nonbendable spring. Let's label those beads as bead $'1'$ and $'2'$ and let r_1 and r_2 be the position vectors of them respectively. Their connector vector is $Q = r_2 - r_1$ and $r_c = \frac{1}{2}(r_1 + r_2)$ is the center of mass of the system.

As the flow field is taken to be homogeneous we can write the fluid velocity as $v = v_0 + [k \cdot r]$, where v_0 is independent of r and k is traceless $trk = 0$ as the fluid is taken to be incompressible.

The distribution function in position-velocity space which is $F(r_1, r_2, \dot{r}_1, \dot{r}_2, t)$ can be written in the form

$$F(r_1, r_2, \dot{r}_1, \dot{r}_2, t) = \Psi(r_1, r_2, t) \cdot \Xi(\dot{r}_1, \dot{r}_2, r_1, r_2, t) \tag{5.1}$$

The configuration space distribution function Ψ is independent of the location of the center of masses of the polymer molecules (it is merely a function of their configuration), whereas the velocity-space distribution function Ξ is taken to be normalized and satisfies

$$\int\int \Xi d\dot{r}_1 d\dot{r}_2 = 1 \tag{5.2}$$

The configuration space distribution function Ψ is assumed to be factored as $\Psi(r_1, r_2, t) = n\psi(Q, t)$. The distribution function $\psi(Q, t)$ satisfies the normalization condition $\int \ \psi(Q, t)dQ = 1$. Furthermore the velocity distribution can be taken to be Maxwellian such that

$$\Xi_{eq}(\dot{r}_1, \dot{r}_2) = \frac{\exp\{-[\frac{1}{2}m(\dot{r}_1 - v)^2 + \frac{1}{2}m(\dot{r}_2 - v)^2]/KT\}}{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \ \exp\{-[\frac{1}{2}m(\dot{r}_1 - v)^2 + \frac{1}{2}m(\dot{r}_2 - v)^2]/KT\} d\dot{r}_1 d\dot{r}_2} \tag{5.3}$$

For a general time-independent function $B(r_1, r_2, \dot{r}_1, \dot{r}_2)$ the velocity-space average is

$$[[B]] = \int\int B\Xi d\dot{r}_1 d\dot{r}_2 \tag{5.4}$$

and the phase-space average of $B(r_1, r_2, \dot{r}_1, \dot{r}_2)$ is

$$\langle B \rangle = \frac{1}{nV}\int\int [[B]]\Psi dr_1 dr_2 \tag{5.5}$$

If B is only a function of Q then

$$\langle B \rangle = \int B\psi dQ \tag{5.6}$$

The kind of forces bead $\nu(\nu = 1, 2)$ is presumed to experience are four, namely:
a)A hydrodynamic drag force $F_\nu^{(h)}$. The force of resistance experienced by a bead as it moves through the solution. This drag force may be isotropic or anisotropic e.t.c
b)A Brownian force $F_\nu^{(b)}$. The irregular manner by which beads are jostled about due to thermal fluctuations in the liquid. It can however be expressed as a function of the configuration distribution function.
c)An intramolecular force $F_\nu^{(\phi)}$. The force that a bead experiences due to the spring in the dumbbell. It is the negative gradient of the potential energy of the system.
d)An external force $F_\nu^{(e)}$. These are gravitational, electrical forces e.t.c

The inertial term (mass × acceleration) can be neglected

As mentioned above when we neglect the inertial terms the equation of motion for bead ν becomes

$$F_\nu^{(h)} + F_\nu^{(b)} + F_\nu^{(\phi)} + F_\nu^{(e)} = 0 \tag{5.7}$$

in which

$$F_\nu^{(h)} = -\zeta \cdot [[[\dot{r}_\nu]] - (v_\nu + v_\nu^{'})] \tag{5.8}$$

$$F_\nu^{(b)} = -\frac{1}{\Psi}\frac{\partial}{\partial t} \cdot [[[m(\dot{r}_\nu - v)(\dot{r}_\nu - v)]]\Psi] \tag{5.9}$$

$$F_\nu^{(\phi)} = -\frac{\partial}{\partial r_\nu}\phi \tag{5.10}$$

Thus the hydrodynamic force acting on bead ν is assumed proportional to the difference between the bead velocity $\dot{r}_\nu$ (averaged with respect to the velocity distribution) and the sum $v_\nu + v_\nu^{'}$. The velocity $v_\nu = v_0 + [k \cdot r_\nu]$ is that of a flow at bead ν though $v_\nu^{'}$ is the perturbation of the flow field at bead ν resulting from the motion of the other bead and will be neglected.

The 'friction tensor' ζ is a symmetric second order tensor and when taken isotropic is written as $\zeta = \delta\zeta$ where the scalar ζ is called the 'friction coefficient'

The Brownian force takes the form of the divergence of the momentum flux with respect to the velocity v at the center of mass of the dumbbell. When equilibration in momentum space is assumed the Brownian force contribution takes the form

$$F_\nu^{(b)} = -KT(\frac{\partial \ln \Psi}{\partial r_\nu}) \tag{5.11}$$

We define $F^{(c)} = F_1^{(\phi)} = -F_2^{(\phi)}$
The equation of motion if the Maxwell velocity distribution is used in the Brownian motion term, takes the form

$$-\zeta([[\dot{r}_\nu]] - v_0 - [k \cdot r_\nu]) - KT\frac{\partial}{\partial r_\nu}\ln(\Psi) + F_\nu^{(\phi)} + F_\nu^{(e)} = 0 \tag{5.12}$$

With the above equation we get

$$[[\dot{r}_c]] = v_0 + [k \cdot r_c] + \frac{1}{2\zeta}\sum_\nu F_\nu^{(e)} \tag{5.13}$$

$$[[\dot{Q}]] = [k \cdot Q] - \frac{2KT}{\zeta}\frac{\partial}{\partial Q}\ln(\psi) - \frac{2}{\zeta}F^{(c)} + \frac{1}{\zeta}[F_2^{(e)} - F_1^{(e)}] \tag{5.14}$$

The equation of continuity for the configuration distribution function is

$$\frac{\partial \Psi}{\partial t} = -(\frac{\partial}{\partial r_1} \cdot [[\dot{r}_1]]\Psi) - (\frac{\partial}{\partial r_2} \cdot [[\dot{r}_2]]\Psi) \tag{5.15}$$

or rewritten in terms of r_c and Q

$$\frac{\partial \Psi}{\partial t} = -(\frac{\partial}{\partial r_c} \cdot [[\dot{r}_c]]\Psi) - (\frac{\partial}{\partial Q} \cdot [[\dot{Q}]]\Psi) = -(\frac{\partial}{\partial Q} \cdot [[\dot{Q}]]\Psi) \tag{5.16}$$

and finally

$$\frac{\partial \psi}{\partial t} = -(\frac{\partial}{\partial Q} \cdot [[\dot{Q}]]\psi) \tag{5.17}$$

and by substituting $[[\dot{Q}]]$ from a former equation we take the diffusion equation

$$\frac{\partial \psi}{\partial t} = -(\frac{\partial}{\partial Q} \cdot \{[k \cdot Q]\psi - \frac{2KT}{\zeta}\frac{\partial}{\partial Q}\psi - \frac{2}{\zeta}F^{(c)}\psi + \frac{1}{\zeta}(F_2^{(e)} - F_1^{(e)})\psi\}) \tag{5.18}$$

5.2 Expressions for the Stress Tensor

The stress tensor π in the polymer solution is given as the sum of the solvent's (π_s) contribution and another contribution (π_p) due to the presence of polymer molecules, so

$$\pi = \pi_s + \pi_p = (p_s\delta + \tau_s) + (p_p\delta + \tau_p) = p\delta + \tau \tag{5.19}$$

where $p = p_s + p_p$ and $\tau = \tau_s + \tau_p = -\eta_s\dot{\gamma} + \tau_p$
η_s:the solvent's viscosity
$\dot{\gamma} : \dot{\gamma} = \nabla v + \nabla v^T$ is the rate of strain tensor

The derivation for the π_p expression will be empirical and quite fundamental. We recognize three kinds of contributions to the stress tensor:
a)A contribution due to the intramolecular potential, $\pi_p^{(c)}$. The two beads of the dumbbell being on opposite sides of an arbitrary plane will contribute a force $[\eta \cdot \pi_p^{(c)}]$ acting on the plane, of tension or compression transmitted through the connectors.
b)A contribution due to different external forces acting on the two beads $\pi_p^{(e)}$. This will cause a force $[\eta \cdot \pi_p^{(e)}]$ acting on the arbitrary surface.
c)A Brownian (bead motion) contribution to the stress tensor. This will cause a force $[\eta \cdot \pi_p^{(b)}]$ acting on the arbitrary plane.

5.2.1 Contribution from the Intramolecular Potential $\pi_p^{(c)}$

Let's consider an arbitrary plane of area S in the solution moving with the solution velocity v. Let η be the unit vector normal to the surface and n the number of dumbbells/unit volume. Then the number of molecules straddling the plane, with bead $'1'$ on the negative side and bead $'2'$ on the positive side is $n(\eta{\cdot}Q){\cdot}S\psi(Q,t)dQ$

The contribution to the force of the 'negative material' on the 'positive material' will be in the amount of $-F_1^{(\phi)}$. Hence the contribution of all orientations with bead $'1'$ in the negative region and bead $'2'$ in the positive region to the stress is

$$\int_{\text{integral over } Q \text{ for which } (\eta\cdot Q)>0} n(\eta \cdot Q)\psi(Q,t)(-F_1^{(\phi)})dQ \tag{5.20}$$

The stress contribution of all orientations with bead $'2'$ in the negative region and bead $'1'$ in the positive region is

$$\int_{\text{integral over } Q \text{ for which } (\eta\cdot Q)<0} n(-\eta \cdot Q)\psi(Q,t)(-F_2^{(\phi)})dQ \tag{5.21}$$

Introducing the 'connector tension' $F^{(c)}$ such that $F^{(c)} = F_1^{(\phi)} = -F_2^{(\phi)}$ the sum of the above integrals is

$$-\int_{\text{integral over all } Q} n(\eta\cdot Q)\psi(Q,t)F^{(c)}dQ = -[\eta\cdot n\int QF^{(c)}\psi(Q,t)dQ] = [\eta\cdot\pi_p^{(c)}] \tag{5.22}$$

So

$$\pi_p^{(c)} = -n\int QF^{(c)}\psi(Q,t)dQ = -n\langle QF^{(c)}\rangle \tag{5.23}$$

Since $F^{(c)}$ can be replaced by $F^{(c)}Q/|Q|$ the tensor $\pi_p^{(c)}$ is shown to be symmetric.

5.2.2 Contribution from the External Forces $\pi_p^{(e)}$

Let's assume that bead $'1'$ is subjected to an external force $F_1^{(e)}$ and bead $'2'$ may be subjected to force $F_2^{(e)}$. Following similar arguments as in case a) the contribution to the stress tensor is

$$\begin{aligned}&\int_{\text{integral over all } Q \text{ for which } (\eta\cdot Q)>0} n(\eta\cdot Q)\psi(Q,t)(-F_1^{(e)})dQ + \\ &\int_{\text{integral over all } Q \text{ for which } (\eta\cdot Q)<0} n(-\eta\cdot Q)\psi(Q,t)(-F_2^{(e)})dQ\end{aligned} \tag{5.24}$$

If we had just calculated the force exerted by the 'positive material' on the 'negative material' this would be

$$\begin{aligned}&\int_{\text{integral over all } Q \text{ for which } (\eta\cdot Q)>0} n(\eta\cdot Q)\psi(Q,t)(-F_2^{(e)})dQ + \\ &\int_{\text{integral over all } Q \text{ for which } (\eta\cdot Q)<0} n(\eta\cdot Q)\psi(Q,t)(-F_1^{(e)})dQ\end{aligned} \tag{5.25}$$

Then by identifying one half of the difference of these last two expressions as $[\eta\cdot\pi_p^{(e)}]$ then $\pi_p^{(e)} = \frac{1}{2}n\langle Q(F_2^{(e)} - F_1^{(e)})\rangle$ which is not necessarily symmetric.

5.2.3 Contribution from Bead Motion $\pi_p^{(b)}$

The motion of beads will contribute to the stress tensor because of momentum transported by the beads.The number of beads with velocity $\dot{r}_1$ that cross an arbitrary surface (whose area is S) in the time interval Δt is

$$n((\dot{r}_1 - v)\cdot S\eta)\Delta t \tag{5.26}$$

Then the amount of momentum transported across the plane is

$$n((\dot{r}_1 - v) \cdot S\eta)m(\dot{r}_1 - v)\Delta t \tag{5.27}$$

Thus the average of the momentum flux resulting from both beads is

$$n\eta \cdot \sum_{\nu=1}^{2} \int [[m(\dot{r}_1 - v)(\dot{r}_1 - v)]]\psi(Q,t)dQ \tag{5.28}$$

and is identified by $[\eta \cdot \pi_p^{(b)}]$ so

$$\pi_p^{(b)} = n \int [[\sum_{\nu=1}^{2} m(\dot{r}_1 - v)(\dot{r}_1 - v)]]\psi(Q,t)dQ \tag{5.29}$$

and integrating using the Maxwellian distribution we get $\pi_p^{(b)} = 2nKT\delta$
The stress tensor is given by the summarizing expression

$$\pi = \pi_s - n\langle QF^{(c)}\rangle + \frac{1}{2}n\langle Q[F_2^{(e)} - F_1^{(e)}]\rangle + nm\sum_{\nu=1}^{2}\langle(\dot{r}_v - v)(\dot{r}_v - v)\rangle \tag{5.30}$$

5.3 Hookean Dumbbells

If we restrict ourselves to hookean spring connectors then $F^{(c)} = HQ$ where H is the spring constant.

Then the polymer contribution to the stress tensor τ_p for the Kramers and the Giesekus case respectively is
Kramers:

$$\tau_p = -nH\langle QQ\rangle + nKT\delta \tag{5.31}$$

Giesekus:

$$\tau_p = \frac{n\zeta}{4}\langle QQ\rangle_{(1)} \tag{5.32}$$

After simple manipulations,one gets $\tau_p + \lambda_H \tau_{p(1)} = -nKT\lambda_H\gamma_{(1)}$(remember $\delta_{(1)} = -\gamma_{(1)}$)
and $\tau + \lambda_1\tau_{(1)} = -\eta_0(\gamma_{(1)} + \lambda_2\gamma_2)$ in terms of τ where
$\eta_0 = \eta_s + nKT\lambda_H$
$\lambda_1 = \lambda_H$
$\lambda = (\frac{\eta_s}{\eta_s + nKT\lambda_H})\lambda_H$

The aforementioned equation is the constitutive equation for the dilute solution and is of the form of the 'convected Jeffreys model'

The Hookean-dumbbell-solution const. eq. may be put into the form

$$\tau = -\eta_s \dot{\gamma} + \int_{-\infty}^{t} \{\frac{nKT}{\lambda_H} e^{-(t-t^{'})/\lambda_H}\} \gamma_{[0]}(t,t^{'}) dt^{'} \tag{5.33}$$

where $\gamma_{[0]}(t,t^{'}) = \delta - B = \delta - E \cdot E$ (B is the Finger strain tensor)

The average value of the square of the end-to-end distance is obtained by taking the trace of 5.31, hence $\frac{\langle Q^2 \rangle}{\langle Q^2 \rangle_{eq}} = 1 - \frac{tr\tau_p}{3nKT}$ a ratio that can be measured by means of light scattering.

Chapter 6

General Phase-Space Theory(based on Bird and Curtiss)

6.1 Abstract

The idea of a general Kinetic theory formulated in the phase space of the entire polymeric liquid was initially captured in 1975 by Curtiss, Bird and Hassager [18].This theory is summarized in [3]. Such a theory was useful for many reasons.For instance it was essential in providing a common framework for the study of rheological,diffusional and thermal phenomena e.t.c.

The framework we will be working in is thus the one of a phase-space kinetic theory for models with no internal constraints. These are commonly called 'bead-spring models', nevertheless we allow any kind of connectivity, e.g chains, rings, stars, combs e.t.c.

The notation we will continually use will be the one that labels the number of the 'bead' on the molecular model after $(\nu, \mu, \eta, ...)$, the chemical species of the molecule after $(\alpha, \beta, \gamma, ...)$ and the number of the molecule of that particular species after $(i, j, k, ...)$ in the liquid mixture. Therefore, symbols involving the interactions of pairs of beads will carry six indices, three for each bead.

6.2 Preliminaries

6.2.1 Coordinates and Momenta for Bead-Spring Models

We consider various types of springs according to the kind of potential:
a)Hookean (or Gaussian) in which $\phi = \frac{1}{2}HQ^2$

b)Fraenkel in which $\phi = \frac{1}{2}H(Q - Q_0)^2$
where Q_0 is the length in the absence of tension.
c)Warner (or 'FENE') in which $\phi = -\frac{1}{2}HQ_0^2 \ln[1-(\frac{Q}{Q_0})^2]$,here Q_0 is the maximum extended length of the spring
in short ϕ is the potential energy of the spring, Q is the interbead distance and H is the spring constant.

Hookean springs are ideal in obtaining analytical expressions e.g in the Rouse and Zimm chain models. Fraenkel springs are useful in describing chains with reduced degrees of freedom e.g constant bond lengths or angles. Finally, Warner springs are used since they approximate roughly the behavior of the inverse Langevin springs.

It is not a good idea to assume that a bead spring chain with Fraenkel connectors and $H \to \infty$ gives the same statistical mechanical results as the bead-rod chain. Indeed, this discrepancy was shown by Hassager and discussed by Gottlieb and van Kampen.

Now it really the time to set forth the notation with the Coordinates and Momenta for the bead-spring model.

We let r_ν, $\nu = 1, 2, ..., N$ be the position vector of bead ν with respect to an arbitrary laboratory fixed coordinate system and m_ν the mass of bead ν. The center-of-mass position vector r_c is defined by

$$r_c = \sum_\nu \frac{m_\nu r_\nu}{\sum_\nu m_\nu} = (\frac{1}{m_m}) \sum_\nu m_\nu r_\nu \tag{6.1}$$

and the relative position vectors Q_k, $k = 1, 2, ..., N - 1$ are defined by

$$Q_k = r_{k+1} - r_k = \sum_{\nu=1}^{N} \bar{B}_{k\nu} r_\nu \tag{6.2}$$

where m_m is the mass of the molecule
Then

$$r_\nu = r_c + \sum_{k=1}^{N-1} B_{\nu k} Q_k \tag{6.3}$$

and by this relation we can introduce position vectors referred to the center of mass

$$R_\nu = r_\nu - r_c = \sum_{k=1}^{N-1} B_{\nu k} Q_k \tag{6.4}$$

Note from the above relation that R_ν are functions of the Q_k and that

$$\sum_\nu m_\nu R_\nu = 0 \tag{6.5}$$

.

Dots indicate time derivatives and we know that $p_\nu = m_\nu \dot{r}_\nu$. The above matrices $\bar{B}_{k\nu}$ and $B_{\nu k}$ that have just been introduced are

$$\bar{B}_{k\nu} = \delta_{k+1,\nu} - \delta_{k\nu} \tag{6.6}$$

and

$$B_{\nu k} = \begin{cases} (\frac{1}{m_m}) \sum_{\mu=1}^{k} m_\mu, & \text{for } k < \nu \\ -(\frac{1}{m_m}) \sum_{\mu=k+1}^{N} m_\mu, & \text{for } k \geq \nu \end{cases} \tag{6.7}$$

those matrices satisfy the following relations

$$\sum_\nu \bar{B}_{k\nu} = 0 \tag{6.8}$$

$$\sum_\nu m_\nu B_{\nu k} = 0 \tag{6.9}$$

$$\sum_\nu \bar{B}_{j\nu} B_{\nu k} = \delta_{jk} \tag{6.10}$$

$$\sum_k B_{\nu k} \bar{B}_{km} = \delta_{\nu\mu} - (\frac{m_\mu}{m_m}) \tag{6.11}$$

We also generally use the $N-1 \times N-1$ matrices A_{jk}, C_{jk} that are named after Rouse and Kramers respectively and are defined by

$$A_{jk} = \sum_\nu \bar{B}_{j\nu} \bar{B}_{k\nu} \tag{6.12}$$

and

$$C_{jk} = \sum_\nu B_{\nu j} B_{\nu k} \tag{6.13}$$

with eigenvalues a_j, c_j respectively.
e.g for the elastic dumbbell model (two beads with mass m, connected by one spring)

$$\bar{B}_{11} = -1, B_{11} = -\frac{1}{2}, A_{11} = a_1 = 2 \tag{6.14}$$

$$\bar{B}_{12} = +1, B_{21} = +\frac{1}{2}, C_{11} = c_1 = \frac{1}{2} \tag{6.15}$$

Now let $f(r_c, Q_1, ...Q_{N-1}, t) = g(r_1, ..., r_N, t)$ then by the chain rule we result that

$$\frac{\partial g}{\partial r_\nu} = \frac{m_\nu}{m_m} \frac{\partial f}{\partial r_c} + \sum_k \bar{b}_{k\nu} \frac{\partial f}{\partial Q_k} \tag{6.16}$$

and the Jacobian of the transformation is

$$|\frac{\partial(r_1, ..., r_N)}{\partial(r_c, Q_1, ..., Q_{N-1})}| = 1 \tag{6.17}$$

Up to this moment we have considered one polymer molecule only. If we need to consider a chemical species α then we denote that by a superscript α:thus corresponding to r_ν, r_c, Q_k, R_ν and $m_m, m_\nu, \bar{B}_{k\nu}, B_{\nu k}$ we write $r_\nu^\alpha, r_c^\alpha, Q_k^\alpha, R_\nu^\alpha$ and $m_m^\alpha, m_\nu^\alpha, \bar{B}_{k\nu}^\alpha, B_{\nu k}^\alpha$. We use the notation N_α for the number of beads in molecules of species α. The various chemical species α, may be solvent molecules or polymer molecules. Solvent molecules are labelled with an $'s'$. Moreover, if we restrict to the i'th molecule of species α then we attach an extra superscript i and corresponding to $r_\nu^\alpha, r_c^\alpha, Q_k^\alpha, R_\nu^\alpha$ and $m_m^\alpha, m_\nu^\alpha, \bar{B}_{k\nu}^\alpha, B_{\nu k}^\alpha$
we read $r_\nu^{\alpha i}, r_c^{\alpha i}, Q_k^{\alpha i}, R_\nu^{\alpha i}$ and $m_m^\alpha, m_\nu^\alpha, \bar{B}_{k\nu}^\alpha, B_{\nu k}^\alpha$

Collections of coordinates or momenta carry special symbols. These sets are:
r^α = set of all N_α coordinates r_ν^α for the beads of a molecule of species α
p^α = set of all N_α coordinates p_ν^α for the beads of a molecule of a species α
Q^α = set of all $N_\alpha - 1$ relative position vectors Q_k^α for a molecule of species α
and $r^{\alpha i}$ = set of all N_α coordinates $r_\nu^{\alpha i}$ for the beads of the i'th molecule of species α
$p^{\alpha i}$ = set of all N_α momenta $p_\nu^{\alpha i}$
We also use the abbreviations dr^α for $dr_1^\alpha ... dr_{N_\alpha}^\alpha$ and dQ^α for $dQ_1^\alpha ... dQ_{N_\alpha - 1}^\alpha$

Finally, we give the following definitions

$$R_{\nu\mu}^{\alpha i} = r_\mu^{\alpha i} - r_\nu^{\alpha i} \tag{6.18}$$

$$R_{\nu\mu}^{\alpha i, \beta j} = r_\mu^{\beta j} - r_\nu^{\alpha i} \tag{6.19}$$

with similar notation without the $i's$ and $j's$ to designate interbead vectors between beads of a molecule of species α, or between the beads of two molecules α and β.
We end with:

$$R_{\alpha\beta} = r_c^\beta - r_c^\alpha \tag{6.20}$$

that is the vector from the center of mass of a molecule of species α to the center of mass of a molecule of species β and

$$r_c^{\alpha\beta} = \frac{m_m^\alpha r_c^\alpha + m_m^\beta r_c^\beta}{m_m^\alpha + m_m^\beta} \tag{6.21}$$

=Center of mass of a pair of molecules α and β

Beads of different molecules are assumed to interact with one another according to a Lennard-Jones type of force which is attractive at large distances and repulsive at small distances. The interbead force is taken to be collinear with the interbead vector. As for the interbead forces within a single molecule those are described by springs and if we want to take into account the 'excluded volume effect' then we can additionally include a Lennard-Jones type of interaction between beads not connected by springs. Here again, the interbead force is taken to be collinear with the interbead vector.

6.2.2 Potentials and Forces for Bead-Spring Models

Here we give the potential energies describing forces between beads, including the 'spring forces' (excluded volume forces) and the 'Lennard-Jones type forces' between molecules:
$\phi^{\alpha i}$:the potential energy of a single molecule αi (intramolecular contribution) which is a function of $r_\nu^{\alpha i}(\nu = 1, 2, ..., N_\alpha)$
$\phi^{(e)\alpha i}$:the potential energy of a single molecule αi (external field contribution) which is also a function of $r_\nu^{\alpha i}(\nu = 1, 2, ..., N_\alpha)$
ϕ:the potential energy of all molecules in the liquid (intramolecular and intermolecular, but not external field, contributions) which is a function of $r_\nu^{\alpha i}(\nu = 1, ...N_\alpha, \alpha = 1, 2..., i = 1, 2, ...)$

The above can be written as sums of pairwise interactions (extra assumption): Thus $\phi^{\alpha i} = \frac{1}{2}\sum_\nu \sum_\mu \phi_{\nu\mu}^{\alpha i}$ in which, if $\nu \neq \mu$ then $\phi_{\nu\mu}^{\alpha i}$ is a function of $|R_{\nu\mu}^{\alpha i}| = |r_\mu^{\alpha i} - r_\nu^{\alpha i}|$ and if $\nu = \mu$ then $\phi_{\nu\mu}^{\alpha i} = 0$
$\phi^{(e)\alpha i} = \sum_\nu \phi_\nu^{(e)\alpha i}$ in which $\phi_\nu^{(e)\alpha i}$ is a function of $r_\nu^{\alpha i}$
$\Phi = \frac{1}{2}\sum_{\alpha i\nu}\sum_{\beta j\mu} \phi_{\nu\mu}^{\alpha i,\beta j}$ in which $\phi_{\nu\mu}^{\alpha i,\beta j}$ is a function of $|R_{\nu\mu}^{\alpha i,\beta j}| = |r_\mu^{\beta j} - r_\nu^{\alpha i}|$,$\phi_{\nu\nu}^{\alpha i,\alpha i}$ are defined to be zero and $\phi_{\nu\mu}^{\alpha i,\alpha i} = \phi_{\nu\mu}^{\alpha i}$

Sometimes, we write
$\Phi = \frac{1}{2}\sum_\nu\sum_\mu \phi_{\nu\mu}^{\alpha i} + \frac{1}{2}\sum_{\alpha i\nu}\sum_{\beta j\mu} \phi_{\nu\mu}^{(d)\alpha i,\beta j}$, where $\phi_{\nu\mu}^{(d)\alpha i,\beta j}$ differs from $\phi_{\nu\mu}^{\alpha i,\beta j}$ in that in the former, if $\alpha = \beta$ those terms with $i = j$ are zero.

We also define the forces acting on bead ν of molecule αi, corresponding to the potential energies

$$F_\nu^{(\phi)\alpha i} = -\frac{\partial}{\partial r_\nu^{\alpha i}}\phi^{\alpha i} = -\frac{\partial}{\partial r_\nu^{\alpha i}}\sum_\mu \phi_{\nu\mu}^{\alpha i} = \sum_\mu F_{\nu\mu}^{(\phi)\alpha i} \tag{6.22}$$

= force resulting from 'springs' within one molecule.

$$F_\nu^{(e)\alpha i} = -\frac{\partial}{\partial r_\nu^{\alpha i}}\phi^{(e)\alpha i} = -\frac{\partial}{\partial r_\nu^{\alpha i}}\phi_\nu^{(e)\alpha i} \tag{6.23}$$

= force exerted by an external field .

$$F_\nu^{(\phi)\alpha i} = -\frac{\partial}{\partial r_\nu^{\alpha i}}\Phi = -\frac{\partial}{\partial r_\nu^{\alpha i}}\sum_{\beta j\mu} \phi_{\nu\mu}^{\alpha i,\beta j} = \sum_{\beta j\mu} F_{\nu\mu}^{(\Phi)\alpha i,\beta j} \tag{6.24}$$

= force due to all other 'beads' in the liquid ($\alpha i\nu \neq \beta j\mu$)

Additionally, we define

$$F_\nu^{(d)\alpha i} = -\frac{\partial}{\partial r_\nu^{\alpha i}} \sum_{\beta j\mu} \phi_{\nu\mu}^{(d)\alpha i,\beta j} = \sum_{\beta j\mu} F_{\nu\mu}^{(d)\alpha i,\beta j} \tag{6.25}$$

and the total force on bead ν of molecule αi is

$$F_\nu^{\alpha i} = F_\nu^{(\Phi)\alpha i} + F_\nu^{(e)\alpha i} = F_\nu^{(\phi)\alpha i} + F_\nu^{(d)\alpha i} + F_\nu^{(e)\alpha i}. \tag{6.26}$$

Then according to Newton's second law of motion:
$F_\nu^{\alpha i} = \dot{p}_\nu^{\alpha i}$ and $p_\nu^{\alpha i} = m_\nu^\alpha \dot{r}_\nu^{\alpha i}$

Finally, we define symbols for forces on the center of mass of αi,

$$F^{(e)\alpha i} = -\frac{\partial}{\partial r_c^{\alpha i}} \phi^{(e)\alpha i} \tag{6.27}$$

=force due to external force

$$F^{(d)\alpha i} = -\frac{\partial}{\partial r_c^{\alpha i}} \Phi \tag{6.28}$$

=force due to all other molecules.

6.2.3 The Liouville Equation and the General Equation of Change

The dynamical state of a polymeric liquid mixture in a fixed instant of time is described by a point in the phase-space (i.e $r_\nu^{\alpha i}, p_\nu^{\alpha i}, \nu = 1, 2, ..., N_\alpha, \alpha = 0, 1, 2, ..., i = 1, 2, ...$). We denote by r, p and x the complete set of position, momentum and phase-space coordinates respectively.

The state of an ensemble of isolated systems is described by a distribution function $f(x, t)$ in the system phase-space, which is normalized to unity

$$\int f(x, t) dx = 1 \tag{6.29}$$

The average value of a function $B(x)$ is given by

$$\int B(x) f(x, t) dx = \langle B(x) \rangle \tag{6.30}$$

We define the configuration space distribution function $\Psi(r, t)$ by

$$\int f(x, t) dp = \Psi(r, t) \tag{6.31}$$

and the average value of function $B(r)$ is

$$\int B(r)f(x,t)dx = \int B(r)\Psi(r,t)dr = \langle B\rangle \tag{6.32}$$

The Liouville equation reads

$$\frac{\partial}{\partial t}f = -\sum_{\alpha i\nu}(\frac{p_\nu^{\alpha i}}{m_\nu^\alpha}\cdot\frac{\partial}{\partial r_\nu^{\alpha i}}f + F_\nu^{\alpha i}\cdot\frac{\partial}{\partial p_\nu^{\alpha i}}f) \equiv -\L f \tag{6.33}$$

where Ł is the Liouville operator.
The general equation of change is
$\frac{\partial}{\partial t}\langle B\rangle = \langle \L f\rangle$ and by making various choices of B we can get:
a)The Continuity Equation
b)The Momentum Transport Equation
c)The Hydrodynamic Energy Equation
d)The Hydrodynamic Equation for the Angular Momentum
e)The Equation for the time evolution of the Singlet Distribution Function
in short all the kinetic theory equations

6.3 Distribution Functions in the Phase -Configuration space of one or two molecules

We are about to present definitions and results for contracted distribution functions, essential for further developments.

6.3.1 Singlet Distribution Function

The definition of the Singlet phase-space distribution function is:

$$\begin{aligned} f_\alpha(r^\alpha, p^\alpha, t) &= \langle\sum_i \delta(r_i^{\alpha i} - r_1^\alpha)\delta(r_2^{\alpha i} - r_2^\alpha)...\delta(p_1^{\alpha i} - p_1^\alpha)\delta(p_2^{\alpha i} - p_2^\alpha)...\rangle \\ &= \langle\sum_i \delta(r^{\alpha i} - r^\alpha)\delta(p^{\alpha i} - p^\alpha)\rangle \end{aligned} \tag{6.34}$$

The interpretation of the singlet distribution function is :

$$f_\alpha(r_1^\alpha, r_2^\alpha, ..., r_{N_\alpha}^\alpha, p_1^\alpha, p_2^\alpha, ..., p_{N_\alpha}^\alpha, t)dr_1^\alpha dr_2^\alpha dr_{N_\alpha}^\alpha dp_1^\alpha dp_2^\alpha ... dp_{N_\alpha}^\alpha =$$

the ensemble average of the number of molecules of species α,for which bead "1" is located in the range dr_1^α about r_1^α with momentum in the range dp_1^α about

p_1^α,bead "2" is located in the range dr_2^α about r^α with momentum in the range dp_2^α about p_2^α etc
The normalization of $f_\alpha(r^\alpha, p^\alpha, t)$ is the following

$$\int\int f_\alpha(r^\alpha, p^\alpha, t)\delta(r_c^\alpha - r)dr^\alpha dp^\alpha = n_\alpha(r, t) \tag{6.35}$$

where $n_\alpha(r, t)$ is the ensemble average of the number density of centers-of-mass of species α at position r and time t.We define the singlet configurational distribution function

$$\bar{\Psi}_\alpha(r^\alpha, t) = \int f_\alpha(r^\alpha, p^\alpha, t)dp^\alpha = \langle\sum_i \delta(r^{\alpha i} - r^\alpha)\rangle \tag{6.36}$$

$\bar{\Psi}_\alpha$ is expected to vary slowly with respect to the location of the center of mass over a macroscopic length scale.Therefore it may seem reasonable to introduce a configuration function that carries the same amount of information but is defined on a different set that spans the same space.Thus

$$\Psi_\alpha(r_c^\alpha, Q^\alpha, t) = \bar{\Psi}_\alpha(r^\alpha, t) \tag{6.37}$$

which is normalized by:

$$\int \Psi_\alpha(r_c^\alpha, Q^\alpha, t)\delta(r_c^\alpha - r)dr_c^\alpha dQ^\alpha = \int \Psi_\alpha(r, Q^\alpha, t)dQ^\alpha = n_\alpha(r, t) \tag{6.38}$$

6.3.2 Doublet Distribution Functions

The doublet distribution function for a pair of molecules α β is defined by:

$$f_{\alpha\beta}(r^\alpha, p^\alpha, r^\beta, p^\beta, t) = \langle\sum_i\sum_j \delta(r^{\alpha i} - r^\alpha)\delta(p^{\alpha i} - p^\alpha)\delta(r^{\beta j} - r^\beta)\delta(p^{\beta j} - p^\beta)\rangle \tag{6.39}$$

If $\alpha = \beta$ terms with $i = j$ are to be ommited.We go on with the interpretation of the doublet distribution function:

$$f_{\alpha\beta}(r_1^\alpha, ..., r_{N_\alpha}^\alpha, p_1^\alpha, ..., p_{N_\alpha}^\alpha, r_1^\beta, ..., r_{N_\beta}^\beta, p_1^\beta, ..., p_{N_\beta}^\beta, t)dr_1^\alpha...dr_{N_\alpha}^\alpha$$

$$dp_1^\alpha...dp_{N_\alpha}^\alpha dr_1^\beta...dr_{N_\beta}^\beta dp_1^\beta...dp_{N_\beta}^\beta =$$

the ensemble average of the number of molecules of species α and β,such that bead "1" of a molecule of α is located within the range dr_1^α about r_1^α with momentum in the range dp_1^α about p_1^α etc and that bead "1" of a molecule of β is located within the range dr_1^β about r_1^β with momentum in the range dp_1^β about p_1^β etc By means already familiar we obtain the configurational distribution function:

$$\bar{\Psi}_{\alpha\beta}(r^\alpha, r^\beta, t) = \int f_{\alpha\beta}(r^\alpha, p^\alpha, r^\beta, p^\beta, t) dp^\alpha dp^\beta$$

$$= \langle \sum_i \sum_j \delta(r^{\alpha i} - r^\alpha)\delta(r^{\beta j} - r^\beta)\rangle \tag{6.40}$$

We also define $\Psi_{\alpha\beta}$ in the following manner

$$\Psi_{\alpha\beta}(r_c^\alpha, Q^\alpha, r_c^\beta, Q^\beta, t) = \bar{\Psi}_{\alpha\beta}(r^\alpha, r^\beta, t) \tag{6.41}$$

6.4 Averages of functions in the Phase-space of one and two molecules

For the sake of future simplicity in the presentation we are about to derive formulas for averages involving functions in the phase-space of one or two molecules.For this we need the following definition:
Let $b^\alpha(r^\alpha, p^\alpha)$ be a function in the phase-space of a single molecule then its average in momentum space is

$$[[b^\alpha]]^\alpha = \int b^\alpha f_\alpha dp^\alpha / \int f_\alpha dp^\alpha \tag{6.42}$$

Similarly,we can define the average value of b^α in the phase-space of a pair of molecules like:

$$[[b^\alpha]]^{\alpha\beta} = \int\int b^\alpha(r^\alpha, p^\alpha) f_{\alpha\beta} dp^\alpha dp^\beta / \int\int f_{\alpha\beta} dp^\alpha dp^\beta \tag{6.43}$$

6.4.1 Averages involving Functions in the Phase-space of one molecule only

Later on we will consider averages of the form

$$\bar{C}_\nu^\alpha = \langle \sum_i b_\nu^{\alpha i} C_\nu^{\alpha i} \delta(r_\nu^{\alpha i} - r)\rangle \tag{6.44}$$

in which in general $b_\nu^{\alpha i}$ will be a function of the $p_\mu^{\alpha i}$ for all μ and $C_\nu^{\alpha i}$ is a function of the $r_\mu^{\alpha i}$ for all μ.Our purpose of this section is to arrive to an expression of this average by means of the single distribution function.

After simple manipulations we write down two equivalent expressions for $\bar{C}_\nu^\alpha$ which are

$$\bar{C}_\nu^\alpha = \int\int\sum_i b_\nu^{\alpha i} C_\nu^{\alpha i} f(x,t)\delta(r_\nu^{\alpha i} - r_\nu^\alpha)\delta(r_\nu^\alpha - r) dr_\nu^\alpha dx \tag{6.45}$$

and

$$\bar{C}_\nu^\alpha = \int\int\int\sum_i b_\nu^{\alpha i} C_\nu^{\alpha i} \delta(r^{\alpha i} - r^\alpha)\delta(p^{\alpha i} - p^\alpha) f(x,t)\delta(r_\nu^\alpha - r) dr^\alpha dp^\alpha dx \tag{6.46}$$

Because of the inclusion of the delta functions $b_\nu^{\alpha i}$ may be written as b_ν^α and similarly $C_\nu^{\alpha i}$ may be written as C_ν^α so we get

$$\bar{C}_\nu^\alpha = \int\int b_\nu^\alpha C_\nu^\alpha f_\alpha(r^\alpha, p^\alpha, t)\delta(r_\nu^\alpha - r) dr^\alpha dp^\alpha \tag{6.47}$$

or

$$\bar{C}_\nu^\alpha = \int [[b_\nu^\alpha]]^\alpha C_\nu^\alpha \bar{\Psi}_\alpha(r^\alpha, t)\delta(r_\nu^\alpha - r) dr^\alpha \tag{6.48}$$

We are now about to shift to another configuration of description:

$$\bar{C}_\nu^\alpha = \int\int [[b_\nu^\alpha]]^\alpha C_\nu^\alpha \Psi_\alpha(r_c^\alpha, Q^\alpha, t)\delta(r_c^\alpha + R_\nu^\alpha - r) dr_c^\alpha dQ^\alpha \tag{6.49}$$

or after integration

$$\bar{C}_\nu^\alpha = \int [[b_\nu^\alpha]]^\alpha C_\nu^\alpha \Psi_\alpha(r - R_\nu^\alpha, Q^\alpha, t) dQ^\alpha \tag{6.50}$$

The last step is to expand the integrand in a Taylor series about r,since Ψ_α is slowly changing with respect to its first argument:So

$$\bar{C}_\nu^\alpha = \int [[b_\nu^\alpha]]^\alpha C_\nu^\alpha \Psi_\alpha(r, Q^\alpha, t) dQ^\alpha - \nabla \cdot \int R_\nu^\alpha [[b_\nu^\alpha]]^\alpha C_\nu^\alpha \Psi_\alpha(r, Q^\alpha, t) dQ^\alpha$$

$$+\nabla\nabla : \int R_\nu^\alpha R_\nu^\alpha [[b_\nu^\alpha]]^\alpha C_\nu^\alpha \Psi_\alpha(r, Q^\alpha, t) dQ^\alpha + ... \tag{6.51}$$

or in an equivalent form

$$\bar{C}_\nu^\alpha = \int [[b_\nu^\alpha]]^\alpha C_\nu^\alpha \Psi_\alpha(r, Q^\alpha, t) dQ^\alpha$$

$$-\nabla \cdot \int\int_0^1 R_\nu^\alpha [[b_\nu^\alpha]]^\alpha C_\nu^\alpha \Psi_\alpha(r - \xi R_\nu^\alpha, Q^\alpha, t) d\xi dQ^\alpha \tag{6.52}$$

6.4.2 Averages involving Functions in the Phase-space of a pair of molecules

This time we are concerned with averages involving interactions between pairs of beads belonging to different molecules.We will find expressions for averages of the form:

$$\bar{C}_{\nu}^{\alpha\beta} = \langle \sum_{i} \sum_{j}{}^{'} b_{\nu}^{\alpha i} C_{\nu}^{\alpha i,\beta j} \delta(r_{\nu}^{\alpha i} - r) \rangle \tag{6.53}$$

where the prime symbol indicates that $\alpha i \neq \beta j$ as for $b_{\nu}^{\alpha i}$ it is a function of the $p_{\mu}^{\alpha i}$ for all μ and $C_{\nu}^{\alpha i,\beta j}$ is a function of $r_{\mu}^{\alpha i}$ for all μ and $r_{\mu}^{\beta j}$ for all μ

The expressions we finally obtain are

$$\bar{C}_{\nu}^{\alpha\beta} = \int\int\int [[b_{\nu}^{\alpha}]]^{\alpha\beta} C_{\nu}^{\alpha\beta} \tilde{\Psi}_{\alpha\beta}(r - R_{\nu}^{\alpha} + \frac{m_{m}^{\beta}}{m_{m}^{\alpha} + m_{m}^{\beta}} R_{\alpha\beta}, R_{\alpha\beta}, Q^{\alpha}, Q^{\beta}, t) dR_{\alpha\beta} dQ^{\alpha} dQ^{\beta} \tag{6.54}$$

or

$$\begin{aligned} \bar{C}_{\nu}^{\alpha\beta} = & \int\int\int [[b_{\nu}^{\alpha}]]^{\alpha\beta} C_{\nu}^{\alpha\beta} \tilde{\Psi}_{\alpha\beta}(r, R_{\alpha\beta}, Q^{\alpha}, Q^{\beta}, t) dR_{\alpha\beta} dQ^{\alpha} d^{\beta} \\ & -\nabla \cdot \int\int\int (R_{\nu}^{\alpha} - \frac{m_{m}^{\beta}}{m_{m}^{\alpha} + m_{m}^{\beta}} R_{\alpha\beta}) [[b_{\nu}^{\alpha}]]^{\alpha\beta} \\ & C_{\nu}^{\alpha\beta} \tilde{\Psi}_{\alpha\beta}(r, R_{\alpha\beta}, Q^{\alpha}, Q^{\beta}, t) dR_{\alpha\beta} dQ^{\alpha} dQ^{\beta} + ... \end{aligned} \tag{6.55}$$

where $\tilde{\Psi}_{\alpha\beta}$ contains the same amount of information as $\Psi_{\alpha\beta}$ with the only difference in the arguments.Since

$$\tilde{\Psi}_{\alpha\beta}(r_{c}^{\alpha\beta}, R_{\alpha\beta}, Q^{\alpha}, Q^{\beta}, t) = \Psi_{\alpha\beta}(r_{c}^{\alpha}, Q^{\alpha}, r_{c}^{\beta}, Q^{\beta}, t) \tag{6.56}$$

6.5 The Hydrodynamic Equation of Continuity

The equation of continuity for a species α in a multicomponent mixture is:

$$\frac{\partial}{\partial t} \rho_{\alpha} = -(\nabla \cdot \rho_{\alpha} v_{\alpha}) = -(\nabla \cdot \rho_{\alpha} v) - (\nabla \cdot j_{\alpha}) (\alpha = 1, 2, 3, ...) \tag{6.57}$$

where
ρ_{α}:mass concentration of species α
v_{α}:velocity of species α
j_{α}:mass-flux vector of species α
The physical interpretation of quantity j_{α}, is that for a surface element dS and a unit vector η normal to dS then $(\eta \cdot j_{\alpha})dS$ is the mass of species α that passes through dS/per unit time from the negative to the positive side of dS.

One can easily see the following relations

$$\rho(r,t) = \sum_\alpha \rho_\alpha(r,t) \tag{6.58}$$

$$\rho(r,t)v(r,t) = \sum_\alpha \rho_\alpha(r,t)v_\alpha(r,t) \tag{6.59}$$

$$j_\alpha(r,t) = \rho_\alpha(r,t)(v_\alpha(r,t) - v(r,t)) \tag{6.60}$$

$$\sum_\alpha j_\alpha(r,t) = 0 \tag{6.61}$$

and by adding the equation of continuity for each species we get the equation of continuity $\frac{\partial}{\partial t}\rho = -(\nabla \cdot \rho v)$ for the liquid mixture.

What we need is a function B_α in the phase-space such that $\langle B_\alpha \rangle$ is the concentration ρ_α of species α and hence we can generate the equation of continuity and find a proper expression for the mass-flux vector j_α. We thus need to localize the mass of α in a unit volume surrounding position r.
That is $B_\alpha = \sum_i \sum_\nu m_\nu^\alpha \delta(r_\nu^{\alpha i} - r)$
and $\rho_\alpha = \langle B_\alpha \rangle$

Using results already shown we have

$$\rho_\alpha = \sum_\nu m_\nu^\alpha \int \bar{\Psi}_\alpha(r^\alpha, t)\delta(r_\nu^\alpha - r)dr^\alpha = \sum_\nu m_\nu^\alpha \int \Psi_\alpha(r - R_\nu^\alpha, Q^\alpha, t)dQ^\alpha$$

$$= \sum_\nu m_\nu^\alpha \int \Psi_\alpha(r, Q, t)dQ^\alpha - \nabla \cdot \sum_\nu m_\nu^\alpha \int R_\nu^\alpha \Psi_\alpha(r, Q^\alpha, t)dQ^\alpha + ...$$

$$n_\alpha m_m^\alpha - 0 + \frac{1}{2}\nabla\nabla : \sum_\nu m_\nu^\alpha \int R_\nu^\alpha R_\nu^\alpha \Psi_\alpha(r, Q^\alpha, t)dQ^\alpha - ... \tag{6.62}$$

The relation $\rho_\alpha = n_\alpha m_\nu^\alpha$ is not true, since the mass of a molecule is not localized at the center of mass.

The general equation of change gives

$$\frac{\partial}{\partial t}\rho_\alpha = \langle \sum_{\beta i \mu} \frac{p_\mu^{\beta j}}{m_\mu^\beta} \cdot \frac{\partial}{\partial r_\mu^{\beta j}}(\sum_i \sum_\nu m_\nu^\alpha \delta(r_\nu^{\alpha i} - r))\rangle$$

$$= \langle \sum_i \sum_\nu \frac{p_\nu^{\alpha i}}{m_\nu^\alpha} \cdot \frac{\partial}{\partial r_\nu^{\alpha i}}(m_\nu^\alpha \delta(r_\nu^{\alpha i} - r))\rangle$$

$$= -\langle \sum_i \sum_\nu (p_\nu^{\alpha i} \cdot \frac{\partial}{\partial r}\delta(r_\nu^{\alpha i} - r))\rangle$$

$$= -(\nabla \cdot \langle \sum_i \sum_\nu p_\nu^{\alpha i} \delta(r_\nu^{\alpha i} - r) \rangle). \tag{6.63}$$

We have used the fact that $(\frac{\partial}{\partial x})\delta(x-y) = -(\frac{\partial}{\partial y})\delta(x-y)$ and that $\frac{\partial}{\partial r}, \nabla$ are identical operators. The quantity in brackets in the last relation is realized as $\rho_\alpha v_\alpha$. We can now write

$$\rho_\alpha v_\alpha = \sum_\nu \int [[p_\nu^\alpha]]^\alpha \bar{\Psi}_\alpha(r^\alpha, t)\delta(r_\nu^\alpha - r) dr^\alpha$$

$$= \sum_\nu \int [[p_\nu^\alpha]]^\alpha \Psi_\alpha(r - R_\nu^\alpha, Q^\alpha, t) dQ^\alpha$$

$$= \sum_\nu \int [[p_\nu^\alpha]]^\alpha \Psi_\alpha(r, Q^\alpha, t) dQ^\alpha - \nabla \cdot \sum_\nu \int R_\nu^\alpha [[p_\nu^\alpha]]^\alpha \Psi_\alpha(r, Q^\alpha, t) dQ^\alpha + ... \tag{6.64}$$

and

$$j_\alpha(r,t) = \sum_\nu \int ([[p_\nu^\alpha]]^\alpha - m_\nu^\alpha v(r,t)) \bar{\Psi}_\alpha(r^\alpha, t)\delta(r_\nu^\alpha - r) dr^\alpha$$

$$\sum_\nu \int [[p_\nu^\alpha]]^\alpha \Psi_\alpha(r - R_\nu^\alpha, Q^\alpha, t) dQ^\alpha - v(r,t) \sum_\nu m_\nu^\alpha \int \Psi_\alpha(r - R_\nu^\alpha, Q^\alpha, t) dQ^\alpha \tag{6.65}$$

We make Taylor expansion for each term in 6.65. Thus

$$j_\alpha(r,t) = \sum_\nu m_\nu^\alpha \int [[\dot{r}_\nu^\alpha]]^\alpha \Psi_\alpha(r, Q^\alpha, t) dQ^\alpha$$

$$-\nabla \cdot \sum_\nu m_\nu^\alpha \int R_\nu^\alpha [[\dot{r}_\nu^\alpha]]^\alpha \Psi_\alpha(r, Q^\alpha, t) dQ^\alpha$$

$$+\frac{1}{2}\nabla\nabla : \sum_\nu m_\nu^\alpha \int R_\nu^\alpha R_\nu^\alpha [[\dot{r}_\nu^\alpha]]^\alpha \Psi_\alpha(r, Q^\alpha, t) dQ^\alpha + ...$$

$$-v(r,t) \sum_\nu m_\nu^\alpha \int \Psi_\alpha(r, Q^\alpha, t) dQ^\alpha + 0$$

$$-\frac{1}{2} v(r,t) : \sum_\nu m_\nu^\alpha \int R_\nu^\alpha R_\nu^\alpha \Psi_\alpha(r, Q^\alpha, t) dQ^\alpha + ... \tag{6.66}$$

6.6 The Hydrodynamic Equation of Motion

The equation of motion for a fluid mixture is known to be

$$\frac{\partial}{\partial t}[\rho v] = -[\nabla \cdot \rho v v] - [\nabla \cdot \pi] + G \tag{6.67}$$

where
π: is the stress tensor
G: external force/unit volume
The stress tensor is defined in a way, such that for a surface element dS and a unit vector η normal to dS the $[\eta \cdot \pi]dS$ is the force exerted from the negative to the positive side of dS.

As done before, we need to find a vector function B in the phase space such that $\langle B\rangle$ is the momentum flux ρv at position r and time t. We take $B = \sum_{\alpha i \nu} p_\nu^{\alpha i}\delta(r_\nu^{\alpha i} - r)$ and insert it into the general equation of change, thus we have

$$\frac{\partial}{\partial t}\rho v = -\nabla \cdot \langle \sum_{\alpha i \nu} \frac{1}{m_\nu^\alpha} p_\nu^{\alpha i} p_\nu^{\alpha i} \delta(r_\nu^{\alpha i} - r)\rangle + \langle \sum_{\alpha i \nu} F_\nu^{\alpha i}\delta(r_\nu^{\alpha i} - r)\rangle \tag{6.68}$$

The last term is idealized as a 'momentum source' term S and we have

$$S = S^{(\phi)} + S^{(d)} + S^{(e)} = \langle \sum_{\alpha i \nu} (F_\nu^{(\phi)\alpha i} + F_\nu^{(d)\alpha i} + F_\nu^{(e)\alpha i})\delta(r_\nu^{\alpha i} - r)\rangle \tag{6.69}$$

we can also see the stress tensor as the sum of four different contributions

$$\pi = \pi^{(k)} + \pi^{(\phi)} + \pi^{(d)} + \pi^{(e)} \tag{6.70}$$

the kinetic, intramolecular, intermolecular and external field contribution.

6.6.1 The kinetic Contribution to the Stress Tensor

We rewrite the first $< ... >$ term in 6.68 by replacing $p_\nu^{\alpha i}$ by $m_\nu^\alpha(\dot{r}_\nu^{\alpha i} - r)$ and supplying compensating terms. That is:

$$\langle \sum_{\alpha i \nu} \frac{1}{m_\nu^\alpha} p_\nu^{\alpha i} p_\nu^{\alpha i} \delta(r_\nu^{\alpha i} - r)\rangle = \langle \sum_{\alpha i \nu} m_\nu^\alpha (\dot{r}_\nu^{\alpha i} - v)(\dot{r}_\nu^{\alpha i} - v)\delta(r_\nu^{\alpha i} - r)\rangle$$

$$+\langle \sum_{\alpha i \nu} m_\nu^\alpha (\dot{r}_\nu^{\alpha i} v + v\dot{r}_\nu^{\alpha i} - vv)\delta(r_\nu^{\alpha i} - r)\rangle \tag{6.71}$$

One has to keep in mind that the last term gives

$$\langle \sum_{\alpha i \nu} m_\nu^\alpha (\dot{r}_\nu^{\alpha i} v + v\dot{r}_\nu^{\alpha i} - vv)\delta(r_\nu^{\alpha i} - r)\rangle$$

$$= \sum_\alpha [\rho_\alpha v_\alpha v + v\rho_\alpha v_\alpha - \rho_\alpha vv] = \rho vv \tag{6.72}$$

and the equation of motion takes the form

$$\frac{\partial}{\partial t}[\rho v] = -[\nabla \cdot \rho vv] - [\nabla \cdot \pi^{(k)}] + S. \tag{6.73}$$

We can write $\pi^{(k)} = \langle \sum_{\alpha i \nu} m_\nu^\alpha (\dot{r}_\nu^{\alpha i} - v)(\dot{r}_\nu^{\alpha i} - v)\delta(r_\nu^{\alpha i} - r)\rangle$

$$= \sum_{\alpha\nu} \int \ m_\nu^\alpha [[(\dot{r}_\nu^\alpha - v)(\dot{r}_\nu^\alpha - v)]]^\alpha \Psi_\alpha(r - R_\nu^\alpha, Q^\alpha, t)dQ^\alpha$$

$$= \sum_{\alpha\nu} m_\nu^\alpha \int \ [[(\dot{r}_\nu^\alpha - v)(\dot{r}_\nu^\alpha - v)]]^\alpha \Psi_\alpha(r, Q^\alpha, t)dQ^\alpha + ... \tag{6.74}$$

6.6.2 The external Force Contribution to the Stress Tensor

The external force contribution to the Stress Tensor is:

$$S^{(e)} = \langle \sum_{\alpha i \nu} F_\nu^{(e)\alpha i} \delta(r_\nu^{\alpha i} - r)\rangle$$

$$= \sum_\alpha \sum_\nu \int \ F_\nu^{(e)\alpha} \Psi_\alpha(r - R_\nu^\alpha, Q^\alpha, t)dQ^\alpha$$

$$\sum_\alpha \int \ F^{(e)\alpha} \Psi_\alpha(r, Q^\alpha, t)dQ^\alpha - [\nabla \cdot \sum_\alpha \sum_\nu \int \int_0^1 \ R_\nu^\alpha F_\nu^{(e)\alpha} \Psi_\alpha(r - \xi R_\nu^\alpha, Q^\alpha, t)d\xi dQ^\alpha] \tag{6.75}$$

We make further identifications

$$G = \sum_\alpha \int \ F^{(e)\alpha} \Psi_\alpha(r, Q^\alpha, t)dQ^\alpha \tag{6.76}$$

and $\pi^{(e)} = \sum_\alpha \sum_\nu \int \int_0^1 R_\nu^\alpha F_\nu^{(e)\alpha} \Psi_\alpha(r - \xi R_\nu^\alpha, Q^\alpha, t)d\xi dQ^\alpha$

$$= \sum_\alpha \sum_\nu \int \ R_\nu^\alpha F_\nu^{(e)\alpha} \Psi_\alpha(r, Q^\alpha, t)dQ^\alpha + ... \tag{6.77}$$

If the external forces/unit mass are the same for all beads of a given molecule, so that all $F_\nu^{(e)\alpha}/m_\nu^\alpha$ are constant and equal to g_α then $G = \sum_\alpha \rho_\alpha g_\alpha$ and $\pi^{(e)}$ is equal to zero.

6.6.3 The Intramolecular Contribution to the Stress Tensor

The intramolecular contribution to the source term $S^{(\phi)}$ is,

$$S^{(\phi)} = \langle \sum_{\alpha i \nu} F_{\nu}^{(\phi)\alpha i} \delta(r_{\nu}^{\alpha i} - r) \rangle \tag{6.78}$$

Using results of Section 6.3 we have

$$S^{(\phi)} = \sum_{\alpha} \sum_{\nu} \int \; F_{\nu}^{(\phi)\alpha} \Psi_{\alpha}(r - R_{\nu}^{\alpha}, Q^{\alpha}, t) dQ^{\alpha}$$

$$= \sum_{\alpha} \sum_{\nu} \int \; F_{\nu}^{(\phi)\alpha} \Psi_{\alpha}(r, Q^{\alpha}, t) dQ^{\alpha} - [\nabla \cdot \sum_{\alpha} \sum_{\nu} \int \int_{0}^{1} \; R_{\nu}^{\alpha} F_{\nu}^{(\phi)\alpha} \Psi_{\alpha}(r - \xi R_{\nu}^{\alpha}, Q^{\alpha}, t) d\xi dQ^{\alpha}] \tag{6.79}$$

The first term vanishes since $\sum_{\nu} F_{\nu}^{(\phi)\alpha} = \sum_{\nu} \sum_{\mu} F_{\nu\mu}^{(\phi)\alpha} = 0$ and we identify $\pi^{(\phi)}$ as

$$\begin{aligned} \pi^{(\phi)} &= \sum_{\alpha} \sum_{\nu} \int \int_{0}^{1} R_{\nu}^{\alpha} F_{\nu}^{(\phi)\alpha} \Psi_{\alpha}(r - \xi R_{\nu}^{\alpha}, Q^{\alpha}, t) d\xi dQ^{\alpha} \\ &= \frac{1}{2} \sum_{\alpha\nu\mu} \int \; R_{\nu\mu}^{\alpha} F_{\nu\mu}^{(\phi)\alpha} \Psi_{\alpha}(r, Q^{\alpha}, t) dQ^{\alpha} + ... \end{aligned} \tag{6.80}$$

6.6.4 The Intermolecular Contribution to the Stress Tensor

As done in 7.3 we write

$$S^{(d)} = \langle \sum_{\alpha i \nu} F_{\nu}^{(d)\alpha i} \delta(r_{\nu}^{\alpha i} - r) \rangle = \langle \sum_{\alpha i \nu} \sum_{\beta j \mu} F_{\nu\mu}^{(d)\alpha i, \beta j} \delta(r_{\nu}^{\alpha i} - r) \rangle \tag{6.81}$$

$$\pi^{(d)} = \sum_{\alpha\beta\nu\mu} \int \int \int (R_{\nu}^{\alpha} - \frac{m_{m}^{\beta}}{m_{\mu}^{\alpha} + m_{\mu}^{\beta}} R_{\alpha\beta}) F_{\nu\mu}^{(d)\alpha\beta} \tilde{\Psi}_{\alpha\beta}(r, R_{\alpha\beta}, Q^{\alpha}, Q^{\beta}, t) dR_{\alpha\beta} dQ^{\alpha} dQ^{\beta} \tag{6.82}$$

We now make use of the symmetry property of $\tilde{\Psi}_{\alpha\beta}$ and using Newton's Third law the second term can be rewritten as

$$\pi^{(d)} = \sum_{\alpha\beta\nu\mu} \int \int \int (R_{\nu}^{\alpha} - \frac{1}{2} R_{\alpha\beta}) F_{\nu\mu}^{(d)\alpha\beta} \tilde{\Psi}_{\alpha\beta}(r, R_{\alpha\beta}, Q^{\alpha}, Q^{\beta}, t) dR_{\alpha\beta} dQ^{\alpha} dQ^{\beta} \tag{6.83}$$

or

$$\pi^{(d)} = \frac{1}{2} \sum_{\alpha\beta\nu\mu} \int \int \int R_{\mu\nu}^{\beta\alpha} F_{\nu\mu}^{(d)\alpha\beta} \tilde{\Psi}_{\alpha\beta}(r, R_{\alpha\beta}, Q^{\alpha}, Q^{\beta}, t) dR_{\alpha\beta} dQ^{\alpha} dQ^{\beta} \tag{6.84}$$

6.7 The Hydrodynamic Energy Equation

The energy equation for the multicomponent mixture is

$$\frac{\partial}{\partial t}(\frac{1}{2}\rho u^2+\rho\hat{U}) = -(\nabla\cdot(\frac{1}{2}\rho v^2+\rho\hat{U})v)-(\nabla\cdot q)-(\nabla\cdot[\pi\cdot v])+(v\cdot G)+J \tag{6.85}$$

where the last three terms are respectively the work done on an element of the fluid by the stresses, external forces and diffussional effects.
q is the heat-flux vector
and $\hat{U}$ is the internal energy/unit mass (excluding the energy associated with the kinetic energy and any contribution associated with external forces).

We have to find a function B in the phase-space such that $\langle B\rangle = \frac{1}{2}\rho u^2+\rho\hat{U}$ is the total energy/unit volume. We therefore take

$$B = \sum_{\alpha i\nu}(\frac{1}{2m_\nu^\alpha}p_\nu^{\alpha i}\cdot p_\nu^{\alpha i}+U_\nu^{\alpha i})\delta(r_\nu^{\alpha i}-r) \tag{6.86}$$

in which we have localized the potential energies associated with each of the beads resulting from intra. and intermolecular bead-bead interactions. We have done this by assigning to each bead a 'fair share' of the energy of the pair of interaction for the pair of beads,
so

$$U_\nu^{\alpha i} = \frac{1}{2}\sum_{\beta j\mu}\phi_{\nu\mu}^{\alpha i,\beta j} = \frac{1}{2}\sum_{\mu}\phi_{\nu\mu}^{\alpha i}+\frac{1}{2}\sum_{\beta j\mu}\phi_{\nu\mu}^{(d)\alpha i,\beta j} \tag{6.87}$$

Thus

$$\langle B\rangle = \langle\sum_{\alpha i\nu}(\frac{1}{2}m_\nu^\alpha u^2+\frac{1}{2}m_\nu^\alpha(\frac{p_\nu^{\alpha i}}{m_\nu^\alpha}-v)^2+U_\nu^{\alpha i})\delta(r_\nu^{\alpha i}-r)\rangle \tag{6.88}$$

or $\langle B\rangle = \frac{1}{2}\rho u^2+\rho\hat{U}$
in which $\frac{1}{2}\rho u^2$ is the kinetic energy associated with the mean motion and $\rho\hat{U}$ is the kinetic energy of the beads relative to the flow velocity v plus the potential energies, excluding potential energies associated with the external forces.

The general equation of change for B results

$$\begin{aligned}\frac{\partial}{\partial t}(\frac{1}{2}\rho u^2+\rho\hat{U}) &= -\nabla\cdot\langle\sum_{\alpha i\nu}\dot{r}_\nu^{\alpha i}(\frac{1}{2}m_\nu^\alpha(\dot{r}_\nu^{\alpha i}\cdot\dot{r}_\nu^{\alpha i})+U_\nu^{\alpha i})\delta(r_\nu^{\alpha i}-r)\rangle \\ &+\langle\sum_{\alpha i\nu}\sum_{\beta j\mu}(\dot{r}_\nu^{\alpha i}\cdot\frac{\partial}{\partial r_\nu^{\alpha i}}U_\mu^{\beta j})\delta(r_\mu^{\beta j}-r)\rangle \\ &\langle\sum_{\alpha i\nu}(\dot{r}_\nu^{\alpha i}\cdot F_\nu^{\alpha i})\delta(r_\nu^{\alpha i}-r)\rangle\end{aligned} \tag{6.89}$$

To transform the aforementioned equation into the form of the energy equation we begin by replacing the $\dot{r}_\nu^{\alpha i}$ just after the summation sign in the first line by $\dot{r}_\nu^{\alpha i} - v$ and add the appropriate compensating term.

We then get

$$\frac{\partial}{\partial t}(\frac{1}{2}\rho u^2 + \rho\hat{U}) = -(\nabla \cdot (\frac{1}{2}\rho u^2 + \rho\hat{U})v) + Q^{(k)} + Q^{(e)} + Q^{(\phi)} \tag{6.90}$$

where

$$Q^{(k)} = -\nabla \cdot \langle \sum_{\alpha i \nu} (\dot{r}_\nu^{\alpha i} - v)(\frac{1}{2} m_\nu^\alpha \dot{r}_\nu^{\alpha i} \cdot \dot{r}_\nu^{\alpha i} + U_\nu^{\alpha i})\delta(r_\nu^{\alpha i} - r)\rangle \tag{6.91}$$

$$Q^{(\phi)} = \langle \sum_{\alpha i \nu} (\dot{r}_\nu^{\alpha i} \cdot F_\nu^{(\phi)\alpha i})\delta(r_\nu^{\alpha i} - r)\rangle + \frac{1}{2}\langle \sum_{\alpha i \nu}\sum_{\beta j \mu} (\dot{r}_\nu^{\alpha i} \cdot \frac{\partial}{\partial r_\nu^{\alpha i}} \sum_{\gamma k \eta} \phi_{\mu\eta}^{\beta j, \gamma k})\delta(r_\mu^{\beta j} - r)\rangle \tag{6.92}$$

$$Q^{(e)} = \langle \sum_{\alpha i \nu} (\dot{r}_\nu^{\alpha i} \cdot F_\nu^{(e)\alpha i})\delta(r_\nu^{\alpha i} - r)\rangle \tag{6.93}$$

We now try to express the heat-flux vector q by various manipulations.

6.7.1 The Kinetic Contribution to the Heat Flux Vector

In the contribution $Q^{(k)}$ we replace both of the $\dot{r}_\nu^{\alpha i}$ in the dot product by $\dot{r}_\nu^{\alpha i} - v$ and use the appropriate compensating terms; We have

$$\begin{aligned} Q^{(k)} &= -\nabla \cdot \langle \sum_{\alpha i \nu} (\dot{r}_\nu^{\alpha i} - v)(\frac{1}{2} m_\nu^\alpha (\dot{r}_\nu^{\alpha i} - v)^2 + U_\nu^{\alpha i}\delta(r_\nu^{\alpha i} - r)\rangle \\ &\quad -\nabla \cdot \langle \sum_{\alpha i \nu} m_\nu^\alpha (\dot{r}_\nu^{\alpha i} - v)(\dot{r}_\nu^{\alpha i} - v) \cdot v\delta(r_\nu^{\alpha i} - r)\rangle \\ &= -(\nabla \cdot q^{(k)}) - (\nabla \cdot [\pi^{(k)} \cdot v]) \end{aligned} \tag{6.94}$$

where we define $q^{(k)}$ as the kinetic contribution to the heat-flux vector and using previous results we go on with the analysis

$$\begin{aligned} q^{(k)} &= \sum_{\alpha\nu} \frac{1}{2} m_\nu^\alpha \int [[(\dot{r}_\nu^\alpha - v)(\dot{r}_\nu^\alpha - v)^2]]^\alpha \Psi_\alpha(r - R_\nu^\alpha, Q^\alpha, t)dQ^\alpha \\ &\quad + \frac{1}{2}\sum_{\alpha\nu\mu} \int \phi_{\nu\mu}^\alpha [[\dot{r}_\nu^\alpha - v]]^\alpha \Psi_\alpha(r - R_\nu^\alpha, Q^\alpha, t)dQ^\alpha \\ &\quad + \frac{1}{2}\sum_{\alpha\beta\nu\mu} \int\int\int \phi_{\nu\mu}^{(d)\alpha\beta}[[\dot{r}_\nu^\alpha - v]]^{\alpha\beta}\tilde{\Psi}_{\alpha\beta}(r - R_\nu^\alpha + \frac{m_m^\beta}{m_m^\alpha + m_m^\beta}R_{\alpha\beta}, R_{\alpha\beta}, Q^\alpha, Q^\beta, t)dR_{\alpha\beta}dQ^\alpha dQ^\beta. \end{aligned} \tag{6.95}$$

One has to note that for a surface element dS the first term of $q^{(k)}$ multiplied by η reveals the rate of diffusion of kinetic energy across dS, so just because of $\eta \cdot (\dot{r}_\nu^{\alpha i} - v)$ we have that diffusion at a small angle to the surface is less effective for transporting kinetic energy than diffusion at a large angle. The second and third term dotted into η and multiplied by dS, describe the rate of diffusion of intra- and intermolecular potential energy across dS.

6.7.2 The External Force Contribution to the Heat Flux Vector

We have denoted

$$Q^{(e)} = \langle \sum_{\alpha i \nu} (\dot{r}_\nu^{\alpha i} \cdot F_\nu^{(e)\alpha i}) \delta(r_\nu^{\alpha i} - r) \rangle \tag{6.96}$$

and using simple manipulations

$$\begin{aligned} Q^{(e)} &= \sum_{\alpha\nu} \int [[\dot{r}_\nu^\alpha]]^\alpha \cdot F_\nu^{(e)\alpha} \Psi_\alpha(r - R_\nu^\alpha, Q^\alpha, t) dQ^\alpha \\ &= \sum_{\alpha\nu} \int [[\dot{r}_\nu^\alpha]]^\alpha \cdot F_\nu^{(e)\alpha} \Psi_\alpha(r, Q^\alpha, t) dQ^\alpha \\ -[\nabla \cdot \sum_{\alpha\nu} &\int \int_0^1 R_\nu^\alpha F_\nu^{(e)\alpha} \cdot [[\dot{r}_\nu^{\alpha i}]]^\alpha \Psi_\alpha(r - \xi R_\nu^\alpha, Q^\alpha, t) d\xi dQ^\alpha] \end{aligned} \tag{6.97}$$

We for once more replace $\dot{r}_\nu^{\alpha i}$ with $\dot{r}_\nu^{\alpha i} - v$ and add compensating terms. We get:

$$\begin{aligned} Q^{(e)} &= \sum_{\alpha\nu} \int [[\dot{r}_\nu^\alpha - v(r,t)]]^\alpha \cdot F_\nu^{(e)\alpha} \Psi_\alpha(r, Q^\alpha, t) dQ^\alpha \\ &+ v(r,t) \cdot \sum_{\alpha\nu} \int F_\nu^{(e)\alpha} \Psi_\alpha(r, Q^\alpha, t) dQ^\alpha \\ -\nabla \cdot \sum_{\alpha\nu} &\int \int_0^1 R_\nu^\alpha F_\nu^{(e)\alpha} \cdot [[\dot{r}_\nu^\alpha - v(r,t)]]^\alpha \Psi_\alpha(r - \xi R_\nu^\alpha, Q^\alpha, t) d\xi dQ^\alpha \\ -\nabla \cdot [\sum_{\alpha\nu} &\int \int_0^1 R_\nu^\alpha F_\nu^{(e)\alpha} \Psi_\alpha(r - \xi R_\nu^\alpha, Q^\alpha, t) d\xi dQ^\alpha \cdot v(r,t)] \\ &= J + (v \cdot G) - (\nabla \cdot q^{(e)}) - (\nabla \cdot [\pi^{(e)} \cdot v]) \end{aligned} \tag{6.98}$$

The third term is the divergence of the external force contribution to the heat-flux vector, which is

$$q^{(e)} = \sum_{\alpha\nu} \int \int_0^1 R_\nu^\alpha F_\nu^{(e)\alpha} \cdot [[\dot{r}_\nu^\alpha - v]]^\alpha \Psi_\alpha(r - \xi R_\nu^\alpha, Q^\alpha, t) d\xi dQ^\alpha$$

$$= \sum_{\alpha\nu} \int \; R^{\alpha}_{\nu} F^{(e)\alpha}_{\nu} \cdot [[\dot{r}^{\alpha}_{\nu} - v]]^{\alpha} \Psi_{\alpha}(r, Q^{\alpha}, t) dQ^{\alpha} + ... \tag{6.99}$$

The first term J is the 'diffussional source' term

$$J = \sum_{\alpha\nu} \int \; [[\dot{r}^{\alpha}_{\nu} - v]]^{\alpha} \cdot F^{(e)\alpha}_{\nu} \Psi_{\alpha}(r, Q^{\alpha}, t) dQ^{\alpha} \tag{6.100}$$

Let $g_{\alpha} = \frac{F^{(e)\alpha}_{\nu}}{m^{\alpha}_{\nu}}$ and suppose that g_{α} are constant and independent of v, then $J = \sum_{\alpha} (j_{\alpha} \cdot g_{\alpha})$ and this expression is generally seen in continuum mechanics treatments.

We also note that $(\eta \cdot q^{(e)}) dS$ is the rate of work that is done as the beads diffuse under the external force that is acting on the beads.

6.7.3 The Intramolecular Contribution to the Heat Flux Vector

We turn now to the source term $Q^{(\phi)}$

$$\begin{aligned}
Q^{(\phi)} &= + \langle \sum_{\alpha i \nu} \sum_{\beta j \mu} (\dot{r}^{\alpha i}_{\nu} \cdot F^{(\phi)\alpha i, \beta j}_{\nu\mu}) \delta(r^{\alpha i} - r) \rangle \\
&\quad - \frac{1}{2} \langle \sum_{\alpha i \nu} \sum_{\gamma k \eta} (\dot{r}^{\alpha i}_{\nu} \cdot F^{(\phi)\alpha i, \gamma k}_{\nu\mu}) \delta(r^{\alpha i}_{\nu} - r) \rangle \\
&\quad - \frac{1}{2} \langle \sum_{\alpha i \nu} \sum_{\beta j \mu} (\dot{r}^{\alpha i}_{\nu} \cdot F^{(\phi)\alpha i, \beta j}_{\nu\mu}) \delta(r^{\beta j}_{\mu} - r) \rangle \\
&= \frac{1}{2} \langle \sum_{\alpha i \nu} \sum_{\beta j \mu} ((\dot{r}^{\alpha i}_{\nu} + \dot{r}^{\beta j}_{\mu}) \cdot F^{(\phi)\alpha i, \beta j}_{\nu\mu}) \delta(r^{\alpha i}_{\nu} - r) \rangle
\end{aligned} \tag{6.101}$$

We now only consider terms for which $\alpha i = \beta j$ that is the intramolecular contribution $Q^{(\phi)}$

$$\begin{aligned}
Q^{(\phi)} &= \frac{1}{2} \langle \sum_{\alpha i \nu \mu} ((\dot{r}^{\alpha i}_{\nu} + \dot{r}^{\alpha i}_{\mu}) \cdot F^{(\phi)\alpha i}_{\nu\mu}) \delta(r^{\alpha i}_{\nu} - r) \rangle \\
&= \frac{1}{2} \sum_{\alpha\nu\mu} \int \; [[\dot{r}^{\alpha}_{\nu} + \dot{r}^{\alpha}_{\mu}]]^{\alpha} \cdot F^{(\phi)\alpha}_{\nu\mu} \psi_{\alpha}(r - R^{\alpha}_{\nu}, Q^{\alpha}, t) dQ^{\alpha} \\
&\quad - \nabla \cdot \frac{1}{2} \sum_{\alpha\nu\mu} \int \int_{0}^{1} \; R^{\alpha}_{\nu} F^{(\phi)\alpha}_{\nu\mu} \cdot [[\dot{r}^{\alpha}_{\nu} + \dot{r}^{\alpha}_{\mu}]]^{\alpha} \cdot \psi_{\alpha}(r - \xi R^{\alpha}_{\nu}, Q^{\alpha}, t) d\xi dQ^{\alpha} \\
&\quad - \nabla \cdot \frac{1}{2} \sum_{\alpha\nu\mu} \int \int_{0}^{1} \; R^{\alpha}_{\nu} F^{(\phi)\alpha}_{\nu\mu} \cdot [[\dot{r}^{\alpha}_{\nu} + \dot{r}^{\alpha}_{\mu}]]^{\alpha} \psi_{\alpha}(r - \xi R^{\alpha}_{\nu}, Q^{\alpha}, t) d\xi dQ^{\alpha}
\end{aligned}$$

$$-\nabla \cdot [\sum_{\alpha\nu\mu} \int \int_0^1 \; R_\nu^\alpha F_{\nu\mu}^{(\phi)\alpha} \cdot [[(\dot{r}_\nu^\alpha) + (\dot{r}_\mu^\alpha - v)]]^\alpha \cdot \psi_\alpha(r - \xi R_\nu^\alpha, Q^\alpha, t) d\xi dQ^\alpha$$

$$-\nabla \cdot \int \int_0^1 \; R_\nu^\alpha F_{\nu\mu}^{(\phi)\alpha} \psi_\alpha(r - \xi R_\nu^\alpha, Q^\alpha, t) d\xi dQ^\alpha \cdot v(r,t)]$$

$$= -(\nabla \cdot q^{(\phi)}) - (\nabla \cdot [\pi^{(\phi)} \cdot v]) \tag{6.102}$$

We have thus defined the intramolecular potential contribution $q^{(\phi)}$ to the heat flux vector.
Then

$$q^{(\phi)} = \frac{1}{2} \sum_{\alpha\nu\mu} \int \int_0^1 \; R_\nu^\alpha F_{\nu\mu}^{(\phi)\alpha} \cdot [[(\dot{r}_\nu^\alpha - v) + (\dot{r}_\mu^\alpha - v)]]^\alpha \Psi_\alpha(r - \xi R_\nu^\alpha, Q^\alpha, t) d\xi dQ^\alpha$$

$$= \frac{1}{2} \sum_{\alpha\nu\mu} \int \; R_{\nu\mu}^\alpha F_{\nu\mu}^{(\phi)\alpha} \cdot [[\dot{r}_\nu^\alpha - v]]^\alpha \Psi_\alpha(r, Q^\alpha, t) dQ^\alpha + ... \tag{6.103}$$

where we have used Newton's third law for pairs of beads on one molecule and the definition that $R_{\mu\nu}^\alpha = r_\nu^\alpha - r_\mu^\alpha$

Finally, $(\eta \cdot q^{(\phi)})dS$ is the rate at which work is done on the fluid on the positive side of dS by the fluid on the negative side. The dot product of η with $R_{\mu\nu}^\alpha$ indicates that springs that make a small angle with the plane of dS contribute less in the averaging process than springs that make a large angle.

6.7.4 The Intermolecular Contribution to the Heat Flux Vector

We can get the intermolecular contribution to the heat flux vector by considering terms for which $\alpha i \neq \beta j$. The first term drops out by Newton's third law.

$$Q^{(d)} = \frac{1}{2} \langle \sum_{\alpha i \nu} \sum_{\beta j \mu} ((\dot{r}_\nu^{\alpha i} + \dot{r}_\mu^{\beta j}) \cdot F_{\nu\mu}^{(d)\alpha i, \beta j}) \delta(r_\nu^{\alpha i} - r) \rangle$$

$$= \frac{1}{2} \sum_{\alpha\beta\nu\mu} \int \int \int \; [[\dot{r}_\nu^\alpha + \dot{r}_\mu^\beta]]^{\alpha\beta} \cdot F_{\nu\mu}^{(d)\alpha\beta} \tilde{\Psi}_{\alpha\beta} dR_{\alpha\beta} dQ^\alpha dQ^\beta$$

$$-\nabla \cdot \frac{1}{2} \sum_{\alpha\beta\nu\mu} \int \int \int \; (R_\nu^\alpha - \frac{m_m^\beta}{m_m^\alpha + m_m^\beta} R_{\alpha\beta}) [[\dot{r}_\nu^\alpha + \dot{r}_\mu^\beta]]^{\alpha\beta} \cdot F_{\nu\mu}^{(d)\alpha\beta} \tilde{\Psi}_{\alpha\beta} dR_{\alpha\beta} dQ^\alpha dQ^\beta$$

$$-\nabla \frac{1}{2} \sum_{\alpha\beta\nu\mu} \int \int \int \; (R_\nu^\alpha - \frac{m_m^\beta}{m_m^\alpha + m_m^\beta} R_{\alpha\beta}) F_{\nu\mu}^{(d)\alpha\beta} \tilde{\Psi}_{\alpha\beta} dR_{\alpha\beta} dQ^\alpha dQ^\beta \cdot v(r,t)$$

$$= -(\nabla \cdot q^{(d)}) - (\nabla \cdot [\pi^{(d)} \cdot v]) \tag{6.104}$$

so after modifications

$$q^{(d)} = \frac{1}{2} \sum_{\alpha\beta\nu\mu} \int\int\int (R_{\nu}^{\alpha} - \frac{1}{2} R_{\alpha\beta})[[(\dot{r}_{\nu}^{\alpha} - v)(\dot{r}_{\mu}^{\beta} - v)]]^{\alpha\beta} \cdot F_{\nu\mu}^{(d)\alpha\beta} \tilde{\Psi}_{\alpha\beta} dR_{\alpha\beta} dQ^{\alpha} dQ^{\beta} \tag{6.105}$$

or finally

$$q^{(d)} = \frac{1}{2} \sum_{\alpha\beta\nu\mu} \int R_{\mu\nu}^{\beta\alpha} F_{\nu\mu}^{(d)\alpha\beta} \cdot [[\dot{r}_{\nu}^{\alpha} - v]]^{\alpha\beta} \tilde{\Psi}_{\alpha\beta}(r, R_{\alpha\beta}, Q^{\alpha}, Q^{\beta}, t) dR_{\alpha\beta} dQ^{\alpha} dQ^{\beta} \tag{6.106}$$

and $(\eta \cdot q^{(d)})dS$ is the rate at which work is done on the fluid on the positive side of dS by the fluid on the negative side, as a result of bead-bead interactions between beads on different molecules.

6.8 The Hydrodynamic Equation for the Angular Momentum

The conservation of the angular momentum as applied to a system in which there is no intrinsic angular momentum can be set formally as

$$\frac{\partial}{\partial t}[r \times \rho v] = -[\nabla \cdot v[r \times \rho v]] - [\nabla \cdot \{\pi \times r\}] + [r \times G] + T \tag{6.107}$$

where T is the external torque/unit volume applied to the fluid and G is the external force/unit volume.

The cross product of the position vector r with the hydrodynamic equation of motion leads to

$$\frac{\partial}{\partial t}[r \times \rho v] = -[\nabla \cdot v[r \times \rho v]] - [\nabla \cdot \{\pi \times r\}] + [r \times G] - [\varepsilon : \pi] \tag{6.108}$$

ε is the third-order tensor and its elements ε_{ijk} are the permutation symbols. By those two equations we get that $T = -[\varepsilon : \pi]$ which shows that the antisymmetrical part of the stress tensor is related to the external torque.

We now shift to the statistical mechanics aspects and seek a phase-space function $B^{'}$ such that $< B^{'} >$ is the density of the total angular momentum. We note that $[r_{\nu}^{\alpha i} \times p_{\nu}^{\alpha i}]$ is the angular momentum of a bead with respect to some arbitrarily chosen fixed reference frame.

Let

$$B^{'} = \sum_{\alpha i \nu} [r_{\nu}^{\alpha i} \times p_{\nu}^{\alpha i}] \delta(r_{\nu}^{\alpha i} - r) \tag{6.109}$$

then

$$\langle B^{'}\rangle = \langle\sum_{\alpha i\nu}[r_\nu^{\alpha i} \times p_\nu^{\alpha i}]\delta(r_\nu^{\alpha i} - r)\rangle = r \times \langle\sum_{\alpha i\nu} p_\nu^{\alpha i}\delta(r_\nu^{\alpha i} - r)\rangle = [r \times \langle B\rangle] = [r \times \rho v] \tag{6.110}$$

where $B = \sum_{\alpha i\nu} p_\nu^{\alpha i}\delta(r_\nu^{\alpha i} - r)$
and we can also find that the general equation of change is

$$\langle LB^{'}\rangle = [r \times \langle LB\rangle]. \tag{6.111}$$

6.9 An Equation of Motion for the Singlet Distribution Function

In this part of the development we are concerned with a formal derivation of the differential equation for the singlet distribution function.

We start by applying the quantity

$$B = \sum_i B_i = \sum_i \delta(r^{\alpha i} - r^\alpha)\delta(p^{\alpha i} - p^\alpha), \tag{6.112}$$

for which $\langle B\rangle = f_\alpha(r^\alpha, p^\alpha, t)$

The general equation of change is
$\frac{\partial}{\partial t}\langle B\rangle = \langle \text{Ł}B\rangle$ so we have

$$\begin{aligned}\frac{\partial}{\partial t}f_\alpha &= \langle\sum_{\beta j\nu}(\frac{p_\nu^{\beta j}}{m_\nu^\beta} \cdot \frac{\partial}{\partial r_\nu^{\beta j}}\sum_i B_i + F_\nu^{\beta j} \cdot \frac{\partial}{\partial p_\nu^{\beta j}}\sum_i B_i)\rangle \\ &= -\sum_{i\nu}(\frac{1}{m_\nu^\alpha} \cdot \frac{\partial}{\partial r_\nu^\alpha} \cdot \langle p_\nu^{\alpha i}B_i\rangle + \frac{\partial}{\partial p_\nu^\alpha} \cdot \langle F_\nu^{\alpha i} \cdot B_i\rangle)\end{aligned} \tag{6.113}$$

and the last equality is due to the fact that contribution comes from terms with $\beta = \alpha$ and $j = i$

We can also write $\langle p_\nu^\alpha B_i\rangle$ instead of $\langle p_\nu^{\alpha i}B_i\rangle$ and $\langle F_\nu^{(e)\alpha}B_i\rangle$, $\langle F_\nu^{(\phi)\alpha}B_i\rangle$ instead of $\langle F_\nu^{(e)\alpha i}B_i\rangle$ and $\langle F_\nu^{(\phi)\alpha i}B_i\rangle$ respectively due to the fact that the integration over the phase-space involves delta functions. The term $\langle F_\nu^{(d)\alpha i}B_i\rangle$ requires special treatment (remember that $F_\nu^{\alpha i} = F_\nu^{(e)\alpha i} + F_\nu^{(\phi)\alpha i} + F_\nu^{(d)\alpha i}$).

We make various manipulations

$$\sum_i\sum_{\beta j\mu}\int F_{\nu\mu}^{(d)\alpha i,\beta j}\delta(r^{\alpha i} - r^\alpha)\delta(p^{\alpha i} - p^\alpha)f(x,t)dx$$

$$= \sum_i \sum_{\beta j\mu} \int\int\int \; F_{\nu\mu}^{(d)\alpha i,\beta j} \delta(r^\alpha - r^\alpha)\delta(p^{\alpha i} - p^\alpha)\delta(r^{\beta j} - r^\beta)\delta(p^{\beta j} - p^\beta) f(x,t) dr^\beta dp^\beta dx$$

$$= \sum_{\beta\mu} \int\int \; F_{\nu\mu}^{(d)\alpha\beta} \langle \sum_i \sum_j \delta(r^{\alpha i} - r^\alpha)\delta(p^{\alpha i} - p^\alpha)\delta(r^{\beta j} - r^\beta)\delta(p^{\beta j} - p^\beta)\rangle dr^\beta dp^\beta$$

$$\sum_{\beta\mu} \int\int \; F_{\nu\mu}^{(d)\alpha\beta} f_{\alpha\beta}(r^\alpha, p^\alpha, r^\beta, p^\beta, t) dr^\beta dp^\beta \tag{6.114}$$

and get

$$\frac{\partial}{\partial t} f_\alpha = -\sum_\nu \left(\frac{p_\nu}{m_\nu^\alpha} \cdot \frac{\partial}{\partial r_\nu^\alpha} f_\alpha + F_\nu^{(e)\alpha} \cdot \frac{\partial}{\partial p_\nu^\alpha} f_\alpha + F_\nu^{(\phi)\alpha} \cdot \frac{\partial}{\partial p_\nu^\alpha} f_\alpha\right)$$

$$-\sum_\nu \left(\frac{\partial}{\partial p_\nu^\alpha} \cdot \sum_{\beta\mu} \int\int \; F_{\nu\mu}^{(d)\alpha\beta} f_{\alpha\beta}(r^\alpha, p^\alpha, r^\beta, p^\beta, t) dr^\beta dp^\beta\right) \tag{6.115}$$

Finally, after integrating over all momenta p_ν^α we have

$$\frac{\partial}{\partial t} \bar{\Psi}_\alpha(r^\alpha, t) = -\sum_\nu \left(\frac{\partial}{\partial r_\nu^\alpha} \cdot [[\dot{r}_\nu^\alpha]]^\alpha \bar{\Psi}_\alpha\right) \tag{6.116}$$

or the equation for $\Psi_\alpha(r_c^\alpha, Q^\alpha, t)$,that is

$$\frac{\partial}{\partial t} \Psi_\alpha(r_c^\alpha, Q^\alpha, t) = -\left(\frac{\partial}{\partial r_c^\alpha} \cdot [[\dot{r}_c^\alpha]]^\alpha \Psi_\alpha\right) - \sum_j \left(\frac{\partial}{\partial Q_j^\alpha} \cdot [[\dot{Q}_j^\alpha]]^\alpha \Psi_\alpha\right) \tag{6.117}$$

after a simple chain differentiation.
We note that we can only use the aforementioned equations when we know more about the momentum-averaged quantities.

6.10 Equations of Internal Motion for the Molecules Hydrodynamic and Brownian Forces

Simple manipulations on the equation for time-evolution of the singlet distribution function gives

$$m_\nu^\alpha \frac{\partial}{\partial t} [[\dot{r}_\nu^\alpha]]^\alpha \bar{\Psi}_\alpha = -m_\nu^\alpha \sum_\mu \left(\frac{\partial}{\partial r_\mu^\alpha} \cdot [[\dot{r}_\mu^\alpha \dot{r}_\nu^\alpha]]^\alpha \bar{\Psi}_\alpha\right)$$

$$+F_\nu^{(e)\alpha} \bar{\Psi}_\alpha + F_\nu^{(\phi)\alpha} \bar{\Psi}_\alpha + \sum_\beta \int \; F_\nu^{(d)\alpha\beta} \bar{\Psi}_{\alpha\beta} dr^\beta \tag{6.118}$$

and using the notation $u_\nu^{\alpha i}(r^\alpha, t) = [[\dot{r}_\nu^\alpha]]^\alpha$ as well as introducing the quantity $[[(\dot{r}_\mu^\alpha - u_\mu^\alpha)(\dot{r}_\nu^\alpha - u_\nu^\alpha]]^\alpha$ together with the appropriate compensating terms, we get:

$$
\begin{aligned}
m_\nu^\alpha \frac{\partial}{\partial t} u_\nu^\alpha \bar{\Psi}_\alpha + m_\nu^\alpha \sum_\mu \left(\frac{\partial}{\partial r_\mu^\alpha} \cdot u_\mu^\alpha u_\nu^\alpha \bar{\Psi}_\alpha\right) \\
= -m_\nu^\alpha \sum_\mu \left(\frac{\partial}{\partial r_\mu^\alpha} \cdot [[(\dot{r}_\mu^\alpha - u_\mu^\alpha)(\dot{r}_\nu^\alpha - u_\nu^\alpha)]]^\alpha \bar{\Psi}_\alpha\right) \\
F_\nu^{(e)\alpha} \bar{\Psi}_\alpha + F_\nu^{(\phi)\alpha} \bar{\Psi}_\alpha + \sum_\beta \int F^{(d)\alpha\beta} \bar{\Psi}_{\alpha\beta} dr^\beta
\end{aligned}
\tag{6.119}
$$

The terms on the left side after calculations give

$$
m_\nu^\alpha \bar{\Psi}_\alpha \frac{\partial}{\partial t} u_\nu^\alpha + m_\nu^\alpha \bar{\Psi}_\alpha \sum_\mu \left(u_\mu^\alpha \cdot \frac{\partial}{\partial r_\mu^\alpha} u_\nu^\alpha\right) \tag{6.120}
$$

and dividing by $\bar{\Psi}_\alpha$ 6.120 we get

$$
m_\nu^\alpha \left(\frac{\partial}{\partial t} u_\nu^\alpha + \sum_\mu \left(u_\mu^\alpha \cdot \frac{\partial}{\partial r_\mu^\alpha} u_\nu^\alpha\right)\right) = F_\nu^{(b)\alpha} + F_\nu^{(e)\alpha} + F_\nu^{(\phi)\alpha} + F_\nu^{(h)\alpha} \tag{6.121}
$$

Therefore we have introduced the averaged Brownian and Hydrodynamic force acting on bead ν of molecule α.

$$
F_\nu^{(b)\alpha}(r^\alpha, t) = -\frac{1}{\bar{\Psi}_\alpha} \cdot m_\nu^\alpha [[(\dot{r}_\mu^\alpha - u_\mu^\alpha)(\dot{r}_\nu^\alpha - u_\nu^\alpha)]]^\alpha \bar{\Psi}_\alpha) \tag{6.122}
$$

and

$$
F_\nu^{(h)\alpha}(r^\alpha, t) = \frac{1}{\bar{\Psi}_\alpha} \sum_{\beta\mu} \int F_{\nu\mu}^{(d)\alpha\beta} \bar{\Psi}_{\alpha\beta} dr^\beta \tag{6.123}
$$

this specification follows quite naturally although especially 6.123 has not been evaluated for any molecular model or flow.Therefore, we have introduced empirical expressions involving the so called 'friction coefficient'.

Chapter 7

Appendix

7.1 Canonical Transformations

The fact that the Jacobian of a canonical transformation is unity was first proved by Liouville.

Consider a system with N degrees of freedom that passes via a canonical transformation from state (q,p) to state (q',p'). Thus the Jacobian of the transformation

$$|\frac{\partial(q^{'},p^{'})}{\partial(q,p)}| = det\begin{pmatrix} \frac{\partial q_1^{'}}{\partial q_1} & \frac{\partial q_2^{'}}{\partial q_1} & \cdots \\ . & . & . \end{pmatrix} \tag{7.1}$$

is a $2N \times 2N$ determinant.

Recalling that $|\frac{\partial(q^{'},p^{'})}{\partial(q,p)}| = |\frac{\partial(q^{'},p^{'})}{\partial(q,p^{'})}|/|\frac{\partial(q,p)}{\partial(q,p^{'})}|$

the Jacobian reduces to the quotient of two $N \times N$ determinants, namely

$$J = \frac{\partial q^{'}/\partial q|_{p'}}{\partial p/\partial p'|_{q}} \equiv \frac{J_n}{J_d} \tag{7.2}$$

the subscripts p' and q in the numerator and denominator respectively denote variables that are kept fixed during differentiation.

The ik element of J_n is

$$J_n^{ik} = \frac{\partial q_i^{'}}{\partial q_k} \tag{7.3}$$

and since the transformation $(q,p) \rightarrow (q^{'},p^{'})$ is canonical there exists a generating function G such that

$$J_n^{ik} = \frac{\partial^2 G}{\partial p_i^{'} \partial q_k} \tag{7.4}$$

in a similar manner the ik element of the denominator is

$$J_d^{ik} = \frac{\partial^2 G}{\partial q_i \partial p_k^{'}} \tag{7.5}$$

so $J_n^{ik} = J_d^{ki}$ Thus

$$\frac{\partial(q^{'}, p^{'})}{\partial(q, p)} = J = \frac{J_n}{J_d} = 1 \tag{7.6}$$

Remark: The geometric significance of the Liouville theorem is that under a canonical transformation a volume Ω transforms into Ω' in Γ-space in a way that $m(\Omega) = m(\Omega')$. In other words volume elements in Γ-space are canonical invariants.

The time has come to prove a useful lemma:

Lemma:If the same canonical transformation $e^{[G]r}$(for an arbitrary dynamical function G and a parameter r)is applied to both factors in the integrand $\int dpdqb(q,p;x,t)c(q,p;x,t)$ then its value remains unchanged.

Proof:If we remember that

$$\int dqdp[e^{[G]r}b(q,p;x,t)][e^{[G]r}c(q,p;x,t)] = \int dqdpb(q_r,p_r;x,t)c(q_r,p_r;x,t) \tag{7.7}$$

where

$$q_r = e^{[G]r}q \tag{7.8}$$
$$p_r = e^{[G]r}p \tag{7.9}$$

the only thing left is a change of integration variables

$$\int dqdpb(q_r,p_r;x,t)c(q_r,p_r;x,t) = \int dq_r dp_r|J|b(q_r,p_r;x,t)c(q_r,p_r;x,t) \tag{7.10}$$

where J is equal to $\frac{\partial(q,p)}{\partial(q_r,p_r)}$ and since the Jacobian of a canonical transformation is unity we have obtained the desired conclusion

Remark:We can generalize the aforementioned lemma up to integrands that contain a finite number of dynamical functions

7.2 A second derivation of the Liouville equation

Let $f(q,p,t)$ be the phase space distribution function, properly normalized in a Hamiltonian system with N particles and $d\Omega$ a volume element in the phase space.If dN is the number of particles in $d\Omega$ at time t then

$$dN = Nf(q,p,t)d\Omega = Nf(q,p,t)dpdq \tag{7.11}$$

Those particles following the systems trajectories will occupy after time dt the volume element $d\Omega'$
So

$$dN = Nf(q(t+dt), p(t+dt), t+dt)d\Omega' \tag{7.12}$$

We already know that the motion of these points comprises a canonical transformation so $d\Omega' = d\Omega$ and $f(q,p,t)$ remains constant on system trajectories so $\frac{df}{dt} = 0$ or equivalently

$$\frac{\partial f}{\partial t} = -\sum_{n=1}^{N} \{ \frac{\partial f}{\partial p_n} \cdot \frac{\partial p_n}{\partial t} + \frac{\partial f}{\partial q_n} \cdot \frac{\partial q_n}{\partial t} \} \tag{7.13}$$

7.3 The normal modes for the Rouse Model

We consider the linear transformation of $R_n(t)$

$$X_p(t) = \int_0^N dn \phi_{pn} R_n(t) \tag{7.14}$$

ϕ_{pn} chosen in the way that

$$\zeta_p \frac{\partial}{\partial t} X_p = -k_p X_p + f_p \tag{7.15}$$

we have

$$\begin{aligned} \zeta_p \frac{\partial X_p}{\partial t} = \zeta_p \frac{\partial}{\partial t} \int_0^N dn \phi_{pn} R_n(t) &= \zeta_p \int_0^N dn \phi_{pn} \frac{\partial R_n(t)}{\partial t} \\ &\frac{\zeta_p}{\zeta} \int_0^N dn \phi_{pn} (k \frac{\partial^2 R_n}{\partial n^2} + f_n) \\ = \frac{\zeta_p}{\zeta} \int_0^N dn \phi_{pn} k \frac{\partial^2 R_n}{\partial n^2} &+ \frac{\zeta_p}{\zeta} \int_0^N dn \phi_{pn} f_n \end{aligned} \tag{7.16}$$

The right hand side can be rewritten after integrating by parts

$$\begin{aligned} rhs = \frac{\zeta_p}{\zeta} [\phi_{pn} k \frac{\partial R_n}{\partial n}]_0^N \frac{\zeta_p}{\zeta} [k \frac{\partial \phi_{pn}}{\partial n} R_n]_0^N \\ + \frac{\zeta_p}{\zeta} \int_0^N dn [k \frac{\partial^2 \phi_{pn}}{\partial n^2} R_n + \phi_{pn} f_n] \end{aligned} \tag{7.17}$$

So we can write down 7.16 in the form

$$\begin{aligned} -\frac{\zeta_p}{\zeta} [k \frac{\partial \phi_{pn}}{\partial n} R_n]_0^N + \frac{\zeta_p}{\zeta} \int_0^N dn [k \frac{\partial^2 \phi_{pn}}{\partial n^2} R_n + \phi_{pn} f_n] \\ = \int_0^N dn (-k_p \phi_{pn} R_n) + f_p \end{aligned} \tag{7.18}$$

In order that the last equation holds we must have

$$\frac{\zeta_p}{\zeta} k \frac{\partial^2 \phi_{pn}}{\partial n^2} = -k_p \phi_{pn} \tag{7.19}$$

with

$$\frac{\partial \phi_{pn}}{\partial n} = 0$$

at $n = 0$ and $n = N$
and $f_p = \frac{\zeta_p}{\zeta} \int_0^N \ dn \phi_{pn} f_n$
The solution to 7.19 together with the boundary conditions is

$$\phi_{pn} = \frac{1}{N} \cos(\frac{p\pi n}{N})(p = 0, 1, 2, ...) \tag{7.20}$$

and $k_p = k \frac{\zeta_p}{\zeta} (\frac{p\pi}{N})^2$
The ζ_p can be arbitrarily chosen so that

$$\langle f_{px}(t) f_{px}(0) \rangle = 2\zeta_p k_B T \delta(t) \tag{7.21}$$

We calculate the left hand side

$$\langle f_{p\alpha}(t) f_{q\beta}(t) \rangle = \frac{\zeta_p \zeta_q}{N^2 \zeta^2} \int_0^N \ dn \int_0^N \ dm \cos(\frac{p\pi n}{N}) \cos(\frac{q\pi m}{N}) \tag{7.22}$$

$$\langle f_{n\alpha}(t) f_{m\beta}(0) \rangle = \frac{\zeta_p \zeta_p}{N^2 \zeta^2} \int_0^N \ dn \cos(\frac{p\pi n}{N}) \cos(\frac{q\pi m}{N}) \tag{7.23}$$

$$2\zeta k_B T \delta_{\alpha\beta} \delta(t) = \frac{\zeta_p^2}{N^2 \zeta^2} \frac{1 + \delta_{p0}}{2} N \delta_{pq} 2\zeta k_B T \delta_{\alpha\beta} \delta(t) \tag{7.24}$$

7.4 Treatment of systems with Rigid Constraints

We now present two general ways in treating systems with rigid constraints. This is essential in studying for example models like rigid dumbbells or a rodlike polymer. Constraints we are considering are those that can be written in form $C_p(\{R\}) = 0 p = 1, 2, ..., N_c$.

The hydrodynamic relation we are considering is

$$V_m = k \cdot R_m + \sum_n H_{nm} \cdot F_n \tag{7.25}$$

and we are solving this equation under the constraints given. One way to do this is by introducing generalized coordinates and specify the configuration of the beads uniquely. Another way to do this is by the use of Lagrangian multipliers for the constraints. Both methods have their pros and cons (e.g the method of the generalized coordinates is impractical to the freely jointed model).

7.4.1 The Method of the Generalized Coordinates

Let $\{Q\} \equiv \{Q_1, Q_2, ..., Q_{N_f}\}$ the set of the generalized coordinates. Then the position vectors R_m are expressed in the form $R_m = R_m(\{Q\})m = 1, ..., N$
and

$$V_m = \sum_{\alpha=1}^{N_f} \frac{\partial R_m}{\partial Q_\alpha} V_\alpha = \frac{\partial R_m}{\partial Q_\alpha} V_\alpha (summationconvention) \tag{7.26}$$

where V_a is the velocity of the generalized coordinate Q_a (e.g $V_\alpha = \frac{dQ_\alpha}{dt}$).

To obtain F_m we use the principle of virtual work, which is the work necessary to change Q_α by δQ_α. If we recall that the total energy of the system is $U + K_B T \ln(\Psi)$ then the work done is

$$\delta(U + K_B T \ln(\Psi)) = [\frac{\partial}{\partial Q_\alpha}(U + K_B T \ln(\Psi)]\delta Q_\alpha \tag{7.27}$$

and it can be also calculated by

$$\delta(U + K_B T \ln(\Psi) = -F_m \cdot \delta R_m \tag{7.28}$$

where $\delta R_m = \frac{\partial R_m}{\partial Q_\alpha} \delta Q_\alpha$
Thus we have

$$F_m \cdot \frac{\partial R_m}{\partial Q_\alpha} = -\frac{\partial}{\partial Q_\alpha}(K_B T \ln(\Psi) + U) \tag{7.29}$$

By 7.25,7.26,7.29 we determine V_a and F_m.

$$F_n = (H^{-1})_{nm} \cdot (U_m - k \cdot R_m) = (H^{-1})_{nm}(\frac{\partial R_m}{\partial Q_\alpha} V_\alpha - k \cdot R_m) \tag{7.30}$$

where $(H^{-1})_{nm} \cdot H_{mk} = \delta_{nk} I$
Substituting into 7.29 we get

$$\frac{\partial R_n}{\partial Q_\alpha} \cdot (H^{-1})_{nm} \cdot [\frac{\partial R_m}{\partial Q_b} V_b - k \cdot R_m] = -\frac{\partial}{\partial Q_\alpha}(U + K_B T \ln(\Psi) \tag{7.31}$$

We can denote

$$(h^{-1})_{\alpha\beta} = \frac{\partial R_n}{\partial Q_\alpha} \cdot (H^{-1})_{nm} \cdot \frac{\partial R_m}{\partial Q_\beta} \tag{7.32}$$

$$F_\alpha^{(E)} = -\frac{\partial}{\partial Q_\alpha}(U + K_B T \ln(\Psi) \tag{7.33}$$

and

$$V_\alpha^{(V)} = h_{\alpha\beta} \frac{\partial R_n}{\partial Q_\beta} \cdot (H^{-1})_{nm} \cdot k \cdot R_m \tag{7.34}$$

We can rewrite 7.31 in the form

$$(h^{-1})_{\alpha\beta}(V_\beta - V_b^{(V)}) = F_\alpha^{(E)} \tag{7.35}$$

or

$$\begin{aligned} V_\alpha &= V_\alpha^{(V)} + h_{\alpha\beta} F_b^{(E)} \\ &= -h_{\alpha\beta}\frac{\partial}{\partial Q_\beta}(U + K_B T \ln(\Psi)) + V_\alpha^{(V)} \end{aligned} \tag{7.36}$$

hence

$$F_n = (H^{-1})_{nm} \cdot (\frac{\partial R_m}{\partial Q_\alpha} h_{\alpha\beta} F_b^{(E)} + \frac{\partial R_m}{\partial Q_\alpha} V_\alpha^{(V)} - kR_m) \tag{7.37}$$

7.4.2 The Method of Lagrangian Multipliers

Another method of dealing with systems of rigid constraints is by the use of the Lagrangian multipliers.Our endeavor will be to minimize the chemical potential $K_B T \ln \Psi + U$ under the system of constraints $C_p(\{R\}) = 0$.
We are thus solving the system

$$\frac{\partial}{\partial R_m}(K_B T \ln \Psi + U) = \lambda_p \frac{\partial C_p}{\partial R_m} \tag{7.38}$$

$$C_p(\{R\}) = 0 \tag{7.39}$$

or better

$$\frac{\partial}{\partial R_m}(K_b T \ln \Psi + U) = \lambda_p \frac{\partial C_p}{\partial R_m} \tag{7.40}$$

$$\frac{\partial C_p}{\partial R_m} \cdot V_m = 0 \tag{7.41}$$

One needs to keep in mind the hydrodynamic equation

$$V_m = \kappa \cdot R_m + \sum_n H_{nm} \cdot F_n \tag{7.42}$$

and also that the force F_m may now be expressed as

$$F_m = -\frac{\partial}{\partial R_m}(K_B T \ln \Psi + U) + \lambda_p \frac{\partial C_p}{\partial R_m} \tag{7.43}$$

The coefficients may now be calculated by 7.38,7.41 and 7.43 so our calculation leads to

$$\lambda_p = (\tilde{h}^{-1})_{pq} \frac{\partial C_p}{\partial R_n} \cdot H_{nm} \cdot \frac{\partial}{\partial R_m}[K_B T \ln \Psi + U] - (\tilde{h}^{-1})_{pq} \frac{\partial C_q}{\partial R_n} \cdot \kappa \cdot R_n \tag{7.44}$$

where $(\tilde{h}^{-1})_{pq}$ is the inverse of the matrix

$$(\tilde{h})_{pq} \equiv \frac{\partial C_p}{\partial R_n} \cdot H_{nm} \cdot \frac{\partial C_q}{\partial R_m} \tag{7.45}$$

The Smoluchowski equation may be obtained by the continuity equation :

$$\frac{\partial \Psi}{\partial t} = -\frac{\partial}{\partial R_m} \cdot (V_m \Psi)$$

$$= \frac{\partial}{\partial R_n} \cdot H_{nm} \cdot \Psi(\frac{\partial}{\partial R_m} - \frac{\partial C_p}{\partial R_m}(\tilde{h}^{-1})_{pq}\frac{\partial C_q}{\partial R_k} \cdot H_{ki} \cdot \frac{\partial}{\partial R_i})(K_B T \ln \Psi + U)$$

$$-\frac{\partial}{\partial R_m} \cdot (\kappa \cdot R_m - H_{mk} \cdot \frac{\partial C_p}{\partial R_k}(\tilde{h}^{-1})_{pq}\frac{\partial C_q}{\partial R_n} \cdot \kappa \cdot R_n) \tag{7.46}$$

7.5 Elements of Probability Theory

Elements of probability theory that are essential in understanding the concepts in chapters that deal with polymer dynamics are reviwed here.The pattern we are following is the measure theoretic one.

7.5.1 Probability Spaces and Random Variables

The probability space of a random experiment is a general measure space(Ω, F, P) in which measure P is called a probability measure and possesses the extra property that is normalized to unity.

The space Ω is called the outcome space and its elements ω are outcomes of the experiment.F is a σ-algebra (σ-field) on Ω (a set of subsets of Ω) that satisfies the following requirements
1. If $A \in F$ then $A^c \in F$
2. If $A_1, A_2, ... \in F$ then $\bigcup_{n=1}^{\infty} A_n \in F$

A σ-algebra can be found to be closed under complementarity, countable union and countable intersection with use of simple set theoretic properties.

The probability measure P is a real valued set function $P : F \rightarrow [0, 1]$ satisfying
1.$P(\Omega) = 1$
2.$P(A) \geq 0$ for all $A \in F$
3.If $A_1, A_2, ... \in F$ are disjoint then $P(\bigcup_{n=1}^{\infty} A_n) = \sum_{n=1}^{\infty} P(A_n)$
A random variable X is simply a measurable function $(X : \Omega \longrightarrow \Re)$,that is,for every Borel measurable set B then $X^{-1}(B) \in F$.

7.5.2 Moments

The expectation of the random variable X is $E(X) = \int_{\Omega} X(\omega)dP(\omega) = \int_R xdF_X(x)$ where x are the realizations of X.
We also define for a Borel measurable function g

$$E(g(X)) = \int_{\Omega} g(X(\omega))dP(\omega) = \int_R g(x)dF_X(x) \tag{7.47}$$

7.6 Elements from Tensor Analysis

7.6.1 Notational Preliminaries;Vectors and Tensors

We are about to give a brief summary on the most common vector operations treated from an analytical viewpoint (we will avoid the interpretation with the various geometric properties of these operations).

We will begin with the definition of the permutation symbol ϵ_{ijk} which takes values $+1, -1$ for even and odd permutations of the indices ijk respectively or the value 0 if any two indices are alike.

Vectors

Let $\delta_1, \delta_2, \delta_3$ be the unit vectors in the direction of the x, y, z axes.The definitions of the dot and cross products of the vectors are

$$(\delta_i \cdot \delta_j) = \delta_{ij} \tag{7.48}$$

and

$$[\delta_i \times \delta_j] = \sum_{k=1}^{3} \epsilon_{ijk}\delta_k \tag{7.49}$$

Any vector in the physical configuration space can be expanded in terms of its components.So if v_1, v_2, v_3 are the projections on the coordinate axes then the vector v can be written as

$$v = \sum_{i=1}^{3} \delta_i v_i \tag{7.50}$$

Let v_1, v_2, v_3 and w_1, w_2, w_3 be the components of vectors v, w respectively.Then the most common vector operations are:
The addition (subtraction) of vectors

$$v + w = \sum_i \delta_i(v_i + w_i) \tag{7.51}$$

Multiplication of a vector by a scalar s

$$sv = \sum_i \delta_i \{sv_i\} \tag{7.52}$$

The dot product of two vectors

$$(v \cdot w) = \sum_i \sum_j \delta_{ij} v_i w_j = \sum_i v_i w_i \tag{7.53}$$

The cross product of two vectors

$$[v \times w] = \sum_i \sum_j \sum_k \epsilon_{ijk} \delta_i v_j w_k \tag{7.54}$$

The multiple vector product

$$(u \cdot [v \times w]) = \sum_i \sum_j \sum_k \epsilon_{ijk} u_i v_j w_k \tag{7.55}$$

Tensors

The key point when one deals with tensor operations is to define a new kind of product,namely the dyadic product $\delta_i \delta_j$.Operations that have to do with tensors will be defined according to the following table:

$$(\delta_i \delta_j : \delta_k \delta_l) = (\delta_j \cdot \delta_k)(\delta_i \cdot \delta_l) = \delta_{jk} \delta_{il} \tag{7.56}$$

$$[\delta_i \delta_j \cdot \delta_k] = \delta_i (\delta_j \cdot \delta_k) = \delta_i \delta_{jk} \tag{7.57}$$

$$[\delta_i \cdot \delta_j \delta_k] = (\delta_i \cdot \delta_j) \delta_k = \delta_{ij} \delta_k \tag{7.58}$$

$$\{\delta_i \delta_j \cdot \delta_k \delta_l\} = \delta_i (\delta_j \cdot \delta_k) \delta_l = \delta_{jk} \delta_i \delta_l \tag{7.59}$$

$$\{\delta_i \delta_j \times \delta_k\} = \delta_i [\delta_j \times \delta_k] = \sum_{l=1}^{3} \epsilon_{jkl} \delta_i \delta_l \tag{7.60}$$

$$\{\delta_i \times \delta_j \delta_k\} = [\delta_i \times \delta_j] \delta_k = \sum_{l=1}^{3} \epsilon_{ijl} \delta_l \delta_k \tag{7.61}$$

If τ_{ij} are the components of tensor τ then τ can be written as

$$\tau = \sum_{i=1}^{3} \sum_{j=1}^{3} \delta_i \delta_j \tau_{ij} \tag{7.62}$$

Addition of tensors

$$\sigma + \tau = \sum_i \sum_j \delta_i \delta_j (\sigma_{ij} + \tau_{ij}) \tag{7.63}$$

Multiplication of a tensor by a scalar s

$$s\tau = \sum_i \sum_j \delta_i \delta_j \{s\tau_{ij}\} \tag{7.64}$$

The double dot product of two tensors

$$(\sigma : \tau) = \sum_i \sum_j \sigma_{ij}\tau_{ji} \tag{7.65}$$

Dot product of a tensor with a vector

$$[\tau \cdot v] = \sum_i \delta_i \{\sum_j \tau_{ij} v_j\} \tag{7.66}$$

The cross product of a tensor with a vector

$$\{\tau \times v\} = \sum_i \sum_l \delta_i \delta_l \{\sum_j \sum_k \epsilon_{jkl} \tau_{ij} v_k\} \tag{7.67}$$

Differential Operations

The first object to define is the "nabla" operator which is defined as

$$\nabla = \sum_i \delta_i \frac{\partial}{\partial x_i} \tag{7.68}$$

For a scalar function s we define the gradient of s as

$$\nabla s = \sum_i \delta_i \frac{\partial s}{\partial x_i} \tag{7.69}$$

The divergence of the vector field v (a vector function of the variables x_1, x_2, x_3) is

$$(\nabla \cdot v) = \sum_i \frac{\partial v_i}{\partial x_i} \tag{7.70}$$

The Curl of a vector field v is

$$[\nabla \times v] = \sum_i \sum_j \sum_k \epsilon_{ijk} \delta_i \frac{\partial}{\partial x_j} v_k \tag{7.71}$$

The gradient of the vector field v is

$$\nabla v = \sum_i \sum_j \delta_i \delta_j \frac{\partial}{\partial x_i} v_j \tag{7.72}$$

The divergence of a tensor field τ is

$$[\nabla \cdot \tau] = \sum_k \delta_k \{\sum_i \frac{\partial}{\partial x_i} \tau_{ij}\} \tag{7.73}$$

The Laplacian of a Scalar field is

$$(\nabla \cdot \nabla s) = \{\sum_i \frac{\partial^2}{\partial x_i^2} s\} \tag{7.74}$$

The Laplacian of a vector field is

$$[\nabla \cdot \nabla v] = \sum_k \delta_k (\sum_i \frac{\partial^2}{\partial x_i^2} v_k) \tag{7.75}$$

7.6.2 Integral Theorems

- The Gauss Divergence Theorem.

If V is a closed region with surface S then

$$\int_V (\nabla \cdot v) dV = \int_S (\eta \cdot v) dS \tag{7.76}$$

in which η is the outwardly directed unit normal vector.
In the case of a tensor τ Gauss' Theorem reads

$$\int_V [\nabla \cdot \tau] dV = \int_S [\eta \cdot \tau] dS \tag{7.77}$$

where we can replace straightforwardly the tensor τ with the dyadic product vw of two vectors v, w and thus get

$$\int_V [\nabla \cdot vw] dV = \int_S [\eta \cdot vw] dS \tag{7.78}$$

- The Stokes Curl Theorem

If S is a surface bounded by a closed curve C then

$$\int_S (\eta \cdot [\nabla \times v]) dS = \oint_C (t \cdot v) dC \tag{7.79}$$

where t is the unit tangential vector in the direction of integration along C.
Stokes Theorem for Tensors is:

$$\int_S [\eta \cdot \{\nabla \times \tau\}] dS = \oint_C [t \cdot \tau] dC \tag{7.80}$$

7.6.3 Transformation of Coordinates

To get along with the high number of indices that we are going to use in this section, we will start by stating two items that may help us avoid too much confusion. The first one is a 'mnemonic' trick, namely 'The Conservation of Indices' that states that lower and upper tensor indices are balanced across equal signs. The other is an 'abbreviation convention' which states that repeated indices are summed unless otherwise noted and bears the name 'Einstein summation formula'

Starting, let q^i and $\bar{q}^i$ be two sets of (generally) non-orthogonal, curvilinear coordinates that are related to one another by the coordinate transformations:

$$\bar{q}^i = \bar{q}^i(q^1, q^2, q^3); q^i = q^i(\bar{q}^1, \bar{q}^2, \bar{q}^3) \tag{7.81}$$

We make use of the chain rule of differentiation and write

$$d\bar{q}^i = (\frac{\partial \bar{q}^i}{\partial q^j})dq^j; dq^i = (\frac{\partial q^i}{\partial \bar{q}^j})d\bar{q}^j \tag{7.82}$$

Let g_i and $\bar{g}_i$ be the base vectors in the original and barred coordinate system respectively. Then
$dr = g_i dq^i$ and $dr = \bar{g}_i d\bar{q}^i$
The above two relations are essential to obtain the transformation rules for the base vectors:

$$g_i = \frac{\partial \bar{q}^j}{\partial q^i}\bar{g}_j \tag{7.83}$$

and

$$\bar{g}_i = \frac{\partial q^j}{\partial \bar{q}^i}g_j \tag{7.84}$$

Now its time to introduce the notation for the contravariant base vectors. These are inserted in such a way that

$$g^i \cdot g_j = \delta^i_j; g_i \cdot g^j = \delta^j_i \tag{7.85}$$

and

$$\bar{g}^i \cdot \bar{g}_j = \delta^i_j; \bar{g}_i \cdot \bar{g}^j = \delta^j_i \tag{7.86}$$

We define the contravariant (or reciprocal) base vectors by

$$g^1 = \frac{[g_2 \times g_3]}{(g_1 \cdot [g_2 \times g_3])} \tag{7.87}$$

and g^2, g^3 are obtained by cyclic permutations
where the denominator is the volume of the parallelepiped formed by g_1, g_2, g_3 (or $\bar{g}_1, \bar{g}_2, \bar{g}_3$ in the second case)

Thus the transformation rules for the contravariant base vectors are $g^i = \frac{\partial q^i}{\partial \bar{q}^j}\bar{g}^j$ and $\bar{g}^i = \frac{\partial \bar{q}^i}{\partial q^j} g^j$

Now a vector v may be written in two forms in both coordinate systems $v = g_i v^i = \bar{g}_i \bar{v}^i$ or $v = g^i v_i = \bar{g}^i \bar{v}_i$

We can easily get from the above relations that

$$v^i = \frac{\partial q^i}{\partial \bar{q}^j}\bar{v}^j ; \bar{v}^i = \frac{\partial \bar{q}^i}{\partial q^j} v^j \tag{7.88}$$

$$v_i = \frac{\partial \bar{q}^j}{\partial q^i}\bar{v}_j ; \bar{v}_i = \frac{\partial q^j}{\partial \bar{q}^i} v_j \tag{7.89}$$

The time has come to introduce the metric tensors g_{ij} and g^{ij} by

$$g_i \cdot g_j = g_{ij} \tag{7.90}$$

and

$$g^i \cdot g^j = g^{ij} \tag{7.91}$$

We note that $\sqrt{g}$ is equal to $(g_1 \cdot [g_2 \times g_3])$

The distance between two points in a manifold is now given by

$$dr^2 = g_{ij} dq^i dq^j = g^{ij} dq_i dq_j \tag{7.92}$$

We have expressed vectors in terms of base vectors, analogously we can do that with tensors

$$\tau = g_i g_j \tau^{ij} = g^i g^j \tau_{ij} = g_i g^j \tau^i_j = g^i g_j \tau^j_i \tag{7.93}$$

the τ^{ij}, τ_{ij} and (τ^i_j or τ^j_i) are the covariant, contravariant and mixed components of tensor τ, respectively.

The covariant and contravariant components are simply related (remember the conservation of indices)

$$v_j = g_{ij} v^i \tag{7.94}$$

and

$$\tau^{ij} = g^{ik} g^{jl} \tau_{kl} \tag{7.95}$$

We are now in position to define the Cristoffel symbols Γ^k_{ij} by

$$\Gamma^k_{ij} = \frac{1}{2}\sum_l g^{kl}\left(\frac{\partial g_{il}}{\partial q^j} + \frac{\partial g_{jl}}{\partial q^i} - \frac{\partial g_{ij}}{\partial q^l}\right) \tag{7.96}$$

Recall that the g_i are the base vectors of the q^i coordinates and one can prove that the following hold

$$\frac{\partial}{\partial q^j} g_i = \Gamma^k_{ij} g_k \tag{7.97}$$

and

$$\frac{\partial}{\partial q^j} g^i = -\Gamma^i_{kj} g^k \tag{7.98}$$

Finally, defining the gradient operator ∇ as $\nabla = g^i \frac{\partial}{\partial q^i}$ we can verify that

$$(\nabla \cdot v) = \frac{1}{\sqrt{g}} \frac{\partial}{\partial q^i} (\sqrt{g} v^i) \tag{7.99}$$

and

$$\nabla^2 s = \frac{1}{\sqrt{g}} \frac{\partial}{\partial q^i} (\sqrt{g} g^{ij} \frac{\partial s}{\partial x^j}) \tag{7.100}$$

7.7 The Fourier Transform

For a function $v \in L_1(R^d)$ we define its Fourier transform for $\xi = (\xi_1, ..., \xi_d) \in R^d$ by

$$Fv(\xi) = \hat{v}(\xi) = \int_{R^d} v(x) e^{-ix\cdot\xi} dx \tag{7.101}$$

and the inverse Fourier transform by

$$F^{-1}v(x) = \check{v}(x) = (2\pi)^{-d} \int_{R^d} v(\xi) e^{ix\cdot\xi} d\xi = (2\pi)^{-d} \hat{v}(-x) \tag{7.102}$$

Defining the inner product of two integrable real (or complex) valued functions v, w as

$$(v, w) = \int_{R^d} v(x) w(x) dx ((v, w) = \int_{R^d} v(x) \overline{w(x)} dx) \tag{7.103}$$

then Parsevals formula states

$$\int_{R^d} v(x) \overline{w(x)} dx = (2\pi)^{-d} \int_{R^d} \hat{v}(\xi) \overline{\hat{w}(\xi)} d\xi \tag{7.104}$$

A norm can be defined by $\parallel v \parallel = (\int_{R^d} v^2(x) dx)^{1/2}$ so Parsevals formula states

$$\parallel v \parallel = (2\pi)^{-d/2} \parallel \hat{v} \parallel \tag{7.105}$$

We state some other properties of the Fourier transform

- $Fv(\cdot + y)(\xi) = e^{iy\cdot\xi} \hat{v}(\xi)$ transformation of the argument of the function y units right.
- $Fv(\alpha \cdot)(\xi) = \alpha^{-d} \hat{v}(\alpha^{-1}\xi) y$ for $\alpha > 0$
- $F(D^\alpha v)(\xi) = (i\xi)^\alpha \hat{v}(\xi)$

Finally a convolution of the two functions v, w is defined by

$$(v * w)(x) = \int_{R^d} v(x-y)w(y)dy = \int_{R^d} v(y)w(x-y)dy \tag{7.106}$$

For the Fourier transform of the convolution we obtain

$$F(v * w)(\xi) = Fv(\xi)Fw(\xi) \tag{7.107}$$

7.8 The Stress Tensor at Equilibrium (A proof on the uniqueness of the stress tensor)

Questions may arise that deal with the uniqueness of the stress tensor.
a)The equation of motion in continuum mechanics is $\frac{\partial}{\partial t}(\rho v) + (div\rho vv) = -(\nabla \cdot \pi) + G$ and thus we are led to the fact that adding a divergencefree tensor will not affect the equation of motion.On the other hand that will cause a change to the force acting on a surface element which is $[\eta \cdot \pi]dS$.
b)One could identify the $S^{(e)}$ with the G and set $\pi^{(e)}$ equal to zero. This would also lead to a different result for the force $[\eta \cdot \pi]dS$ on a surface element.

To overcome these difficulties we will derive an expression for the stress tensor at equilibrium and show that none of the above actions are legal in the equilibrium state. This discussion will be restricted to systems for which the external forces are independent of position and the total external force on a single molecule is zero.

In the phase space we have

$$\frac{d}{dt} r_\nu^{\alpha i} p_\nu^{\alpha i} = \frac{1}{m_\nu^\alpha} p_\nu^{\alpha i} p_\nu^{\alpha i} + r_\nu^{\alpha i} \tilde{F}_\nu^{\alpha i} = \frac{1}{m_\nu^\alpha} p_\nu^{\alpha i} p_\nu^{\alpha i} + r_\nu^{\alpha i}(F_\nu^{\alpha i} + F_\nu^{(w)\alpha i}) \tag{7.108}$$

where $\widetilde{F}_\nu^{\alpha i}$ is the total force on a bead;that is the sum of $F_\nu^{\alpha i}$ (inter- and intramolecular plus external forces) and the force $F_\nu^{(w)\alpha i}$ due to the walls of the container enclosing the liquid.

Summing over all beads in the system integrating w.r.t time from 0 to τ we get:

$$\frac{1}{\tau} \sum_{\alpha i \nu} r_\nu^{\alpha i} p_\nu^{\alpha i}|_0^\tau = K + \Xi + \Xi^{(w)} \tag{7.109}$$

where

$$K = \sum_{\alpha i \nu} \frac{1}{m_\nu^\alpha} \langle p_\nu^{\alpha i} p_\nu^{\alpha i} \rangle_\tau = \sum_{\alpha i \nu} \frac{1}{\tau} \int_0^\tau p_\nu^{\alpha i} p_\nu^{\alpha i} dt \tag{7.110}$$

$$\Xi = \sum_{\alpha i \nu} \langle r_\nu^{\alpha i} F_\nu^{\alpha i} \rangle_\tau = \sum_{\alpha i \nu} \frac{1}{\tau} \int_0^\tau r_\nu^{\alpha i} F_\nu^{\alpha i} dt \tag{7.111}$$

$$\Xi^{(w)} = \sum_{\alpha i \nu} \langle r_\nu^{\alpha i} F_\nu^{(w)\alpha i} \rangle_\tau = \sum_{\alpha i \nu} \frac{1}{\tau} \int_0^\tau r_\nu^{\alpha i} F_\nu^{(w)\alpha i} dt \tag{7.112}$$

In the equilibrium state the term on the left of 7.109 becomes 0 as $\tau \to \infty$, because the position vectors are bounded and the momenta will be very large only over very small time intervals. In the same limit, the time averages of the first two terms on the right side may be replaced by the phase space averages, using the equilibrium distribution function.
Hence

$$K = \sum_{\alpha i \nu} \frac{1}{m_\nu^\alpha} \langle p_\nu^{\alpha i} p_\nu^{\alpha i} \rangle = \sum_{\alpha i \nu} \frac{1}{m_\nu^\alpha} \int p_\nu^{\alpha i} p_\nu^{\alpha i} f_{eq}(x) dx \tag{7.113}$$

and

$$\begin{aligned} \Xi = \sum_{\alpha i \nu} \langle r_\nu^{\alpha i} F_\nu^{\alpha i} \rangle &= \sum_{\alpha i \nu} \int r_\nu^{\alpha i} F_\nu^{\alpha i} f_{eq} dx \\ &= \sum_{\alpha i \nu} \int r_\nu^{\alpha i} F_\nu^{\alpha i} \Psi_{eq} dr \end{aligned} \tag{7.114}$$

where the last average is w.r.t the equilibrium distribution function.

We only need to evaluate $\Xi^{(w)}$. For this we note that the time average of the sum of all forces on the beads due to the wall is the negative of the time average force on the wall by the beads. From continuum arguments, this force (per unit area) is $[\eta \cdot \pi]$.

To show now that the choice of the expression for π is the correct one we define a quantity $\hat{\pi}$ as follows:

$$\hat{\pi} = \pi + c_1 \pi^{(e)} + c_2 \beta \tag{7.115}$$

in which π is the sum of four contributions, $\pi^{(e)}$ is the external field contribution to the stress tensor,β is a divergencefree tensor, and c_1, c_2 are arbitrary constants. If $\hat{\pi}$ is taken to be the stress tensor then the force /unit area on a wall is$[\eta \cdot \hat{\pi}]$ and thus

$$\Xi^{(w)} = -\int r[\eta \cdot \hat{\pi}] ds = -\{\int \eta \cdot \hat{\pi} r ds\}^T \tag{7.116}$$

Applying Gauss theorem we obtain

$$\Xi^{(w)} = -\{\int \nabla \cdot \hat{\pi} r dr\}^T = -\int r[\nabla \cdot \hat{\pi}] dr - \int \hat{\pi} dr \tag{7.117}$$

For the fluid under consideration, namely a fluid at rest with the total external force per molecule being zero the equation of motion simplifies to $[\nabla \cdot \pi] = 0$, substitution into 7.109 for $\hat{\pi}$, gives us

$$\Xi^{(w)} = c_1 \int r[\nabla \cdot \pi^{(e)}]dr - \int (\pi + c_1\pi^{(e)} + c_2\beta)dr \tag{7.118}$$

or

$$-(K + \Xi) = -c_1 \int r[\nabla \cdot \pi^{(e)}]dr - \int \pi dr - c_1 \int \pi^{(e)}dr - c_2 \int \beta dr \tag{7.119}$$

We will show later that the left side of the equation is equal to $-\int \pi dr$ and therefore we obtain:

$$0 = -c_1 \int r[\nabla \cdot \pi^{(e)}]dr - c_1\pi_b^{(e)}V - c_1 \int (\pi^{(e)} - \pi_b^{(e)})dr - c_2 \int \beta dr \tag{7.120}$$

in which the subscript b indicates the value in the bulk of the fluid (not in the thin layer near the wall).

We now want to determine c_1 and c_2. The second term on the right depends on the magnitude of V but not the shape of the container. The values of the $1, 3$ and $4'th$ term depend on the shape of the container.
(a)Case I:β is a constant tensor.In this case the fourth term becomes $-c_2\beta V$ and is independent of the container. Therefore the sum of the first and third terms must be equal to zero (shape-independent terms).
It can be concluded from the latter relation that c_1, c_2 are zero.
(b)Case II: β is not a constant tensor. In this case the second term is the only shape-independent term and setting it equal to zero gives c_1 equal to zero. Then setting the sum of the shape-dependent terms equal to zero gives c_2 equal to zero.

We are thus led to the conclusion that π and $\hat{\pi}$ are the same.
It remains to be shown that $-(K + \Xi)$ is equal to $-\int \pi dr$ or

$$\int \pi dr = \sum_{\alpha i\nu} \frac{1}{m_\nu^\alpha} \int p_\nu^{\alpha i} p_\nu^{\alpha i} f_{eq}(x)dx + \sum_{\alpha i\nu} \int r_\nu^{\alpha i} F_\nu^{\alpha i} \Psi_{eq}(r)dr \tag{7.121}$$

We can replace $r_\nu^{\alpha i}$ by $R_\nu^{\alpha i}$ just because we have restricted the discussion to systems for which the total external force on a molecule is zero.

$$\int \pi dr = \sum_{\alpha i\nu} \int p_\nu^{\alpha i} p_\nu^{\alpha i} f_{eq}(x)dx = \sum_{\alpha i\nu} \int R_\nu^{\alpha i} F_\nu^{\alpha i} \Psi_{eq}(r)dr \tag{7.122}$$

We then write

$$\begin{aligned}\sum_{\alpha i\nu} \frac{1}{m_\nu^\alpha} \int p_\nu^{\alpha i} p_\nu^{\alpha i} f_{eq}(x)dx &= \sum_{\alpha i\nu} \frac{1}{m_\nu^\alpha} \int\int p_\nu^{\alpha i} p_\nu^{\alpha i} f_{eq}(x)\delta(r_\nu^{\alpha i} - r)drdx \\ &= \int \sum_{\alpha i\nu} \frac{1}{m_\nu^\alpha} \int p_\nu^{\alpha i} p_\nu^{\alpha i} f_{eq}(x)\delta(r_\nu^{\alpha i} - r)dxdr \end{aligned} \tag{7.123}$$

and the internal integral is equal to $\pi^{(k)}$
Exactly the same steps may be carried for the second term of 7.109.

Chapter 8

Biographical Notes

8.1 Ludwig Boltzmann

Ludwig Boltzmann (1844 Vienna -1906 Duino) son of a taxation official was awarded a doctorate from the University of Vienna in 1866 for a thesis on the kinetic theory of gases supervised by Joseph Stefan. Soon after his doctorate dissertation Boltzmann started travelling and teaching , moving from one place to another (e.g Graz, Heidelberg, Berlin) and studied under brilliant names of his time. Boltzmann's nature made him subject to rapid swings between happiness and sadness and nowadays it seems that he suffered a kind of depression with elevated expansive or irritable moods (a manic-depressive illness or else bipolar-disorder would fit to the features of a modern psychiatric diagnosis). In 1900 he moved to Leipzig for occupational reasons and became a colleague with one of his strongest scientific opponents, Wilhelm Ostwald. Depressed by his conflict with Ostwald he made his first major suicide attempt. In 1902 Boltzmann moved back to Vienna where he held his chair of theoretical physics, giving philosophy lectures.

Boltzmann's main contribution is the invention of statistical mechanics, which he did independently of Willard Gibbs in a more physical manner. His monumental work included the derivation of the Maxwell-Boltzmann distribution in 1871, the derivation of the Boltzmann equation and the H-theorem in 1872, the derivation of Stefan's empirical T^4 law for black-body radiation using principles of thermodynamics in 1884 e.t.c. The strong opposition to his work on statistical mechanics by Ostwald, Zermelo, Loschmidt and many others made him more volnurable and Boltzmann had to defend every opposing argument. The main reason for the strong conflict he faced is that the probabilistic character of his description that departed from the laws of exact mechanics and his famous 'Stosszahlansatz' assumption in the derivation of his celebrated equation could not be conceived as 'healthy'.

Finally, on a holiday with his family at the bay of Duino near Trieste, Boltzmann hanged himself while his wife and daughter were swimming.

8.2 Josiah Willard Gibbs

Josiah Willard Gibbs (1839 New Haven -1903 New Haven) son of a Yale's professor showed early commitment to academic work and was described as withdrawn. In 1854 he entered Yale college where he excelled in Latin and Mathematics and attained his doctorate in 1863 in engineering (the first engineering doctorate to be conferred in the United States). In his dissertation he used geometric methods to study the design of gears. Gibbs went to Europe for the time interval between 1866 to 1869 spending one year in Paris, Berlin and Heidelberg respectively. He then returned to Yale and two years later he was appointed a professor of Mathematical Physics at Yale while he had not yet produced any scientific work!

Gibbs first papers appeared in 1873 and were Graphical Methods in the Thermodynamics of Fluids and A method of Geometrical Representation of the Thermodynamic Properties of Substances by Means of Surfaces. In 1876 and 1878 he published the two parts of his work On the Equilibrium of Heterogeneous Substances. He also made great contribution on vector analysis, he developed a method of finding the orbit of a comet using three observations (the latter was successively applied in the case of Swift's comet of 1880) and he published on the area of electromagnetic theory of light. His contribution on Statistical Mechanics came in his very late years when he published the monumental Elementary Principles in Statistical Mechanics setting the foundation of Statistical Mechanics on a firm basis.

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