

B 1 Statistical Mechanics

Jan K.G. Dhont

Institut für Festkörperforschung

Forschungszentrum Jülich GmbH

Contents

1	Introduction	3
2	Probability Density Functions (pdf's)	4
2.1	Phase space, pdf's and ensemble averages	4
2.2	Conditional probability density functions	5
2.3	Reduced probability density functions	7
2.4	The pair-correlation function	8
3	Time-Correlation Functions	11
4	Equations of Motion for Probability Density Functions	12
4.1	The Liouville equation	13
4.2	The Smoluchowski equation	15
4.3	The dynamic structure factor for non-interacting colloids	18
5	Hydrodynamics	19
5.1	The continuity equation	20
5.2	The Navier-Stokes equation	20
5.3	The creeping flow equations	22
5.4	The Oseen tensor	24
5.5	Hydrodynamic interactions	26
6	Linear Response Theory	28
6.1	Derivation of the linear response equations	29

6.2	Static and dynamic response of the number density	31
7	The Green-Kubo Formula	33
7.1	Derivation of the Green-Kubo formula	34
7.2	Self-diffusion	35
7.3	Sedimentation	37
8	Onsager's Regression Hypothesis	37
8.1	Formulation of Onsager's regression hypothesis	38
8.2	Collective-diffusion	38
8.3	The shear viscosity	40
8.4	Some remarks on the Onsager approach	43
9	Additional Reading	44

1 Introduction

Classical statistical mechanics is formulated in terms of the probability that interacting particles attain certain positions and velocities. Each given set of positions and velocities is referred to as microstate. The probability for the occurrence of such microstates can be expressed in terms of the interaction potential between the particles. In that sense, statistical mechanics is a microscopic theory. In principle, equations of motion for macroscopic variables can be derived from statistical mechanics. In this way, a microscopic basis can be given to many phenomenological theories. In particular, microscopic expressions can be derived for phenomenological transport coefficients in terms of correlation functions. Examples of such transport coefficients are diffusion coefficients and the shear viscosity of a fluid. These correlation functions can be measured by computer simulations, which then allows the determination of numerical values for transport coefficients once the inter-particle potential is specified.

The aim of this chapter is to introduce the fundamental concepts and theories of classical (non-quantum mechanical) statistical mechanics. The emphasis is on dynamics and response to small external perturbations. Both atomic/molecular and colloidal systems will be treated. In section 2, the fundamental concepts in terms of which statistical mechanics is formulated are introduced. The central quantity here is the probability density function, which specifies the probability of microstates. In section 3, time-correlation functions are introduced, which characterize the dynamics of particles. These correlation functions can be formulated in terms of the so-called time-evolution operator, which is defined through the equation of motion of probability density functions, as shown in section 4. Explicit forms for time evolution operators are derived in terms of inter-particle potentials in the same section. Two cases are considered : atomic/molecular systems and colloidal systems. Colloidal systems are solutions of very large particles, so-called colloidal particles. Here, the interest is in the properties of the subset of these colloidal particles. The solvent is considered as a continuous background on the length scale set by the size of the colloidal particles. The most fundamental equation of motion within classical mechanics is the Liouville equation for atomic/molecular systems. For colloidal particles, the so-called Smoluchowski equation is the relevant equation of motion. The latter equation of motion involves only the position coordinates of the colloidal particles. The derivation of this equation of motion relies on a separation of time scales on which the solvent molecules and the momenta of the colloidal particles evolve, and on which the positions of the colloids evolve. The Smoluchowski equation involves interaction contributions between colloidal particles mediated via the solvent, so-called hydrodynamic interactions. These interactions can be described on the basis of phenomenological equations of motion for fluid flow. Such a phenomenological description of hydrodynamic interactions is the subject of section 5. In section 6, the explicit forms of the time evolution operators are used to calculate the response of observables to small, conservative external fields. This theory is known as "linear response theory". On the basis of this theory, linear transport coefficients are expressed in terms of current-current correlation functions in section 7. These expressions are known as "the Green-Kubo formulas". Explicit expressions for the self-diffusion coefficient and the sedimentation coefficient of colloids are derived from the general Green-Kubo formula. Such formulas can be used to obtain numerical values for transport coefficients by measuring the appropriate current-current correlation functions in a simulation. For non-conservative external fields, like a shear flow, or for transport coefficients where the driving force is proportional to gradients of observables, like the collective-diffusion coefficient, the general Green-Kubo formula can not be applied. Here, an intuitively appealing Ansatz as formulated by Onsager can be employed to obtain Green-Kubo-

like relations. This so-called "Onsager's regression hypothesis" is formulated in section 8. Two transport coefficients are worked out explicitly : the collective-diffusion coefficient of colloids and the shear viscosity of a molecular fluid.

2 Probability Density Functions (pdf's)

It is not feasible nor meaningful to solve Newton's equations of motion for a collection of many particles : the problem is too complicated and the initial values for the position coordinates and momenta that must be specified are not known when an experiment is performed. This is where statistical approaches are useful, where one asks for the probability that, for example, the position coordinates and momenta take certain specified values at some specified time.

2.1 Phase space, pdf's and ensemble averages

Imagine a collection of macroscopically identical systems containing N molecules. Thermodynamic variables for each system are the same, but of course microscopically each of the systems is generally in a different state, that is, the position coordinates and momenta of the molecules in each system at a certain instant in time are generally different. Such a collection of macroscopically identical systems is referred to as an *ensemble*. The *phase space* for spherical molecules is defined as the $6N$ -dimensional space spanned by the position coordinates $\mathbf{r}_1, \dots, \mathbf{r}_N$ and momenta $\mathbf{p}_1, \dots, \mathbf{p}_N$ of all N molecules in each system. The instantaneous values of positions and momenta specify the *microstate* of a system, and is represented by a single point in phase space. The evolution of positions and momenta in a system is described by a curve in phase space. Now suppose that we made a photograph of the entire ensemble, and that the microstate of each system in the ensemble is determined from that photograph.¹ In this way a single point in phase space is assigned to each of the systems, resulting in a point distribution for the ensemble. The density of points is proportional to the probability of finding a single system in that microstate at that particular time. The *probability density function* (abbreviated hereafter as *pdf*) $P(\mathbf{X}, t)$ of the phase space variable,

$$\mathbf{X} \equiv (\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{p}_1, \dots, \mathbf{p}_N), \quad (1)$$

is now defined as,

$$P(\mathbf{X}, t) d\mathbf{X} = \text{the probability that positions and momenta are in } (\mathbf{X}, \mathbf{X} + d\mathbf{X}) \text{ at time } t. \quad (2)$$

Here, $(\mathbf{X}, \mathbf{X} + d\mathbf{X})$ denotes an infinitesimal neighbourhood of \mathbf{X} of extent,

$$d\mathbf{X} = d\mathbf{r}_1 \cdots d\mathbf{r}_N d\mathbf{p}_1 \cdots d\mathbf{p}_N. \quad (3)$$

The pdf is normalized in the sense that,

$$\int d\mathbf{X} P(\mathbf{X}, t) = 1, \quad (4)$$

which expresses the fact that the probability to find a system in some state is unity. Consider a function $f \equiv f(\mathbf{X})$ of position coordinates and momenta. Such functions are referred to as

¹For the determination of the momenta one should actually make two subsequent photographs.

phase functions, and may be scalar functions or vector fields. Phase functions are the microscopic, thermally fluctuating counterparts of macroscopic variables. Frequently, phase functions, and also (a subset of) the phase space coordinates themselves, are alternatively referred to as *stochastic variables*. The macroscopic variable corresponding to a phase function is obtained by ensemble averaging, and is given by,

$$\langle f \rangle = \int d\mathbf{X} P(\mathbf{X}, t) f(\mathbf{X}) . \quad (5)$$

The brackets $\langle \dots \rangle$ are nothing but a short-hand notation for the integral on the right hand-side. This average is the *ensemble average* of f . Alternatively one may introduce the pdf $P(f, t)$ for a stochastic variable f instead of \mathbf{X} , by rewriting the above equation as,

$$\langle f \rangle = \int df P(f, t) f . \quad (6)$$

This pdf for f is equal to (with δ the delta distribution),

$$P(f, t) = \int d\mathbf{X} P(\mathbf{X}, t) \delta(f - f(\mathbf{X})) , \quad (7)$$

as is easily verified by substitution into eq.(6), noting that $\int df \delta(f - f(\mathbf{X})) f = f(\mathbf{X})$. The above expression for $P(f, t)$ is simply a counting of the extent of the subset in phase space where $f(\mathbf{X})$ attains a particular numerical value f , weighted with the local point density.

Other more complicated pdf's can be defined. For example, $P(\mathbf{X}, t, \mathbf{X}_0, t_0)$ is the pdf for \mathbf{X} to occur at time t and \mathbf{X}_0 at some earlier time t_0 , or more precisely,

$$\begin{aligned} P(\mathbf{X}, t, \mathbf{X}_0, t_0) d\mathbf{X} d\mathbf{X}_0 &= \text{the probability that positions and momenta} \\ &\text{are in } (\mathbf{X}, \mathbf{X} + d\mathbf{X}) \text{ at time } t \\ &\text{and in } (\mathbf{X}_0, \mathbf{X}_0 + d\mathbf{X}_0) \text{ at time } t_0 < t . \end{aligned} \quad (8)$$

By definition, the connection with the earlier defined pdf is,

$$P(\mathbf{X}, t) = \int d\mathbf{X}_0 P(\mathbf{X}, t, \mathbf{X}_0, t_0) . \quad (9)$$

Equivalently, one may define pdf's like $P(f, t, g, t_0)$ where f and g are phase functions. Just as above, we have that, $P(f, t) = \int dg P(f, t, g, t_0)$.

Two stochastic variables f and g are said to be *statistically independent* when,

$$P(f, t, g, t_0) = P(f, t) P(g, t_0) . \quad (10)$$

An ensemble average like $\langle fg \rangle$ is then simply equal to the product of the averages $\langle f \rangle$ and $\langle g \rangle$.

2.2 Conditional probability density functions

Consider again the photograph taken of the ensemble at time t as discussed earlier, which allows for the determination of the microstate of each of the systems in the ensemble. Now consider only those systems which at a certain earlier time $t_0 < t$ were in a particular microstate \mathbf{X}_0 .

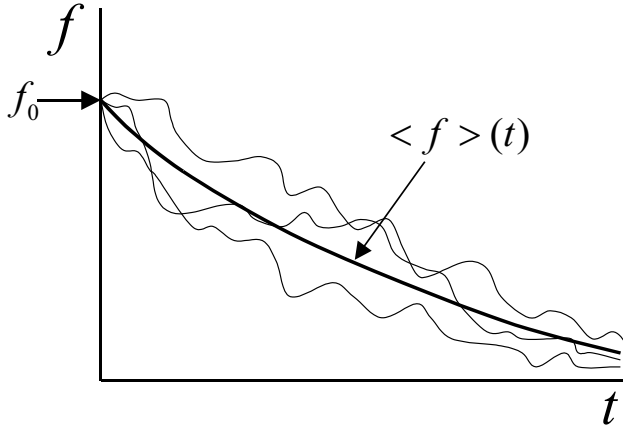


Fig. 1: Three possible realizations of the time evolution of the phase function f , given that at time t_0 the phase function had a particular value f_0 . The smooth curve is the conditional ensemble average $\langle f \rangle_{f_0}$.

This subset of systems in the ensemble is an ensemble itself, and pdf's may be defined as above for this new ensemble. This new ensemble is an ensemble of systems which are prepared in a specified microstate \mathbf{X}_0 at time t_0 . The pdf's for \mathbf{X} are pdf's with the constraint that at an earlier time t_0 the system was in the microstate \mathbf{X}_0 . Such pdf's are called *conditional pdf's*, and are denoted as $P_c(\mathbf{X}, t | \mathbf{X}_0, t_0)$, where the subscript "c" stands for "conditional". Hence,

$$P_c(\mathbf{X}, t | \mathbf{X}_0, t_0) d\mathbf{X} = \begin{array}{l} \text{the probability that positions and momenta} \\ \text{are in } (\mathbf{X}, \mathbf{X} + d\mathbf{X}) \text{ at time } t, \text{ given} \\ \text{that their values were } \mathbf{X}_0 \text{ at time } t_0 < t. \end{array} \quad (11)$$

Similarly, conditional pdf's of phase functions f , given that the phase function had a particular value f_0 at an earlier time may be defined as,

$$P_c(f, t | f_0, t_0) df = \begin{array}{l} \text{the probability that the phase function is} \\ \text{in } (f, f + df) \text{ at time } t, \\ \text{given that its value was } f_0 \text{ at time } t_0 < t. \end{array} \quad (12)$$

By definition, the connection between conditional pdf's and the earlier discussed (unconditional) pdf's reads,

$$P_c(\mathbf{X}, t | \mathbf{X}_0, t_0) = \frac{P(\mathbf{X}, t, \mathbf{X}_0, t_0)}{P(\mathbf{X}_0, t_0)}, \quad (13)$$

and similarly for pdf's of phase functions. The conditional ensemble average of a phase function f , given that $f = f_0$ at some earlier time t_0 , is denoted as $\langle f \rangle_{f_0}$,

$$\langle f \rangle_{f_0} = \int df P_c(f, t | f_0, t_0) f. \quad (14)$$

This ensemble average is in general a function of the time t . The phase function evolves in time for each system in the ensemble differently, since there are many different microstates \mathbf{X}_0 that satisfy $f_0 = f(\mathbf{X}_0)$. Two such different realizations are depicted in Fig.2.2. The conditional ensemble average is the average of all those possible realizations.

One can define time-independent conditional pdf's. For example, one may ask for the probability that particles $3, 4, \dots, N$ have positions $\mathbf{r}_3, \mathbf{r}_4, \dots, \mathbf{r}_N$, given that particles 1 and 2 have prescribed positions \mathbf{r}_1 and \mathbf{r}_2 , respectively. That conditional pdf is, in analogy with eq.(13), equal to,

$$P_c(\mathbf{r}_3, \dots, \mathbf{r}_N | \mathbf{r}_1, \mathbf{r}_2) = \frac{P(\mathbf{r}_1, \dots, \mathbf{r}_N)}{P_2(\mathbf{r}_1, \mathbf{r}_2)}, \quad (15)$$

where $P_2(\mathbf{r}_1, \mathbf{r}_2)$ is the pdf for $(\mathbf{r}_1, \mathbf{r}_2)$, which pdf will be discussed in more detail in the subsequent section.

To determine an ensemble average experimentally, there is no need to actually construct a collection of many macroscopically identical systems. When an experiment on a single system is repeated independently many times, the average of the outcome of these experiments is the ensemble average. In many cases only a single experiment is already sufficient to obtain the ensemble average. When the system is so large that the quantity of interest has many independent realizations within different parts of the system, an ensemble average is measured in a single experiment.

2.3 Reduced probability density functions

According to eq.(5), the ensemble average of a phase function of just two position coordinates, \mathbf{r}_1 and \mathbf{r}_2 say, can be written as,

$$\langle f \rangle = \int d\mathbf{r}_1 \dots \int d\mathbf{r}_N P(\mathbf{r}_1, \dots, \mathbf{r}_N, t) f(\mathbf{r}_1, \mathbf{r}_2) = \int d\mathbf{r}_1 \int d\mathbf{r}_2 P_2(\mathbf{r}_1, \mathbf{r}_2, t) f(\mathbf{r}_1, \mathbf{r}_2), \quad (16)$$

where,

$$P_2(\mathbf{r}_1, \mathbf{r}_2, t) = \int d\mathbf{r}_3 \dots \int d\mathbf{r}_N P(\mathbf{r}_1, \dots, \mathbf{r}_N, t), \quad (17)$$

is referred to as *the reduced pdf of order 2* or *the two-particle pdf*. Similarly, ensemble averages of phase functions of just one position coordinate are averages with respect the first order reduced pdf or the single particle pdf,

$$P_1(\mathbf{r}_1, t) = \int d\mathbf{r}_2 \dots \int d\mathbf{r}_N P(\mathbf{r}_1, \dots, \mathbf{r}_N, t). \quad (18)$$

Higher order reduced pdf's (such as $P_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, t)$) are similarly defined.

The probability of finding a particle at some position \mathbf{r} at time t is proportional to the macroscopic number density $\rho(\mathbf{r}, t)$, which is the average number of particles per unit volume at \mathbf{r} and at time t . Normalization sets the proportionality constant,

$$P_1(\mathbf{r}, t) = \frac{1}{N} \rho(\mathbf{r}, t). \quad (19)$$

A similar relation for P_2 will be discussed later, when the pair-correlation function is introduced.

When the system is in thermal equilibrium, the time-independent pdf for the position coordinates is proportional to the Boltzmann exponential of the total potential energy $\Phi(\mathbf{r}_1, \dots, \mathbf{r}_N)$ of the assembly of N particles,

$$P(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{\exp\{-\beta\Phi(\mathbf{r}_1, \dots, \mathbf{r}_N)\}}{Q(N, T, V)}, \quad (20)$$

with $\beta = 1/k_B T$ (k_B is Boltzmann's constant and T is the absolute temperature) and $Q(N, T, V)$ is the *configurational partition function*,

$$Q(N, T, V) = \int d\mathbf{r}_1 \cdots \int d\mathbf{r}_N \exp\{-\beta\Phi(\mathbf{r}_1, \dots, \mathbf{r}_N)\}. \quad (21)$$

When the total potential energy Φ is known, the reduced pdf's can thus be calculated in principle for systems in equilibrium, except that the integrals in eqs.(17,18) are too complicated. Finding good approximations for the first few reduced pdf's for systems in equilibrium, either from eqs.(17,18) or by other means, is the principle goal of equilibrium statistical mechanics. These equilibrium pdf's are often a necessary input for explicit evaluation of non-equilibrium ensemble averages also.

2.4 The pair-correlation function

When particles do not interact with each other, all reduced pdf's are products of P_1 's. In particular, $P_2(\mathbf{r}_1, \mathbf{r}_2, t) = P_1(\mathbf{r}_1, t) P_1(\mathbf{r}_2, t)$. Interactions can formally be accounted for by an additional factor $g(\mathbf{r}_1, \mathbf{r}_2, t)$, the so-called *pair-correlation function*,

$$P_2(\mathbf{r}_1, \mathbf{r}_2, t) \equiv P_1(\mathbf{r}_1, t) P_1(\mathbf{r}_2, t) g(\mathbf{r}_1, \mathbf{r}_2, t) = \frac{1}{N^2} \rho(\mathbf{r}_1, t) \rho(\mathbf{r}_2, t) g(\mathbf{r}_1, \mathbf{r}_2, t). \quad (22)$$

Similarly, the *three-particle correlation function* g_3 "corrects" for the effect of interactions for the third order pdf P_3 ,

$$\begin{aligned} P_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, t) &= P_1(\mathbf{r}_1, t) P_1(\mathbf{r}_2, t) P_1(\mathbf{r}_3, t) g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, t) \\ &= \frac{1}{N^3} \rho(\mathbf{r}_1, t) \rho(\mathbf{r}_2, t) \rho(\mathbf{r}_3, t) g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, t). \end{aligned} \quad (23)$$

For large distances $|\mathbf{r}_1 - \mathbf{r}_2|$ between two particles, the pair-correlation function attains its value without interactions, which is 1 by definition. The three-particle correlation function becomes equal to 1 when all three particles are well separated.

In case of homogeneous and isotropic fluids in equilibrium, the pair-correlation function is a function of $r = |\mathbf{r}_1 - \mathbf{r}_2|$ only, and can be expanded in a power series of the number density $\bar{\rho} = N/V$ as,

$$g(r) = g_0(r) + \bar{\rho} g_1(r) + \bar{\rho}^2 g_2(r) + \cdots. \quad (24)$$

The leading term g_0 describes interactions between two particles without the intervening effects of other particles. This is nothing but the pair-correlation function for a system containing just two particles. It is the relevant pair-correlation function for systems which are so dilute that events where three or more particles interact simultaneously are unlikely. According to eqs.(20-22), with $P_1 \equiv 1/V$, we thus obtain,

$$g_0(r = |\mathbf{r}_1 - \mathbf{r}_2|) = V^2 \frac{\exp\{-\beta U(r)\}}{\int d\mathbf{r}_1 \int d\mathbf{r}_2 \exp\{-\beta U(r)\}},$$

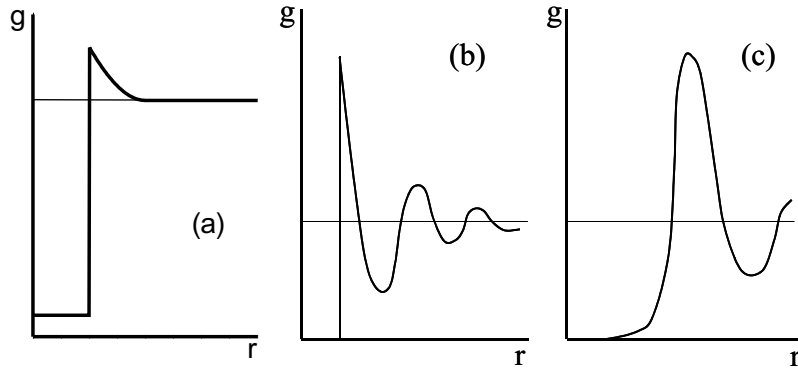


Fig. 2: (a) The pair-correlation function in eq.(27) for a volume fraction $\varphi = 0.1$. (b) A sketch of the pair-correlation function of hard spheres at large concentrations. (c) A sketch of the pair-correlation function for charged spheres. In all three figures, the horizontal line indicates where $g = 1$.

where $U(r)$ is the potential energy of an assembly of just two particles, the pair-interaction potential. Now noting that,

$$\begin{aligned} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \exp\{-\beta U(r)\} &= \int d\mathbf{r}_2 \int d(\mathbf{r}_1 - \mathbf{r}_2) \exp\{-\beta U(r)\} \\ &= V \left\{ \int d\mathbf{r} [\exp\{-\beta U(r)\} - 1] + V \right\} \approx V^2, \end{aligned}$$

since the integral in the last equation is of the order R_V^3 , with R_V the range of the pair-interaction potential, it is found that,

$$g_0(r) = \exp\{-\beta U(r)\}. \quad (25)$$

The phrase "on the pair-level" is generally used whenever interactions between three or more molecules simultaneously are disregarded. Hence, eq.(25) is the pair-correlation function on the pair-level, and can be used to calculate ensemble averages for dilute systems. In general, the pair-correlation function includes "higher order interactions", that is, it includes the intervening effects of the remaining particles on the interaction between two given particles. The next higher order contribution $\sim g_1$ in eq.(24) can be expressed in terms of so-called *Mayer-functions* $f(r) = \exp\{-\beta U(r)\} - 1$ as,

$$g_1(r = |\mathbf{r}_1 - \mathbf{r}_2|) = \exp\{-\beta V(|\mathbf{r}_1 - \mathbf{r}_2|)\} \int d\mathbf{r}_3 f(|\mathbf{r}_1 - \mathbf{r}_3|) f(|\mathbf{r}_2 - \mathbf{r}_3|), \quad (26)$$

This term describes the intervening effect of a single molecule on the effective interactions between two given molecules. The derivation of this result can be found in most standard texts on statistical mechanics.

For hard-sphere spheres, that is, for spherical molecules which do not interact when their cores do not overlap and where the pair-potential is infinite when the cores overlap g_1 is found to be

equal to (the subscript "hs" stands for "hard-spheres"),

$$\begin{aligned}
 g_{hs}(r) = g_0(r) + \bar{\rho}g_1(r) &= 1, \text{ for } r \geq 4a, \\
 &= 1 + \varphi \left[8 - 3\frac{r}{a} + \frac{1}{16} \left(\frac{r}{a} \right)^3 \right], \text{ for } r \in [2a, 4a), \\
 &= 0, \text{ for } r < 2a,
 \end{aligned} \tag{27}$$

where a is the radius of the hard-core and $\varphi = \frac{4\pi}{3}a^3\bar{\rho}$ is the fraction of the total volume that is occupied by the cores of the particles, the so-called *volume fraction*. This pair-correlation function is plotted in Fig.2.4a for $\varphi = 0.1$. At larger concentrations, the pair-correlation function develops a large contact value (defined as the value of g at $r = 2a + \epsilon$ with ϵ arbitrary small), and peaks appear at larger distances, as depicted in Fig.2.4b. A "layered structure" of spheres is formed around the central sphere. The pair-correlation function behaves quite differently in case of long ranged and strongly repulsive interacting particles, such as charged molecules, as depicted in Fig.2.4c. In this case the contact value of g is essentially zero, since the probability that two particles touch is small due to their strong repulsive interaction. The peak position shifts to smaller distances for higher concentrations. This is due to the tendency of the particles to remain far apart from each other so as to minimize their (free) energy. The peak position varies approximately as $1/\bar{\rho}^{1/3}$ for such systems. For the hard-core systems, the peak position is essentially independent of concentration.

Consider a molecule at the origin. One may ask about the average density around that particle, which density is a function of the distance from the particle due to interactions. This density is $N P_1$, as in eq.(19), with the additional condition that there is a particle in the origin. According to eq.(11) (with $t = t_0$, $\mathbf{X}_0 = \mathbf{0}$ = the position of the particle at the origin and $\mathbf{X} = \mathbf{r}$) this conditional probability is equal to $P_2(\mathbf{r}, \mathbf{r}' = \mathbf{0}, t)/P_1(\mathbf{r}' = \mathbf{0}, t)$. Hence, from the definition (22) of the pair-correlation function,

$$\begin{aligned}
 \text{Number density at } \mathbf{r} \text{ with a particle at the origin} &= \\
 N \frac{P_2(\mathbf{r}, \mathbf{r}' = \mathbf{0}, t)}{P_1(\mathbf{r}' = \mathbf{0}, t)} &= \rho(\mathbf{r}, t) g(\mathbf{r}, \mathbf{r}' = \mathbf{0}, t).
 \end{aligned} \tag{28}$$

Well away from the origin, where interaction with the particle at the origin is lost, so that $g(\mathbf{r}, \mathbf{r}' = \mathbf{0}, t) = 1$, this is simply the macroscopic density $\rho(\mathbf{r}, t)$, as it should. The peaks in the Figs.2.4 thus imply enhanced concentrations around a given particle at those distances. For hard-core interactions there is also an enhanced concentration close to contact. This enhancement is due to depletion : particles are expelled from the gap between two nearby particles leaving an uncompensated repulsive force from particles outside the gap that drives the two particles together. Each molecule in a dense liquid, charged or uncharged, is thus surrounded by a "cage" of other particles.

The "effective interaction potential" $U^{eff}(r)$ can be defined for isotropic and homogeneous systems in equilibrium as,

$$g(r) \equiv \exp\{-\beta U^{eff}(r)\}. \tag{29}$$

According to eq.(25), this effective potential is equal to the pair-interaction potential on the pair-level. From the definition of the pair-correlation function and the expressions (20-22), the average force $\mathbf{F}^{eff}(r)$ between two particles for arbitrary concentrations can be shown to be equal to $-\nabla U^{eff}(r)$, provided the system is in equilibrium. The effective force includes the

effects of intervening particles on the interaction between two given molecules. Hence, by definition,

$$\mathbf{F}^{eff}(r) = \beta^{-1} \nabla \ln\{g(r)\} = \beta^{-1} \hat{\mathbf{r}} d \ln\{g(r)\}/dr , \quad (30)$$

so that there is an attraction for those distances where $dg(r)/dr < 0$. For hard-spheres near contact there is thus attraction due to depletion as already explained above. Around the peak in the pair-correlation function the effective force changes from strongly repulsive to attractive. Multi-particle interactions may thus lead to attractions even if the pair-interaction potential is purely repulsive.

3 Time-Correlation Functions

Dynamics of many-body systems can be characterized in terms of so-called *time-correlation functions*. In order to define these correlation functions, consider first the conditional ensemble average,

$$\langle g \rangle_{f_0} = \int dg P_c(g, t | f_0, t_0) g . \quad (31)$$

This ensemble average is a time dependent function, also for systems in equilibrium. It describes the average evolution of the phase function g , given that at time $t_0 < t$ the value of the phase function f was f_0 . When this conditional average is subsequently averaged with respect to f_0 , the result is simply the unconditional ensemble average $\langle g \rangle$: since $P(g, t | f_0, t_0) = P(g, t, f_0, t_0)/P(f_0, t_0)$ we have,

$$\begin{aligned} \langle \langle g \rangle_{f_0} \rangle &= \int df_0 P(f_0, t_0) \int dg P_c(g, t | f_0, t_0) g \\ &= \int dg \underbrace{\int df_0 P(g, t, f_0, t_0)}_{=P(g,t)} g = \langle g \rangle . \end{aligned}$$

The second pair of brackets $\langle \dots \rangle$ on the left hand-side denotes ensemble averaging with respect to the initial condition f_0 . This ensemble average is time independent for systems in equilibrium. The most simple unconditional ensemble average that contains information concerning the dynamics of stochastic variables, also for systems in equilibrium, is the *correlation function of f and g* , defined as,

$$\langle \langle g \rangle_{f_0} f_0 \rangle = \int df_0 P(f_0, t_0) \int dg P_c(g, t | f_0, t_0) g f_0 . \quad (32)$$

In an experiment one usually measures such an unconditional ensemble average, since the system is not prepared in a certain state before the experiment is started. Alternatively, the correlation function may be written in terms of pdf's of phase space coordinates \mathbf{X} . Using that,

$$P(g, t, f_0, t_0) = \int d\mathbf{X} \int d\mathbf{X}_0 P(\mathbf{X}, t, \mathbf{X}_0, t_0) \delta(g - g(\mathbf{X})) \delta(f_0 - f(\mathbf{X}_0)) , \quad (33)$$

which is an alternative formulation of eq.(7), it is easily shown that,

$$\begin{aligned} \langle f(\mathbf{X}(t_0)) g(\mathbf{X}(t)) \rangle &= \int d\mathbf{X} \int d\mathbf{X}_0 f(\mathbf{X}_0) g(\mathbf{X}) P(\mathbf{X}_0, t_0) P_c(\mathbf{X}, t | \mathbf{X}_0, t_0) \\ &= \int d\mathbf{X} \int d\mathbf{X}_0 f(\mathbf{X}_0) g(\mathbf{X}) P(\mathbf{X}, t, \mathbf{X}_0, t_0) , \end{aligned} \quad (34)$$

where the left hand-side is just a more transparent, alternative notation for the correlation function $\langle \langle g \rangle_{f_0} f_0 \rangle$. The correlation function is a function of t and t_0 . For equilibrium systems, however, in which there is no preferred instant in time, the correlation function in eqs.(32,34) depends only on the difference $t - t_0$.

For very large time differences $t - t_0$, the dynamics of g becomes independent of whatever value f had at time t_0 . Formally this means that

$$P(\mathbf{X}_0, t) P_c(\mathbf{X}, t | \mathbf{X}_0, t_0) = P(\mathbf{X}, t, \mathbf{X}_0, t_0) \rightarrow P(\mathbf{X}, t) P(\mathbf{X}_0, t_0) .$$

The correlation function is thus seen to tend to $\langle f \rangle \langle g \rangle$ as $t - t_0 \rightarrow \infty$. The time required to render f and g statistically independent, to within some degree, is referred to as *the correlation time for f and g* .

4 Equations of Motion for Probability Density Functions

In order to calculate time-correlation functions analytically, an equation of motion for the appropriate pdf needs be derived. Before formulating the two most important fundamental equations of motion, let us first see how to calculate time-correlation functions from such equations of motion.

Equations of motion for pdf's are of the form,

$$\frac{\partial}{\partial t} P(\mathbf{X}, t) = \hat{\mathcal{L}} P(\mathbf{X}, t) , \quad (35)$$

where $\hat{\mathcal{L}}$ is *the time evolution operator* (mostly a differential operator) that acts on the phase space variables \mathbf{X} . Depending on the type of system under consideration, the operator $\hat{\mathcal{L}}$ takes different forms, two of which will be discussed at the end of this section. At time t_0 the phase space variables are supposed to be equal to \mathbf{X}_0 . The pdf is thus infinitely sharply peaked around $\mathbf{X} = \mathbf{X}_0$ at time $t = t_0$. From the normalization condition (4) it thus follows that,

$$P(\mathbf{X}, t = t_0) = \delta(\mathbf{X} - \mathbf{X}_0) , \quad (36)$$

with δ the delta distribution. Note that the solution of the equation of motion (35) with this initial condition is actually the conditional pdf $P(\mathbf{X}, t | \mathbf{X}_0, t_0)$. The formal solution of eqs.(35,36) reads,

$$P(\mathbf{X}, t | \mathbf{X}_0, t_0) = \exp\{\hat{\mathcal{L}}(t - t_0)\} \delta(\mathbf{X} - \mathbf{X}_0) , \quad (37)$$

where the *operator exponential* is defined by the Taylor series of the exponential function,

$$\exp\{\hat{\mathcal{L}}(t - t_0)\} \equiv \sum_{n=0}^{\infty} \frac{(t - t_0)^n}{n!} \hat{\mathcal{L}}^n . \quad (38)$$

Here, for $n > 0$, $\hat{\mathcal{L}}^n = \underbrace{\hat{\mathcal{L}} \hat{\mathcal{L}} \cdots \hat{\mathcal{L}}}_{n \times}$, while $\hat{\mathcal{L}}^0 \equiv \hat{\mathcal{I}}$ is the identity operator which leaves phase functions unaltered, that is, $\hat{\mathcal{I}}f = f$ for any phase function f . That the formal expression (37) is indeed the solution of eqs.(35,36) follows from differentiating term by term,

$$\begin{aligned} \frac{\partial}{\partial t} \exp\{\hat{\mathcal{L}}(t - t_0)\} &= \sum_{n=1}^{\infty} \frac{(t - t_0)^{n-1}}{(n-1)!} \hat{\mathcal{L}}^n \\ &= \hat{\mathcal{L}} \sum_{n=0}^{\infty} \frac{(t - t_0)^n}{n!} \hat{\mathcal{L}}^n = \hat{\mathcal{L}} \exp\{\hat{\mathcal{L}}(t - t_0)\} . \end{aligned}$$

Substitution of eq.(37) into eq.(34) and integrating with respect to \mathbf{X}_0 yields,

$$\langle f(\mathbf{X}(t_0)) g(\mathbf{X}(t)) \rangle = \int d\mathbf{X} g(\mathbf{X}) \exp\{\hat{\mathcal{L}}(t - t_0)\} [f(\mathbf{X}) P(\mathbf{X}, t_0)] . \quad (39)$$

For systems in equilibrium, where P is time independent, this expression shows explicitly that the correlation function is a function of the time difference $t - t_0$ only. The advantage of this expression as compared to eq.(34) is that the conditional pdf does not appear explicitly. In principle this expression can be evaluated once the operator $\hat{\mathcal{L}}$ in the equation of motion (35) is specified. A drawback on the expression (39) is that each term in eq.(38) for the operator exponential must be evaluated to obtain the correlation function, and this is in general technically not feasible. Since the n^{th} term in the definition (38) of the operator exponential is $\sim (t - t_0)^n$, evaluation of the first few terms in the expansion leads to an expression that is valid for short times, where t is not much larger than t_0 . Such expansions are referred to as *short-time expansions*. An explicit example for such a short time expansion will be given at the end of the present section.

4.1 The Liouville equation

The most fundamental equation of motion is the *Liouville equation*, which is the equation of motion for the pdf of the position coordinates and the translational momenta of spherical atoms/molecules. Consider an arbitrary volume \mathcal{W} in the $6N$ -dimensional phase space. The total number \mathcal{N} of systems within the ensemble with a microstate inside this volume is proportional to,

$$\mathcal{N}(t) = \int_{\mathcal{W}} d\mathbf{X} P(\mathbf{X}, t) . \quad (40)$$

The rate-of-change of the number of systems with a microstate within \mathcal{W} is due to in- and out-flow through the surface $\partial\mathcal{W}$ of \mathcal{W} . Since only the component of the velocity $d\mathbf{X}/dt$ in phase space that is orthogonal to the surface normal $\hat{\mathbf{X}}$ leads to in- and out-flow, we have,

$$\frac{d\mathcal{N}(t)}{dt} = \int_{\mathcal{W}} d\mathbf{X} \frac{\partial P(\mathbf{X}, t)}{\partial t} = - \oint_{\partial\mathcal{W}} dS \hat{\mathbf{X}} \cdot \left[\frac{d\mathbf{X}}{dt} P(\mathbf{X}, t) \right] , \quad (41)$$

where dS is an infinitesimal surface area. The minus sign in front of the surface integral accounts for the fact that \mathcal{N} decreases in time when $d\mathbf{X}/dt$ is along $\hat{\mathbf{X}}$. Using Gauss's integral theorem to convert the surface integral into a volume integral leads to,

$$\int_{\mathcal{W}} d\mathbf{X} \left\{ \frac{\partial P(\mathbf{X}, t)}{\partial t} + \nabla_{\mathbf{X}} \cdot \left[\frac{d\mathbf{X}}{dt} P(\mathbf{X}, t) \right] \right\} = 0 , \quad (42)$$

Here, ∇_X is the gradient operator with respect to the $6N$ -dimensional phase space variable \mathbf{X} . Since the volume \mathcal{W} is an arbitrary volume, the integrand in eq.(42) is equal to zero. This can be seen as follows. Suppose that the integrand is positive at some point \mathbf{X}_0 . When the integrand is a continuous function of \mathbf{X} , there is by definition a neighbourhood of the point \mathbf{X}_0 where the integrand is strictly positive. Taking \mathcal{W} equal to this neighbourhood shows that eq.(42) is violated. Hence,

$$\begin{aligned} \frac{\partial P(\mathbf{X}, t)}{\partial t} &= -\nabla_X \cdot \left[\frac{d\mathbf{X}}{dt} P(\mathbf{X}, t) \right] \\ &= -\sum_{j=1}^N \left\{ \nabla_{r_j} \cdot \left[\frac{d\mathbf{r}_j}{dt} P(\mathbf{X}, t) \right] + \nabla_{p_j} \cdot \left[\frac{d\mathbf{p}_j}{dt} P(\mathbf{X}, t) \right] \right\}, \end{aligned} \quad (43)$$

where \mathbf{r}_j and \mathbf{p}_j are the position and momentum of particle j , and ∇_{r_j} and ∇_{p_j} are the respective gradient operators. Since,

$$\frac{d\mathbf{r}_j}{dt} = \frac{\mathbf{p}_j}{m} \quad \text{and} \quad \frac{d\mathbf{p}_j}{dt} = \mathbf{F}_j = -\nabla_{r_j} \Phi(\mathbf{r}_1, \dots, \mathbf{r}_N), \quad (44)$$

with m the mass of the particles, \mathbf{F}_j the force on particle j and Φ the total potential, which is due to interactions between the particles and possible due to an external field. Substitution of eq.(44) into eq.(43) thus leads to,

$$\frac{\partial P(\mathbf{X}, t)}{\partial t} = \hat{\mathcal{L}} P(\mathbf{X}, t), \quad (45)$$

where $\hat{\mathcal{L}}$ is the Liouville operator,

$$\hat{\mathcal{L}}(\dots) = \sum_{j=1}^N \left\{ -\frac{\mathbf{p}_j}{m} \cdot \nabla_{r_j}(\dots) + [\nabla_{r_j} \Phi] \cdot \nabla_{p_j}(\dots) \right\}. \quad (46)$$

Sometimes the imaginary unit $i = \sqrt{-1}$ is introduced as a prefactor in eqs.(45,46) to render the Liouville operator Hermitian with respect to the un-weighted inner product. The brackets $[\dots]$ in eq.(46) are used to indicate that the action of the gradient operator is limited to the potential Φ .

One implication of the Liouville equation is that the pdf remains unchanged in time when following a point along its trajectory in phase space, which is sometimes referred to as *Liouville's theorem*. This can be seen as follows. The temporal change DP/Dt of the pdf when one moves along with a point in phase space is equal to,

$$\begin{aligned} \frac{DP(\mathbf{X}, t)}{Dt} &\equiv \frac{dP(\mathbf{X}(t), t)}{dt} = \frac{d\mathbf{X}(t)}{dt} \cdot \nabla_X P(\mathbf{X}, t) + \frac{\partial P(\mathbf{X}, t)}{\partial t} \\ &= \sum_{j=1}^N \left\{ \frac{\mathbf{p}_j}{m} \cdot \nabla_{r_j} P(\mathbf{X}, t) - [\nabla_{r_j} \Phi] \cdot \nabla_{p_j} P(\mathbf{X}, t) \right\} + \frac{\partial P(\mathbf{X}, t)}{\partial t} \\ &= -\hat{\mathcal{L}} P(\mathbf{X}, t) + \frac{\partial P(\mathbf{X}, t)}{\partial t}, \end{aligned} \quad (47)$$

where eqs.(44,46) have been used. According to the Liouville equation (45) this is indeed equal to zero. Since trajectories in phase space can not cross each other, Liouville's theorem implies that the volume of an arbitrary volume element does not change in time during its motion through phase space.

4.2 The Smoluchowski equation

In very asymmetric mixtures of different kinds of particles, there can be a pronounced separation of time scales associated with the various phase space variables of the different species. In that case one can consider the fast species as being always in equilibrium with the instantaneous configuration of the slower species. The fast variables can then be eliminated from the equation of motion by averaging with respect to the equilibrium distribution of these variables in the instantaneous field imposed by the remaining slow species. Such a procedure is referred to as *coarse graining*. Important examples are solutions of large particles, such as colloids and polymers. For such *suspensions*, the dynamics of the large particles is much slower as compared to the relatively small solvent molecules. The solvent molecules are always in instantaneous equilibrium with the field imposed by the slowly moving large particles. In addition, the momentum coordinates of the big particles, hereafter referred to as *colloidal particles* or simply *colloids*, are also fast variables in comparison to their position coordinates. This can be seen as follows. Newton's equation of motion of a single colloidal sphere with mass M can be written as,

$$M \frac{d\mathbf{v}(t)}{dt} = -\zeta \mathbf{v} + \mathbf{f}(t) . \quad (48)$$

The first term on the right-hand side is the average interaction force of the colloidal sphere with the solvent molecules once it attains a certain velocity \mathbf{v} . Since the colloids are much larger than the solvent molecules, this interaction force can be described as a friction force, where ζ is the friction coefficient of the colloid with the solvent. In addition to this friction force there is a fluctuating force \mathbf{f} due to random collisions of the solvent molecules with the surface of the colloid. Equations of motion with a fluctuating contribution are commonly referred to as *Langevin equations*. Since the systematic force is included in the friction contribution, the ensemble average of the fluctuating force is 0. Hence, averaging of the Langevin equation (48) leads to,

$$M \frac{d \langle \mathbf{v}(t) \rangle}{dt} = -\zeta \langle \mathbf{v} \rangle , \quad (49)$$

the solution of which is,

$$\mathbf{v}(t) = \mathbf{v}_0 \exp\{-t/\tau_B\} \quad \text{with} \quad \tau_B = M/\zeta , \quad (50)$$

where \mathbf{v}_0 is the initial velocity. Using that $\zeta = 6\pi\eta_0 a$, with η_0 the shear viscosity of the solvent and a the radius of the spherical colloidal particle (typically of the order of 10 – 1000 nm), the momentum relaxation time τ_B is found to be of the order of 1 ns. If the interest is in time-dependent phenomena in colloidal dispersion on time scales much larger than typically 1 nm, one can regard the momenta as fast variables. The time scale that is larger than τ_B , but still small enough to probe the position coordinates of the colloidal particles is referred to as the *diffusive time scale* τ_D . The minimum resolution in length scale λ_D after coarse graining to the diffusive time scale is equal to the distance that a colloid traverses during the time τ_D . Integration of the velocity in eq.(50) over a time much larger than τ_B gives,

$$\lambda_D = v_0 \int_0^{\tau_D \gg \tau_B} dt' \exp\{-t'/\tau_B\} = v_0 \tau_B . \quad (51)$$

A typical value for the initial velocity can be found from the equipartition theorem as,

$$v_0 \approx \sqrt{3k_B T/M} . \quad (52)$$

Substitution of typical values leads to $\lambda_D \approx 10^{-3} a$. The length resolution after coarse graining to times much larger than τ_B in eq.(50) is thus much smaller than the radius a of the colloid. One should thus be able to coarse grain the Liouville equation for a mixture of solvent molecules and colloidal particles to obtain an equation of motion for the pdf of just the position coordinates of the colloidal particles. This equation of motion is commonly referred to as *the Smoluchowski equation*. Integration of the Liouville equation for such a mixture with respect to the solvent phase space coordinates and the momenta of the colloids [1, 2] is technically quite involved and will not be discussed here. The Smoluchowski equation can be obtained alternatively as follows. First, repeating the arguments leading to the first expression in eq.(43), where now $\mathbf{X} = (\mathbf{r}_1, \dots, \mathbf{r}_N) \equiv \mathbf{R}$ specifies the configuration of the colloids, gives,

$$\frac{\partial P(\mathbf{R}, t)}{\partial t} = -\nabla_{\mathbf{R}} \cdot \left[\frac{d\mathbf{R}}{dt} P(\mathbf{R}, t) \right] = -\sum_{j=1}^N \nabla_{\mathbf{r}_j} \cdot [\mathbf{v}_j^{cg} P(\mathbf{R}, t)] , \quad (53)$$

where $\nabla_{\mathbf{R}}$ is the $3N$ -dimensional gradient operator with respect to the position coordinates of the colloidal particles. Here, the superscript "cg" on the velocities indicates that these velocities are coarse grained to the diffusive time scale, that is, velocities averaged over a time interval equal to the diffusive time scale τ_D . Secondly, an explicit expression for the velocities $d\mathbf{R}/dt = (\mathbf{v}_1^{cg}, \dots, \mathbf{v}_N^{cg})$ can be obtained, noting that on the diffusive time scale the momenta are long relaxed. Relaxation of momenta implies that inertial forces are very small in comparison to all other forces acting on a colloidal particle. These other forces are :

(i) The force due to *direct interactions* between colloids, which is equal to $-\nabla_{\mathbf{r}_j} \Phi$ with Φ the total potential energy of an assembly of N colloids averaged over to the phase space coordinates of the solvent molecules with respect to the equilibrium pdf of the solvent degrees of freedom in the instantaneous field imposed by the colloids.

(ii) The force due to friction with the solvent. When a colloidal sphere moves, it induces a fluid flow which affects other colloids in their motion (see Fig.4.3). These interaction forces are referred to as *hydrodynamic interactions*. Since the hydrodynamic equations that describe the induced fluid flow (as will be discussed in the next section) are linear, the hydrodynamic force \mathbf{F}_j^h on sphere j is linearly related to the velocities of all other spheres,

$$\mathbf{F}_j^h = -\sum_{i=1}^N \Upsilon_{ij} \cdot \mathbf{v}_i^{cg} , \quad (54)$$

where the friction tensors Υ_{ij} are referred to as *hydrodynamic friction tensors*, which are complicated functions of all colloid positions. With the neglect of hydrodynamic interactions these tensors reduce to (with δ_{ij} the Kronecker delta and $\hat{\mathbf{I}}$ the identity tensor),

$$\Upsilon_{ij} = \zeta \hat{\mathbf{I}} \delta_{ij} \quad \text{no hydrodynamic interactions} , \quad (55)$$

that is, $\mathbf{F}_j = -\zeta \mathbf{v}_j^{cg}$, where ζ is the friction coefficient of a sphere with an otherwise quiescent fluid (which was already introduced in connection with the Langevin equation (48).

(iii) Due to coarse graining, a third force is of importance which is of an entropic nature and is referred to as *the Brownian force* \mathbf{F}_j^{Br} . We will specify this force in terms of positions coordinates later.

These forces add up to 0 on the diffusive time scale, as discussed above,

$$-\nabla_{\mathbf{r}_j} \Phi - \sum_{i=1}^N \Upsilon_{ij} \cdot \mathbf{v}_i^{cg} + \mathbf{F}_j^{Br} = \mathbf{0} , \quad (56)$$

or equivalently in $3N$ -vector notation,

$$-\nabla_R \Phi - \Upsilon \cdot \mathbf{v}^{cg} + \mathbf{F}^{Br} = \mathbf{0} , \quad (57)$$

where,

$$\Upsilon = \begin{pmatrix} \Upsilon_{11} & \Upsilon_{12} & \cdots & \Upsilon_{1N} \\ \Upsilon_{21} & \Upsilon_{22} & \cdots & \Upsilon_{2N} \\ \vdots & \vdots & \cdots & \vdots \\ \Upsilon_{N1} & \Upsilon_{N2} & \cdots & \Upsilon_{NN} \end{pmatrix} , \quad (58)$$

is the $3N \times 3N$ -dimensional hydrodynamic friction tensor. Furthermore, $\mathbf{v}^{cg} = (\mathbf{v}_1^{cg}, \dots, \mathbf{v}_N^{cg})$ and $\mathbf{F}^{Br} = (\mathbf{F}_1^h, \dots, \mathbf{F}_N^h)$. Inverting the *force balance equation* (57) leads to the following expression for the velocities (with $\beta = 1/k_B T$),

$$\mathbf{v}^{cg} = \mathbf{D} \cdot \{ -\beta \nabla_R \Phi + \beta \mathbf{F}^{Br} \} , \quad (59)$$

where the *microscopic diffusion tensor* is defined as,

$$\mathbf{D} \equiv k_B T \Upsilon^{-1} , \quad (60)$$

with Υ^{-1} the inverse of the tensor Υ . This tensor can be written analogously to eq.(58) in terms of 3×3 -dimensional tensors \mathbf{D}_{ij} , where the indices are colloidal particles numbers, so that eq.(59) can be written as,

$$\mathbf{v}_i^{cg} = \sum_{j=1}^N \mathbf{D}_{ij} \cdot \{ -\beta \nabla_{r_j} \Phi + \beta \mathbf{F}_j^{Br} \} , \quad (61)$$

Substitution into eq.(53) gives,

$$\frac{\partial P(\mathbf{R}, t)}{\partial t} = \sum_{i,j=1}^N \nabla_{r_i} \cdot \mathbf{D}_{ij}(\mathbf{R}) \cdot \{ \beta P(\mathbf{R}, t) \nabla_{r_j} \Phi(\mathbf{R}) - \beta P(\mathbf{R}, t) \mathbf{F}_j^{Br} \} . \quad (62)$$

The Brownian force can now be specified, noting that $P \sim \exp\{-\beta\Phi\}$ as $t \rightarrow \infty$. According to the above equation of motion, this is the case when,

$$\mathbf{F}_j^{Br} = -k_B T \nabla_{r_j} \ln\{ P(\mathbf{R}, t) \} . \quad (63)$$

Substitution into eq.(62) finally leads to *the Smoluchowski equation*,

$$\frac{\partial P(\mathbf{R}, t)}{\partial t} = \hat{\mathcal{O}} P(\mathbf{R}, t) , \quad (64)$$

where,

$$\hat{\mathcal{O}}(\cdots) = \sum_{i,j=1}^N \nabla_{r_i} \cdot \mathbf{D}_{ij}(\mathbf{R}) \cdot \{ \beta (\cdots) \nabla_{r_j} \Phi(\mathbf{R}) + \nabla_{r_j}(\cdots) \} , \quad (65)$$

is *the Smoluchowski operator*. The Smoluchowski operator is denoted here as $\hat{\mathcal{O}}$ to distinguish it from the Liouville operator. This is the fundamental equation of motion for colloidal and polymeric systems. The equation of motion for the pdf of the positions of the beads for a single polymer chain is obtained from this equation by introducing an appropriate potential Φ that connects the beads to each other. The resulting equation of motion is referred to as *the Zimm or Rouse equation*, depending on whether hydrodynamic interactions are accounted for.

4.3 The dynamic structure factor for non-interacting colloids

As a simple example, let us evaluate the dynamic structure factor for non-interacting colloids, which is valid for very dilute suspensions. Without hydrodynamic interactions, according to eqs.(55,60), the microscopic diffusion tensors reduce to,

$$\mathbf{D}_{ij} = D_0 \hat{\mathbf{I}} \delta_{ij} \quad (66)$$

where,

$$D_0 = \frac{k_B T}{\zeta}, \quad (67)$$

which is the *Einstein diffusion coefficient*. The Smoluchowski equation (64,65) thus reduces to,

$$\frac{\partial P(\mathbf{r}, t)}{\partial t} = D_0 \nabla^2 P(\mathbf{r}, t). \quad (68)$$

where \mathbf{r} is the position coordinate of a single colloidal sphere and ∇ is the gradient operator with respect to \mathbf{r} . This equation of motion is known as *Fick's equation*. It should be noted, however, that this equation is also valid for high concentrations of colloids, provided that gradients in concentration are small on the length scale set by the range of the direct interactions between the colloids. The diffusion coefficient is then different from the Einstein diffusion coefficient D_0 . Fick's law for higher concentrations can actually be derived from the Smoluchowski equation (64,65) by means of a gradient expansion. The dynamic structure factor is defined as (with $i = \sqrt{-1}$),

$$S(k, t) \equiv \langle \exp\{i\mathbf{k} \cdot (\mathbf{r}(t) - \mathbf{r}(t=0))\} \rangle, \quad (69)$$

where the wave vector \mathbf{k} measures the length scale on which the motion of the colloidal sphere is probed. This structure factor is typically measured by means of scattering experiments (light, X-ray and neutron scattering), where the wave vector is connected to the scattering angle, that is, the angle between the incident beam and the detection direction. The dynamic structure factor is a time-correlation function of the form (39), with $t_0 = 0$, $\mathbf{X} \equiv \mathbf{r}$, $f = \exp\{-i\mathbf{k} \cdot \mathbf{r}\}$ and $g = \exp\{i\mathbf{k} \cdot \mathbf{r}\}$. Hence,

$$S(k, t) = \frac{1}{V} \int_V d\mathbf{r} \exp\{i\mathbf{k} \cdot \mathbf{r}\} \exp\{t D_0 \nabla^2\} \exp\{-i\mathbf{k} \cdot \mathbf{r}\}, \quad (70)$$

where it is used that the pdf $P(\mathbf{r}, t) = 1/V$, with V the volume of the system under consideration. It is easily verified that $\nabla^2 \exp\{-i\mathbf{k} \cdot \mathbf{r}\} = -k^2 \exp\{-i\mathbf{k} \cdot \mathbf{r}\}$, and hence, from eq.(38),

$$\exp\{t D_0 \nabla^2\} \exp\{-i\mathbf{k} \cdot \mathbf{r}\} = \exp\{-D_0 k^2 t\} \exp\{-i\mathbf{k} \cdot \mathbf{r}\}. \quad (71)$$

Substitution into eq.(70) thus gives,

$$S(k, t) = \exp\{-D_0 k^2 t\}. \quad (72)$$

The explicit evaluation of the full time dependence is possible due to the fact that $f = \exp\{-i\mathbf{k} \cdot \mathbf{r}\}$ is an eigenfunction of the time-evolution operator $\hat{\mathcal{L}}$. In more general cases this is of course not true, and approximations must be made to evaluate correlation functions. For example, the calculation of $S(k, t)$ for interacting systems, where the Smoluchowski operator in eq.(65) is the relevant time-evolution operator, can not be done exactly.

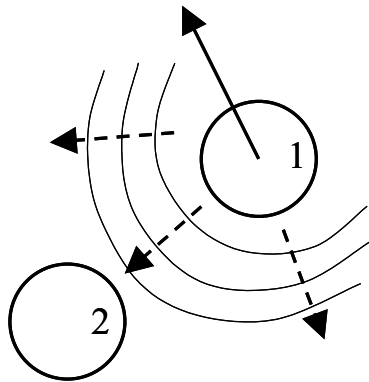


Fig. 3: *Hydrodynamic interactions : when sphere 1 moves it creates a fluid flow that affects sphere 2 in its motion.*

5 Hydrodynamics

In this section we shall consider hydrodynamic interactions between spherical colloids. First of all, the equations which govern fluid flow, the continuity and Navier-Stokes equations, are derived. Inertial terms in the Navier-Stokes equation are then shown to be small for colloids, leading in the so-called creeping flow equations. The Green's functions of the creeping flow equations are calculated, and from that, the hydrodynamic diffusion tensor \mathbf{D}_{ij} is determined to leading order in an expansion with respect to a/R , with a the radius of the spheres and R the distance between the spheres.

The mechanical state of the solvent is characterized by the local velocity $\mathbf{v}(\mathbf{r}, t)$ at position \mathbf{r} at time t , the pressure $p(\mathbf{r}, t)$ and the mass density $\rho(\mathbf{r}, t)$. All these fields are averages over small volume elements that are located at the various positions \mathbf{r} . These volume elements must be so small that the state of the fluid hardly changes within the volume elements. At the same time, the volume elements should contain many fluid molecules, to be able to properly define such averages. In particular we wish to define the thermodynamic state of volume elements, which is possible when they contain a large amount of solvent molecules, and when they are in internal equilibrium, that is, when there is *local equilibrium*. In this way the temperature field $T(\mathbf{r}, t)$ may be defined. The temperature dependence of, for example, the mass density is then described by thermodynamic relations. These thermodynamic relations are an important ingredient in a general theory of hydrodynamics. For our purposes, however, the temperature and mass density may be considered constant. Temperature variations due to viscous dissipation in the solvent are assumed to be negligible. At constant temperature, the only mechanism to change the mass density of the solvent is to vary the pressure. For fluids, however, exceedingly large pressures are needed to change the density significantly, that is, fluids are quite *incompressible*. Brownian motion is not so vigorous to induce such extreme pressure differences, so that the density will also be assumed constant. The assumption of constant temperature and density is also a matter of time scales. Relaxation times for local temperature and pressure differences in the solvent are much faster than typical time scales relevant for Brownian motion.

Assuming constant temperature and mass density leaves just two variables which describe the state of the fluid : the fluid flow velocity $\mathbf{v}(\mathbf{r}, t)$ and the pressure $p(\mathbf{r}, t)$. Thermodynamic relations need not be considered in this case, simplifying the phenomenological analysis considerably.

5.1 The continuity equation

The rate of change of the mass of fluid contained in some arbitrary volume \mathcal{W} is equal to the mass of fluid flowing through its boundary $\partial\mathcal{W}$. The local velocity at surface elements on $\partial\mathcal{W}$ can be written as the sum of its component parallel and perpendicular to the surface. The parallel component does not contribute to in and out flux of mass through the boundary $\partial\mathcal{W}$ (see also the discussion that lead to eq.(41)). Only the component $\mathbf{v} \cdot \hat{\mathbf{n}}$ of the flow perpendicular to the surface gives rise to in and out flux of mass, where $\hat{\mathbf{n}}$ is the unit normal of the corresponding surface element. Hence,

$$\frac{d}{dt} \int_{\mathcal{W}} d\mathbf{r} \rho(\mathbf{r}, t) = - \oint_{\partial\mathcal{W}} d\mathbf{S} \cdot \{\rho(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t)\},$$

where $d\mathbf{S} = \hat{\mathbf{n}} dS$, with dS an infinitesimal surface area. The minus sign on the right hand-side is added, because the mass in \mathcal{W} decreases when \mathbf{v} is along the outward normal. Using Gauss's integral theorem, this leads to,

$$\int_{\mathcal{W}} d\mathbf{r} \left[\frac{\partial}{\partial t} \rho(\mathbf{r}, t) + \nabla \cdot \{\rho(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t)\} \right] = 0,$$

where ∇ is the gradient operator with respect to \mathbf{r} . Since the volume \mathcal{W} is an arbitrary volume, the integrand must be equal to zero, so that,

$$\frac{\partial}{\partial t} \rho(\mathbf{r}, t) + \nabla \cdot \{\rho(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t)\} = 0. \quad (73)$$

This equation expresses conservation of mass, and is referred to as the *continuity equation*.

For a fluid with a constant mass density, the continuity equation reduces to,

$$\nabla \cdot \mathbf{v}(\mathbf{r}, t) = 0. \quad (74)$$

Fluids with an essentially constant mass density are referred to as *incompressible fluids*, and eq.(74) is therefore sometimes referred to as the *incompressibility equation*. Being nothing more than the condition to ensure conservation of mass, this single equation is not sufficient to calculate the fluid flow velocity. It must be supplemented by Newton's equation of motion to obtain a closed set of equations.

5.2 The Navier-Stokes equation

The Navier-Stokes equation is Newton's equation of motion for a small amount of mass contained in a volume element within the fluid. Consider such a mathematically infinitesimally small volume element, the volume of which is denoted as $\delta\mathbf{r}$. The position \mathbf{r} of that volume element as a function of time is set by Newton's equation of motion. The momentum that is carried by the mass element is equal to $\rho(\mathbf{r}, t) (\delta\mathbf{r}) \mathbf{v}(\mathbf{r}, t)$, so that Newton's equation of motion reads,

$$\rho(\mathbf{r}, t) \delta\mathbf{r} \frac{d\mathbf{v}(\mathbf{r}, t)}{dt} = \mathbf{f},$$

where \mathbf{f} is the total force that is exerted on the mass element. Since in Newton's equations of motion \mathbf{r} is the time dependent position coordinate of the volume element, and $d\mathbf{r}/dt = \mathbf{v}$ is the velocity of the volume element, the above equation can be written as,

$$\rho(\mathbf{r}, t) \delta\mathbf{r} \left[\frac{\partial \mathbf{v}(\mathbf{r}, t)}{\partial t} + \mathbf{v}(\mathbf{r}, t) \cdot \nabla \mathbf{v}(\mathbf{r}, t) \right] = \mathbf{f}.$$

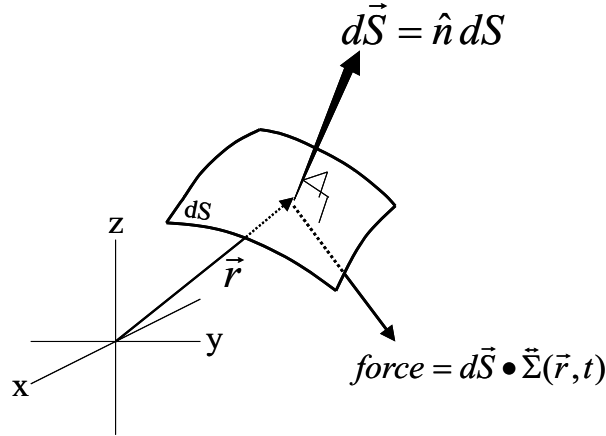


Fig. 4: Definition of the stress tensor Σ .

Here, $\nabla \mathbf{v}$ is a dyadic product, that is, it is a tensor of which the ij^{th} component is equal to $\nabla_i v_j$, with ∇_i the differentiation with respect to r_i , the i^{th} component of \mathbf{r} .

The total force \mathbf{f} on the volume element consists of two parts. First of all, there may be external fields which exert forces on the fluid. These forces are denoted by $(\delta \mathbf{r}) \mathbf{f}^{ext}(\mathbf{r})$, that is, \mathbf{f}^{ext} is the external force on the fluid per unit volume. The second part arises from interactions of the volume element with the surrounding fluid.

The forces due to interactions with the surrounding fluid are formally expressed in terms of the *stress tensor* $\Sigma(\mathbf{r}, t)$, which is defined as follows. Consider an infinitesimally small surface area in the fluid, with surface area dS and a normal unit vector $\hat{\mathbf{n}}$. The force per unit area exerted by the fluid located at the side of the surface area to which the unit normal is directed, on the fluid on the opposite side of the surface area, is by definition equal to $d\mathbf{S} \cdot \Sigma$, with $d\mathbf{S} = \hat{\mathbf{n}} dS$ (see fig.4).

Hence, by definition, the force of surrounding fluid on the volume element $\delta \mathbf{r}$ is equal to,

$$\oint_{\partial \delta \mathbf{r}} d\mathbf{S}' \cdot \Sigma(\mathbf{r}', t) = \int_{\delta \mathbf{r}} d\mathbf{r}' \nabla' \cdot \Sigma(\mathbf{r}', t) = \delta \mathbf{r} \nabla \cdot \Sigma(\mathbf{r}, t),$$

where $\partial \delta \mathbf{r}$ is the boundary of the volume element. We used Gauss's integral theorem to rewrite the surface integral as a volume integral. The last equation is valid due to the infinitesimal size $\delta \mathbf{r}$ of the volume element at position \mathbf{r} . The force \mathbf{f}^h on the volume element due to interaction with the surrounding fluid is thus given by,

$$\mathbf{f}^h(\mathbf{r}, t) = (\delta \mathbf{r}) \nabla \cdot \Sigma(\mathbf{r}, t). \quad (75)$$

There are two contributions to the stress tensor : a contribution resulting from gradients in the fluid flow velocity, and a contribution due to pressure gradients.

Consider first the forces due to pressure gradients. Let us take the volume element $\delta \mathbf{r}$ cubic, with sides of length δl . The pressure p is a force per unit area, so that the force on the volume element in the x -direction is equal to,

$$(\delta l)^2 \left(p(x - \frac{1}{2} \delta l, y, z, t) - p(x + \frac{1}{2} \delta l, y, z, t) \right) = -(\delta l)^3 \frac{\partial}{\partial x} p(x, y, z, t),$$

where $(\delta l)^2$ is the area of the faces of the cube. The force on the volume element is thus $-(\delta \mathbf{r}) \nabla p(\mathbf{r}, t)$. We therefore arrive at, $\nabla \cdot \Sigma = -\nabla p$. The contribution of pressure gradients to

the stress tensor is thus easily seen to be equal to,

$$\Sigma(\mathbf{r}, t) = -p(\mathbf{r}, t) \hat{\mathbf{I}},$$

with $\hat{\mathbf{I}}$ the 3×3 -dimensional unit tensor. This contribution to the stress tensor is referred to as *the isotropic part of the stress tensor*, since it is proportional to the unit tensor and therefore does not have a preferred spatial direction.

Next, consider the forces on the volume element due to gradients in the fluid flow velocity. When the fluid flow velocity is uniform, that is, when there are no gradients in the fluid flow velocity, the only forces on the volume element are due to pressure and possibly external forces. There are friction forces in addition, only in case the volume element attains a velocity which differs from that of the surrounding fluid. The contribution to the stress tensor due to friction forces is therefore a function of spatial derivatives of the flow velocity, not of the velocity itself. This contribution to the stress tensor can be formally expanded in a power series with respect to the gradients in the fluid flow velocity. For not too large gradients (such that the fluid velocity is approximately constant over distances of many times the molecular dimension) the leading term in such an expansion suffices to describe friction forces. The contribution of gradients in the fluid flow velocity to the stress tensor is thus a linear combination of the derivatives $\nabla_i v_j(\mathbf{r}, t)$, where ∇_i is the derivative with respect to the i^{th} component of \mathbf{r} , and $v_j(\mathbf{r}, t)$ is the j^{th} component of $\mathbf{v}(\mathbf{r}, t)$.

There are also no friction forces when the fluid is in uniform rotation, in which case the flow velocity is equal to $\mathbf{v} = \boldsymbol{\Omega} \times \mathbf{r}$, with $\boldsymbol{\Omega}$ the angular velocity. Such a fluid flow corresponds to rotation of the vessel containing the fluid, relative to the observer. Linear combinations of the form,

$$\nabla_i v_j(\mathbf{r}, t) + \nabla_j v_i(\mathbf{r}, t), \quad (76)$$

are easily verified to vanish in case $\mathbf{v} = \boldsymbol{\Omega} \times \mathbf{r}$. The stress tensor is thus proportional to such linear combinations of gradients in the fluid velocity field.

For incompressible isotropic fluids, with no preferred spatial direction, the most general expression for the components Σ_{ij} of the stress tensor as a result of friction is therefore,

$$\Sigma_{D,ij} = \eta_0 \{ \nabla_i v_j + \nabla_j v_i \}, \quad (77)$$

where the subscript "D" stands for *the deviatoric part of the stress tensor*. The terms $\sim \nabla \cdot \mathbf{v}(\mathbf{r}, t)$ on the right hand-side arising from the linear combinations (76) with $i = j$ are zero for incompressible fluids (see eq.74)). For incompressible fluids, the Navier-Stokes equation thus reads,

$$\rho \frac{\partial \mathbf{v}(\mathbf{r}, t)}{\partial t} + \rho \mathbf{v}(\mathbf{r}, t) \cdot \nabla \mathbf{v}(\mathbf{r}, t) = \nabla \cdot \Sigma(\mathbf{r}, t) + \mathbf{f}^{ext}(\mathbf{r}, t) = \eta_0 \nabla^2 \mathbf{v}(\mathbf{r}, t) - \nabla p(\mathbf{r}, t) + \mathbf{f}^{ext}(\mathbf{r}). \quad (78)$$

Together with the continuity equation (74) for incompressible fluids, this equation fully determines the fluid flow and pressure once the external force and boundary conditions are specified.

5.3 The creeping flow equations

The different terms in the Navier-Stokes equation (78) can be very different in magnitude, depending on the problem at hand. In the present case we are interested in fluid flow around

small sized objects (the colloidal spheres). Let us estimate the magnitude of the various terms in the Navier-Stokes equation for this case. A typical value for the fluid flow velocity is the velocity v of the colloidal objects. The fluid flow velocity decreases from a value v , close to a colloidal particle, to a much smaller value, over a distance of the order of the colloid-radius a . Hence, typically, $|\nabla^2 \mathbf{v}| \approx v/a^2$. Similarly, $|\mathbf{v} \cdot \nabla \mathbf{v}| \approx v^2/a$. The rate of change of \mathbf{v} is v divided by the time it takes the colloidal particle to lose its velocity due to friction with the fluid. This time interval is equal to a few times M/ζ , as was discussed in section 4 in connection with the derivation of the Smoluchowski equation. Introducing the rescaled variables,

$$\mathbf{v}' = \mathbf{v}/v, \quad \mathbf{r}' = \mathbf{r}/a \quad \text{and} \quad t' = t/(M/\zeta),$$

transforms the Navier-Stokes equation (78) to,

$$\rho \frac{a^2 \zeta}{M \eta_0} \frac{\partial \mathbf{v}'}{\partial t'} + Re \mathbf{v}' \cdot \nabla' \mathbf{v}' = \nabla'^2 \mathbf{v}' - \nabla' p' + \mathbf{f}'^{ext}. \quad (79)$$

where ∇' is the gradient operator with respect to \mathbf{r}' . Furthermore, the dimensionless pressure and external force are defined here as,

$$p' = \frac{a}{\eta_0 v} p \quad \text{and} \quad \mathbf{f}'^{ext} = \frac{a^2}{\eta_0 v} \mathbf{f}^{ext},$$

The dimensionless number Re is the so-called *Reynolds number*, which is equal to,

$$Re = \frac{\rho a v}{\eta_0}. \quad (80)$$

Using typical values for the various quantities shows that $Re \approx 10^{-3} - 10^{-2}$. By construction we have,

$$|\mathbf{v}' \cdot \nabla' \mathbf{v}'| \approx |\nabla'^2 \mathbf{v}'| \approx 1.$$

Hence, for very small values of the Reynolds number, the term proportional to $\mathbf{v} \cdot \nabla \mathbf{v}$ in the left hand-side in eq.(79) may be neglected. Furthermore, for spherical particles we have $\zeta = 6\pi\eta_0 a$ so that $\rho a^2 \zeta / M \eta_0 = 9\rho/2\rho_p \approx 9/2$, with ρ_p the mass density of the colloidal particle. The prefactor of $\partial \mathbf{v}' / \partial t'$ is thus approximately equal to $9/2$. The time derivative should generally be kept as it stands, also for small Reynolds numbers. Now suppose, however, that one is interested in a description on the diffusive time scale $\tau_D \gg M/\zeta$ (the significance of the diffusive time scale has been discussed in section 4). For such times, the time derivative $\partial \mathbf{v}' / \partial t'$ is long zero, since \mathbf{v} goes to zero as a result of friction during the time interval M/ζ . One may then neglect the contribution to the time derivative which is due to relaxation of momentum of the colloidal sphere as a result of friction with the solvent. The remaining time dependence of \mathbf{v} on the diffusive time scale is due to the possible time dependence of the external force and to interactions with other colloidal particles, which vary significantly only over time intervals larger than the diffusive time scale. The value of the corresponding derivative $\partial \mathbf{v} / \partial t$ can now be estimated as above : the only difference is that the time should not be rescaled with respect to the time M/ζ , but with respect to the diffusive time scale τ_D . We now have, $t' = t/\tau_D$, $\mathbf{v}' = \mathbf{v}/v$, and $|\partial \mathbf{v}' / \partial t'| \approx 1$. The transformed Navier-Stokes equation in this case reads,

$$\frac{9}{2} \frac{\rho}{\rho_p} \frac{M/\zeta}{\tau_D} \frac{\partial \mathbf{v}'}{\partial t'} + Re \mathbf{v}' \cdot \nabla' \mathbf{v}' = \nabla'^2 \mathbf{v}' - \nabla' p' + \mathbf{f}'^{ext},$$

where all derivatives of the fluid flow velocity \mathbf{v}' are of the order 1. Since $\tau_D \gg M/\zeta$, the time derivative due to changes of the fluid flow velocity as a result of the time varying external force and interactions with other colloidal particles may now be neglected.

For small Reynolds numbers and on the diffusive time scale, the Navier-Stokes equation (81), written in terms of the original unprimed quantities, therefore simplifies to,

$$\nabla p(\mathbf{r}, t) - \eta_0 \nabla^2 \mathbf{v}(\mathbf{r}, t) = \mathbf{f}^{ext}(\mathbf{r}) . \quad (81)$$

This equation, together with the incompressibility equation (74), are the *creeping flow equations*. "Creeping" refers to the fact that the Reynolds number is small, which is the case when the typical fluid flow velocity v is small.

5.4 The Oseen tensor

An external force acting only in a single point \mathbf{r}' on the fluid is mathematically described by a delta distribution,

$$\mathbf{f}^{ext}(\mathbf{r}) = \mathbf{f}_0 \delta(\mathbf{r} - \mathbf{r}') . \quad (82)$$

The prefactor \mathbf{f}_0 is the total force $\int d\mathbf{r}' \mathbf{f}^{ext}(\mathbf{r}')$ acting on the fluid. Since the creeping flow equations are linear, the fluid flow velocity at some point \mathbf{r} in the fluid, due to the point force in \mathbf{r}' , is directly proportional to that point force. Hence,

$$\mathbf{v}(\mathbf{r}) = \mathbf{T}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{f}_0 .$$

The tensor \mathbf{T} is commonly referred to as the *Oseen tensor*, named after the scientist who first derived an explicit expression for this tensor [3]. The Oseen tensor connects the point force at a point \mathbf{r}' to the resulting fluid flow velocity at a point \mathbf{r} . Note that \mathbf{T} is only a function of the difference coordinate $\mathbf{r} - \mathbf{r}'$ due to translational invariance for a homogeneous fluid. Similarly, the pressure at a point \mathbf{r} is linearly related to the point force,

$$p(\mathbf{r}) = \mathbf{g}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{f}_0 . \quad (83)$$

The vector \mathbf{g} is referred to here as the *pressure vector*.

Consider an external force which is continuously distributed over the entire fluid. Due to the linearity of the creeping flow equations, the fluid flow velocity at some point \mathbf{r} is simply the superposition of the fluid flow velocities resulting from the forces acting in each point on the fluid. Hence,

$$\mathbf{v}(\mathbf{r}) = \int d\mathbf{r}' \mathbf{T}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{f}^{ext}(\mathbf{r}') . \quad (84)$$

The same holds for the pressure,

$$p(\mathbf{r}) = \int d\mathbf{r}' \mathbf{g}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{f}^{ext}(\mathbf{r}') . \quad (85)$$

In mathematical language, the Oseen tensor and the pressure vector are the Green's functions of the creeping flow equations for the fluid flow velocity and pressure, respectively. Once these Green's functions are known and the external force is specified, the resulting fluid velocity and pressure can be calculated through the evaluation of the above integrals. The calculation of the

Green's functions is thus equivalent to solving the creeping flow equations, provided that the external forces are known.

Let us calculate the Oseen tensor and pressure vector. To this end, substitute eqs.(84,85) into the creeping flow equations (74,81). This leads to,

$$\begin{aligned} \int d\mathbf{r}' [\nabla \cdot \mathbf{T}(\mathbf{r} - \mathbf{r}')] \cdot \mathbf{f}^{ext}(\mathbf{r}') &= 0, \\ \int d\mathbf{r}' [\nabla \mathbf{g}(\mathbf{r} - \mathbf{r}') - \eta_0 \nabla^2 \mathbf{T}(\mathbf{r} - \mathbf{r}') - \hat{\mathbf{I}} \delta(\mathbf{r} - \mathbf{r}')] \cdot \mathbf{f}^{ext}(\mathbf{r}') &= \mathbf{0}, \end{aligned}$$

where, as before, $\hat{\mathbf{I}}$ is the 3×3 -dimensional unit tensor. Since the external force is arbitrary, the expressions in the square brackets must be equal to zero, so that the Green's functions satisfy the following differential equations,

$$\begin{aligned} \nabla \cdot \mathbf{T}(\mathbf{r}) &= \mathbf{0}, \\ \nabla \mathbf{g}(\mathbf{r}) - \eta_0 \nabla^2 \mathbf{T}(\mathbf{r}) &= \hat{\mathbf{I}} \delta(\mathbf{r}). \end{aligned} \quad (86)$$

A single equation for the pressure vector is obtained by taking the divergence of the second equation, with the use of the first equation,

$$\nabla^2 \mathbf{g}(\mathbf{r}) = \nabla \cdot \hat{\mathbf{I}} \delta(\mathbf{r}) = \nabla \delta(\mathbf{r}).$$

Using that $\nabla^2(1/r) = -4\pi \delta(\mathbf{r})$, it follows that $\mathbf{g}(\mathbf{r}) = -(1/4\pi) \nabla(1/r) + \mathbf{G}(\mathbf{r})$, where \mathbf{G} is a vector for which $\nabla^2 \mathbf{G} = \mathbf{0}$, while $\mathbf{G} \rightarrow \mathbf{0}$ as $r \rightarrow \infty$. It can be shown that such a vector is $\mathbf{0}$. Hence,

$$\mathbf{g}(\mathbf{r}) = -\frac{1}{4\pi} \nabla \frac{1}{r} = \frac{1}{4\pi} \frac{\mathbf{r}}{r^3}. \quad (87)$$

The differential equation to be satisfied by the Green's function for the fluid flow velocity (the Oseen tensor), is found by substitution of eq.(87) into eq.(86),

$$\nabla^2 \left[\frac{1}{4\pi} \frac{1}{r} \hat{\mathbf{I}} - \eta_0 \mathbf{T}(\mathbf{r}) \right] = \frac{1}{4\pi} \left[3 \frac{\mathbf{r} \mathbf{r}}{r^5} - \frac{1}{r^3} \hat{\mathbf{I}} \right].$$

An obvious choice for the term between the square brackets on the left hand-side of the above expression is of the form,

$$\frac{1}{4\pi} \frac{1}{r} \hat{\mathbf{I}} - \eta_0 \mathbf{T}(\mathbf{r}) = \alpha_0 \frac{1}{r^n} \hat{\mathbf{I}} + \alpha_1 \frac{1}{r^m} \frac{\mathbf{r} \mathbf{r}}{r^2},$$

with $\alpha_{0,1}$, n and m constants. These constants can indeed be chosen such that this Ansatz is the solution of the differential equation (with the boundary condition that $\mathbf{T}(\mathbf{r}) \rightarrow \mathbf{0}$ as $r \rightarrow \infty$). A somewhat lengthy, but straightforward calculation yields,

$$\mathbf{T}(\mathbf{r}) = \frac{1}{8\pi\eta_0} \frac{1}{r} \left[\hat{\mathbf{I}} + \frac{\mathbf{r} \mathbf{r}}{r^2} \right]. \quad (88)$$

This concludes the determination of the Green's functions for the creeping flow equations.

5.5 Hydrodynamic interactions

The starting point for the calculation of the microscopic diffusion matrices that appear in the Smoluchowski operator (65) is the Green's function representation (84) of the creeping flow equations. In the present situation, the external force \mathbf{f}^{ext} is due to forces that surface elements of the colloidal spheres exert on the fluid. For the multi-sphere problem considered here, the integral in eq.(84) is now a sum of integrals ranging over the surfaces ∂V_j , $j = 1, \dots, N$ of the N spherical Brownian particles,

$$\mathbf{v}(\mathbf{r}) = \sum_{j=1}^N \oint_{\partial V_j} dS' \mathbf{T}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{f}_j(\mathbf{r}'), \quad (89)$$

$$p(\mathbf{r}) = \sum_{j=1}^N \oint_{\partial V_j} dS' \mathbf{g}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{f}_j(\mathbf{r}'), \quad (90)$$

where \mathbf{f}_j is the force per unit area that a surface element with position \mathbf{r}' of colloidal sphere j exerts on the fluid.

We shall assume stick boundary conditions, that is, the velocity of the fluid at the spheres surface is assumed to be equal to the velocity of the corresponding surface element. Hence,

$$\mathbf{v}_i + \boldsymbol{\Omega}_i \times (\mathbf{r} - \mathbf{r}_i) = \sum_{j=1}^N \oint_{\partial V_j} dS' \mathbf{T}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{f}_j(\mathbf{r}'), \quad \mathbf{r} \in \partial V_i, \quad (91)$$

where \mathbf{v}_i and $\boldsymbol{\Omega}_i$ are the translational- and rotational velocity of the i^{th} sphere, respectively. Since this equation is valid for *any* position \mathbf{r} on the surface ∂V_i of particle i , both sides can be integrated over that surface. Due to symmetry, the rotational component on the left hand-side drops out, and we have,

$$\mathbf{v}_i = \frac{1}{4\pi a^2} \oint_{\partial V_i} dS \oint_{\partial V_i} dS' \mathbf{T}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{f}_i(\mathbf{r}') + \frac{1}{4\pi a^2} \sum_{j \neq i}^N \oint_{\partial V_i} dS \oint_{\partial V_j} dS' \mathbf{T}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{f}_j(\mathbf{r}'). \quad (92)$$

Since,

$$\oint_{\partial V_i} dS \mathbf{T}(\mathbf{r} - \mathbf{r}') = \hat{\mathbf{I}} \frac{2a}{3\eta_0}, \quad \text{for } \mathbf{r}' \in \partial V_i, \quad (93)$$

the first term on the right hand-side of eq.(92) is thus equal to,

$$\frac{1}{4\pi a^2} \oint_{\partial V_i} dS \oint_{\partial V_i} dS' \mathbf{T}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{f}_i(\mathbf{r}') = -\frac{1}{6\pi\eta_0 a} \mathbf{F}_i^h,$$

where the total force that the fluid exerts on the i^{th} Brownian particle is equal to,

$$\mathbf{F}_i^h(t) = - \oint_{\partial V_i} dS' \mathbf{f}_i(\mathbf{r}'). \quad (94)$$

The double surface integrals in the second line on the right hand-side of eq.(92) can be approximated, in case the distance between the colloidal spheres is large, as follows. First, the integrations are performed with respect to the translated coordinates $\mathbf{R} = \mathbf{r} - \mathbf{r}_i$ and $\mathbf{R}' = \mathbf{r}' - \mathbf{r}_j$ (see Fig.5).

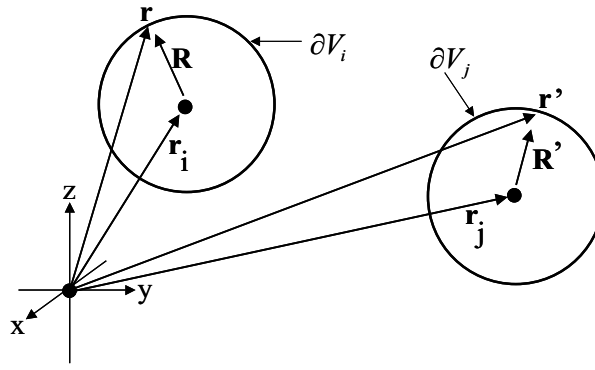


Fig. 5: Definition of the positions \mathbf{R} and \mathbf{R}' on the surface of Brownian particles relative to their position coordinates \mathbf{r}_i and \mathbf{r}_j , respectively.

Let ∂V^0 denote the spherical surface ∂V_i with its center at the origin. The integrals on the right hand-side of eq.(92) are written as,

$$\frac{1}{4\pi a^2} \oint_{\partial V^0} dS \oint_{\partial V^0} dS' \mathbf{T}(\mathbf{R} - \mathbf{R}' + \mathbf{r}_i - \mathbf{r}_j) \cdot \mathbf{f}_j(\mathbf{R}' + \mathbf{r}_j) .$$

Now suppose that the distance $|\mathbf{r}_i - \mathbf{r}_j|$ between the Brownian particles i and j is much larger than $|\mathbf{R} - \mathbf{R}'| \leq 2a$, with a the radius of the sphere. The Oseen tensor $\mathbf{T}(\mathbf{R} - \mathbf{R}' + \mathbf{r}_i - \mathbf{r}_j)$ may then be replaced, to a good approximation, by $\mathbf{T}(\mathbf{r}_i - \mathbf{r}_j)$. With eq.(94) it then follows that,

$$\frac{1}{4\pi a^2} \oint_{\partial V_i} dS \oint_{\partial V_j} dS' \mathbf{T}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{f}_j(\mathbf{r}') \approx -\mathbf{T}(\mathbf{r}_i - \mathbf{r}_j) \cdot \mathbf{F}_j^h .$$

For these large separations between the Brownian spheres, eq.(92) can thus be approximated as,

$$\mathbf{v}_i = -\frac{1}{6\pi\eta_0 a} \mathbf{F}_i^h - \sum_{j \neq i}^N \mathbf{T}(\mathbf{r}_i - \mathbf{r}_j) \cdot \mathbf{F}_j^h . \quad (95)$$

We thus find the following leading order expansion of the microscopic diffusion tensors with respect to a/r_{ij} ,

$$\mathbf{D}_{ii} = D_0 \hat{\mathbf{I}} , \quad (96)$$

$$\mathbf{D}_{ij} = k_B T \mathbf{T}(\mathbf{r}_i - \mathbf{r}_j) = \frac{3}{4} D_0 \frac{a}{r_{ij}} \left[\hat{\mathbf{I}} + \hat{\mathbf{r}}_{ij} \hat{\mathbf{r}}_{ij} \right] , \quad i \neq j , \quad (97)$$

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ is the distance between the spheres i and j , and $\hat{\mathbf{r}}_{ij} = \mathbf{r}_{ij}/r_{ij}$ is a unit vector. Furthermore, $D_0 = k_B T / 6\pi\eta_0 a$ is the same Stokes-Einstein diffusion coefficient that we encountered before.

The above expressions, the Oseen approximation for the microscopic diffusion matrices, are valid for large distances between the Brownian particles, that is, for small values of a/r_{ij} . These results are the leading terms in an expansion with respect to a/r_{ij} .

On the two-particle level, where only two particles interact simultaneously, the general form of the diffusion matrices reads,

$$\begin{aligned} \mathbf{D}_{ii} &= D_0 \hat{\mathbf{I}} + D_0 \sum_{j=1, j \neq i}^N \left\{ A_s(r_{ij}) \hat{\mathbf{r}}_{ij} \hat{\mathbf{r}}_{ij} + B_s(r_{ij}) [\hat{\mathbf{I}} - \hat{\mathbf{r}}_{ij} \hat{\mathbf{r}}_{ij}] \right\}, \\ \mathbf{D}_{ij} &= D_0 \left\{ A_c(r_{ij}) \hat{\mathbf{r}}_{ij} \hat{\mathbf{r}}_{ij} + B_c(r_{ij}) [\hat{\mathbf{I}} - \hat{\mathbf{r}}_{ij} \hat{\mathbf{r}}_{ij}] \right\}, \quad i \neq j. \end{aligned} \quad (98)$$

The summation in the expression for the "self" diffusion matrix \mathbf{D}_{ii} accounts for the fact that *all* particles in suspension reflect the field of the i^{th} particle back to that particle. The scalar functions A_s , B_s , A_c and B_c are referred to as *mobility functions*. These functions depend only on the scalar distance r_{ij} between the two spheres i and j . The mobility functions with $i = j$ are sometimes called *self-mobility functions*, and those with $i \neq j$, *distinct-* or *cross-mobility functions*. The subscripts s and c refer to "self" and "cross", respectively. The mobility functions can be calculated as a Taylor expansion with respect to the inverse distance between two colloidal spheres. The first few terms in such an expansion read,

$$\begin{aligned} A_s &= -\frac{15}{4} \left(\frac{a}{r_{ij}} \right)^4 + \frac{11}{2} \left(\frac{a}{r_{ij}} \right)^6 + O((a/r_{ij})^8), \\ B_s &= -\frac{17}{16} \left(\frac{a}{r_{ij}} \right)^6 + O((a/r_{ij})^8), \\ A_c &= \frac{3}{2} \frac{a}{r_{ij}} - \left(\frac{a}{r_{ij}} \right)^3 + \frac{75}{4} \left(\frac{a}{r_{ij}} \right)^7 + O((a/r_{ij})^9), \\ B_c &= \frac{3}{4} \frac{a}{r_{ij}} + \frac{1}{2} \left(\frac{a}{r_{ij}} \right)^3 + O((a/r_{ij})^9), \end{aligned} \quad (99)$$

where the leading terms correspond to our result in eq.(96). Nowadays, the numerical values of many hundreds of coefficients are known [4]. There are analytical expression for the hydrodynamic interaction tensors for very close approach of two spheres. This so-called *lubrication contribution to hydrodynamic interactions* [5] is not accounted for in the above mentioned expansions. The expansions allow the calculation of transport coefficients up to leading order in concentration, although for attractive interactions lubrication contributions should be taken into account. For higher concentrations, when simultaneous hydrodynamic interactions between more than two particles are important, one should derive expressions involving three and more particles. So far, only the leading order expressions for three particle hydrodynamic interactions are known. Alternatively one can perform simulations to take hydrodynamic interactions into account.

6 Linear Response Theory

Equations of motion for ensemble averaged, macroscopic quantities can be obtained in principle from the equations of motion for probability density functions. Let $F(\mathbf{X})$ be a phase function. The corresponding macroscopic variable that can be measured in an experiment is the ensemble average $\langle F \rangle$, which is referred to as an observable. Multiplying both sides of eq.(35) with $F(\mathbf{X})$ and integrating with respect to the phase-space variables \mathbf{X} leads to,

$$\frac{\partial}{\partial t} \langle F \rangle = \int d\mathbf{X} F(\mathbf{X}) \hat{\mathcal{L}} P(\mathbf{X}, t). \quad (100)$$

The right-hand side should now be expressed in terms of relevant observables to obtain a description on the macroscopic level. Such a microscopic derivation of equations of motion for macroscopic, observable quantities is the main challenge of statistical mechanics. As a special case we shall consider the response of observables to a (possibly time-dependent) external field, which is assumed to be weak enough to linearize appropriate equations of motion with respect to the external perturbation. Such a theory is called "linear response theory".

6.1 Derivation of the linear response equations

Let $\hat{\mathcal{L}}_{eq}$ be the time evolution operator in the absence of the external field and $\hat{\mathcal{L}}^{ext}(t)$ the (possibly time-dependent) contribution due to the external field, that is, $\hat{\mathcal{L}} = \hat{\mathcal{L}}_{eq} + \hat{\mathcal{L}}^{ext}(t)$. The equation of motion (35) is thus written as,

$$\frac{\partial}{\partial t} P(\mathbf{X}, t) = \left\{ \hat{\mathcal{L}}_{eq} + \hat{\mathcal{L}}^{ext}(t) \right\} P(\mathbf{X}, t) . \quad (101)$$

Since the external field is supposed to be weak, the deviation from the probability density function (pdf) $P_{eq} \sim \exp\{-\beta\Phi\}$ without the external field will be small as well. Hence, we shall write,

$$P(\mathbf{X}, t) = P_{eq}(\mathbf{X}) + \Delta P(\mathbf{X}, t) , \quad (102)$$

where ΔP is the small contribution due to the external field. Substitution into eq.(101), using that $\partial P_{eq}/\partial t = \hat{\mathcal{L}}_{eq} P_{eq} = 0$ and neglecting a term $\hat{\mathcal{L}}^{ext}(t) \Delta P$, which is of second order in the strength of the external field, it is found that,

$$\frac{\partial}{\partial t} \Delta P(\mathbf{X}, t) = \hat{\mathcal{L}}^{ext}(t) P_{eq}(\mathbf{X}) + \hat{\mathcal{L}}_{eq} \Delta P(\mathbf{X}, t) . \quad (103)$$

The solution of this equation can be found by variation of constants, leading to,

$$\Delta P(\mathbf{X}, t) = \exp\{\hat{\mathcal{L}}_{eq} t\} \Delta P(\mathbf{X}, t = -\infty) + \int_{-\infty}^t dt' \exp\{\hat{\mathcal{L}}_{eq} (t - t')\} \hat{\mathcal{L}}^{ext}(t') P_{eq}(\mathbf{X}) . \quad (104)$$

To make further progress, we have to specify the operator $\hat{\mathcal{L}}^{ext}$ due to the external field. We shall consider the time evolution according to the Smoluchowski equation (64,65). Liouville dynamics can be treated along similar lines. We chose here to consider Smoluchowski dynamics, since this is not treated in most standard textbooks, contrary to Liouville dynamics. As before, the operators on the diffusive time scale τ_D are denoted as $\hat{\mathcal{O}}$.

In this section we shall consider conservative external fields. By definition, a conservative external field can be incorporated in the time-evolution operator through an additional potential. According to eq.(65), the operator $\hat{\mathcal{O}}^{ext}$ is thus equal to (here, $\mathbf{X} = \mathbf{R} = (\mathbf{r}_1, \dots, \mathbf{r}_N)$),

$$\hat{\mathcal{O}}^{ext}(\dots) = \beta \sum_{i,j=1}^N \nabla_{\mathbf{r}_j} \cdot \mathbf{D}_{ij} \cdot [\nabla_{\mathbf{r}_j} \Phi^{ext}(\mathbf{R}, t)] (\dots) , \quad (105)$$

where Φ^{ext} is the external potential. As an example, consider an external electric field. In that case,

$$\Phi^{ext}(\mathbf{R}, t) = \sum_{j=1}^N q_j \varphi^{ext}(\mathbf{r}_j, t) , \quad (106)$$

where q_j is the charge of particle j and $\varphi^{ext}(\mathbf{r}_j, t)$ is the external electric potential. This can be written as,

$$\Phi^{ext}(\mathbf{R}, t) = \int d\mathbf{r} \rho(\mathbf{r} | \mathbf{R}) \varphi^{ext}(\mathbf{r}, t) , \quad (107)$$

where (with δ the delta distribution),

$$\rho(\mathbf{r} | \mathbf{R}) = \sum_{j=1}^N q_j \delta(\mathbf{r} - \mathbf{r}_j) . \quad (108)$$

This is the phase function that complies with the charge density at point \mathbf{r} : integration of $\rho(\mathbf{r} | \mathbf{R})$ over a volume ΔV gives the charge within that volume at the particular time t . In analogy with eq.(107), the general form of the external potential is written as,

$$\Phi^{ext}(\mathbf{R}, t) = \int d\mathbf{r} B(\mathbf{r} | \mathbf{R}) \varphi^{ext}(\mathbf{r}, t) , \quad (109)$$

where φ^{ext} is the external field and,

$$B(\mathbf{r} | \mathbf{R}) = \sum_{j=1}^N B_j \delta(\mathbf{r} - \mathbf{r}_j) , \quad (110)$$

is the phase function that specifies the microscopic density of a variable B . This phase function describes how the external field couples to the total potential energy. Substitution of eq.(109) into eq.(105) thus leads to,

$$\hat{\mathcal{O}}^{ext}(t)(\dots) = \beta \int d\mathbf{r} \varphi^{ext}(\mathbf{r}, t) \left\{ \sum_{i,j=1}^N \nabla_{r_j} \cdot \mathbf{D}_{ij} \cdot (\dots) \nabla_{r_j} B(\mathbf{r} | \mathbf{R}) \right\} . \quad (111)$$

We shall assume that the external field is absent at $t = -\infty$. In that case,

$$\Delta P(\mathbf{R}, t = -\infty) = 0 . \quad (112)$$

The response of the density of a variable A , defined similarly as the variable B in eq.(110), thus follows from eq.(104) (with \mathbf{X} equal to \mathbf{R}),

$$\langle \Delta A \rangle(\mathbf{r}, t) \equiv \int d\mathbf{R} A(\mathbf{r} | \mathbf{R}) \Delta P(\mathbf{R}, t) = \beta \int_{-\infty}^t dt' \int d\mathbf{r}' \Xi(\mathbf{r} - \mathbf{r}', t - t') \varphi^{ext}(\mathbf{r}', t') , \quad (113)$$

where the response function Ξ is equal to, with $\tau = t - t'$,

$$\Xi(\mathbf{r} - \mathbf{r}', \tau) = \int d\mathbf{R} A(\mathbf{r} | \mathbf{R}) \exp\{\hat{\mathcal{O}}_{eq}\tau\} \sum_{i,j=1}^N \nabla_{r_j} \cdot \mathbf{D}_{ij} \cdot P_{eq}(\mathbf{R}) \nabla_{r_j} B(\mathbf{r}' | \mathbf{R}) , \quad (114)$$

where $\hat{\mathcal{O}}_{eq}$ is the equilibrium Smoluchowski operator. Since $P_{eq} \sim \exp\{-\beta\Phi\}$, it is readily verified that,

$$\sum_{i,j=1}^N \nabla_{r_j} \cdot \mathbf{D}_{ij} \cdot P_{eq}(\mathbf{R}) \nabla_{r_j} B(\mathbf{r} | \mathbf{R}) = \hat{\mathcal{O}}_{eq} [P_{eq}(\mathbf{R}) B(\mathbf{r} | \mathbf{R})] , \quad (115)$$

where the form (65) for the Smoluchowski operator has been used. Substitution into eq.(114) for the response function thus leads to,

$$\Xi(\mathbf{r} - \mathbf{r}', \tau) = \frac{\partial}{\partial \tau} \int d\mathbf{R} A(\mathbf{r}|\mathbf{R}) \exp\{\hat{\mathcal{O}}_{eq}\tau\} [P_{eq}(\mathbf{R}) B(\mathbf{r}'|\mathbf{R})] , \quad (116)$$

and hence, according to eq.(39), in obvious notation,

$$\Xi(\mathbf{r} - \mathbf{r}', \tau) = \frac{\partial}{\partial \tau} \langle B(\mathbf{r}', 0) A(\mathbf{r}, \tau) \rangle_0 , \quad (117)$$

where the subscript "0" is used to indicate that the ensemble average is to be taken in the equilibrium system, without the external field. Note that since the equilibrium system is translationally invariant, the response function is a function of \mathbf{r} and \mathbf{r}' only through their difference $\mathbf{r} - \mathbf{r}'$. The response to an external field is thus expressed in terms of correlations in the equilibrium system, in the absence of the external field. This is of course only valid for small external fields. Also note that in the integral in eq.(113), the time-argument of Ξ is always positive. We could extend the upper time-integration range in eq.(113) to $+\infty$, demanding that,

$$\Xi(\mathbf{r}, t) = 0 \quad , \quad \text{for } t < 0 . \quad (118)$$

This expresses causality : the effect of an external field at time t can not be affected by future events at times $t' > t$.

The time-integration in eq.(113) for the response of an observable A reflects the fact that the response depends on earlier states. This "memory-effect" extends over times on which the variables A and B in the expression eq.(117) become statistically independent. The spatial integration in eq.(113) reflects the effect on the response at a given point from neighbouring points. The range of these "non-local" effects is set by the range of the interactions between particles.

6.2 Static and dynamic response of the number density

As an example, let us consider the response of the number density of colloidal particles due to an external potential. In this case, both A and B are equal to the microscopic density,

$$\rho(\mathbf{r}|\mathbf{R}) = \sum_{j=1}^N \delta(\mathbf{r} - \mathbf{r}_j) , \quad (119)$$

and hence, according to eq.(117)

$$\Xi(\mathbf{r} - \mathbf{r}', t - t') = \frac{\partial}{\partial t} \sum_{i,j=1}^N \langle \delta(\mathbf{r}' - \mathbf{r}_i(t')) \delta(\mathbf{r} - \mathbf{r}_j(t)) \rangle_0 . \quad (120)$$

The response is most conveniently expressed in terms of Fourier transforms. The spatial Fourier transform of a function $f(\mathbf{r})$ is defined here as,

$$f(\mathbf{k}) \equiv \int d\mathbf{r} f(\mathbf{r}) \exp\{-i\mathbf{k} \cdot \mathbf{r}\} , \quad (121)$$

where \mathbf{k} is referred to as a wave vector. The magnitude of $f(\mathbf{k})$ measures the relative contribution of variations of $f(\mathbf{r})$ on a length scale $\sim 1/k$. If, for example, $f(\mathbf{k})$ is relatively small

for large k , the spatial variations of $f(\mathbf{r})$ are predominantly smooth. The temporal Fourier transform of a function $h(t)$ is defined here as,

$$h(\omega) \equiv \int_{-\infty}^{\infty} dt h(t) \exp\{-i\omega t\} , \quad (122)$$

where ω is the frequency. Again, the magnitude of $h(\omega)$ measures the relative contributions to $h(t)$ which vary on a time scale $\sim 1/\omega$. Fourier transformation of eq.(113), using eq.(118), gives,

$$\langle \Delta\rho \rangle (\mathbf{k}, \omega) = \beta \Xi(\mathbf{k}, \omega) \varphi^{ext}(\mathbf{k}, \omega) . \quad (123)$$

From eq.(120) for the example under consideration we have,

$$\Xi(\mathbf{k}, \omega) = i\omega \bar{\rho} S(\mathbf{k}, \omega) , \quad (124)$$

where $\bar{\rho} = N/V$ is the mean number density and $S(\mathbf{k}, t)$ is the time-Fourier transform of the *dynamic structure factor* $S(k, t)$, which is defined as,

$$S(k, t) = \frac{1}{N} \sum_{i,j=1}^N \langle \exp\{-i\mathbf{k} \cdot (\mathbf{r}_i(t) - \mathbf{r}_j(t=0))\} \rangle_0 , \quad \text{for } t \geq 0 , \quad (125)$$

while $S(\mathbf{k}, t) = 0$ for $t < 0$. This function can be measured by scattering experiments, where the wave vector is related to the scattering angle. It has been evaluated for non-interacting colloids in subsection 4.3. In the derivation of eq.(124) we used that,

$$S(k, t = \infty) = \frac{1}{N} \left| \sum_{i=1}^N \langle \exp\{-i\mathbf{k} \cdot \mathbf{r}_i\} \rangle \right|^2 , \quad (126)$$

and,

$$\langle \exp\{-i\mathbf{k} \cdot \mathbf{r}_i\} \rangle = \frac{1}{V} \int d\mathbf{r} \exp\{-i\mathbf{k} \cdot \mathbf{r}\} \sim \delta(\mathbf{k}) , \quad (127)$$

where it is used that the single-particle pdf is nothing but $1/V$. For wave vectors $\mathbf{k} \neq \mathbf{0}$, the delta distribution is zero. Hence, the result in eq.(124) is only valid for non-zero wave vectors, which excludes a position independent external potential. The linear response result in eq.(123) can thus finally be written as,

$$\frac{\langle \Delta\rho \rangle (\mathbf{k}, \omega)}{\bar{\rho}} = i\omega \beta S(k, \omega) \varphi^{ext}(\mathbf{k}, \omega) . \quad (128)$$

S is generally a complex quantity. The imaginary part of S describes the response that is in-phase with the external potential, while the real part describes the out-of-phase response. Since in the derivation of this result we assumed that $\mathbf{k} \neq \mathbf{0}$, which excludes a spatially constant potential. Let us now consider a potential that is constant for times $t > -\tau$, where τ is the time interval during which the density relaxes, that is, the time interval where Ξ is non-zero. For $t > 0$, the response is then due to a constant external potential, independent of both time and position. Physically this means that the state of the system at times $t > 0$ is beyond the time where the system "remembers" previous states during which the potential was switched on.

In the derivation of the Smoluchowski equation, we considered a closed system, since it was assumed that $P \sim \exp\{-\beta\Phi\}$ in equilibrium. The number of particles is thus fixed. A potential that is constant throughout the system therefore can not have an effect on the overall density. In order to analyze the response to a constant potential, we therefore divide the system into two parts : in half of the system the potential is $\varphi_0 > 0$, say, while in the other half the potential is $-\varphi_0$. The increase of the number density in the two parts then cancels, ensuring that the total number of particles remains unchanged. Since the width of the "interface" between the two parts is equal to the range of interaction between particles, which is the range over which Ξ varies with position, one can simply consider one of the parts on the basis of the equations derived above. Interpreting the volume integral in eq.(113) as the zero wave vector limit of the dynamic structure factor (126), it is found that the static response of the density is given by,

$$\frac{\langle \Delta\rho \rangle}{\bar{\rho}} = -\beta \varphi_0 \lim_{k \rightarrow 0} S(k) , \quad (129)$$

where,

$$S(k) \equiv S(k, t = 0) , \quad (130)$$

is the dynamic structure factor (125) for $t = 0$, which is referred to as *the static structure factor*. Clearly, if the potential is positive, the density will decrease, since then the internal energy will be decreased. It can be shown that the static structure factor at zero wave vector is related to the osmotic compressibility as,

$$\lim_{k \rightarrow 0} S(k) = \frac{k_B T}{\partial \Pi(\bar{\rho}, T, \mu_s) / \partial \bar{\rho}} , \quad (131)$$

where Π is the osmotic pressure (here, Π is considered a function of $\bar{\rho}$, T and the chemical potential μ_s of the solvent). The change in density is larger as the system is more easily "compressed", that is, if a relatively large change in density is required to induce a significant change in osmotic pressure.

7 The Green-Kubo Formula

Linear transport coefficients can be related to time-integrals of current-current correlation functions. Such relations are referred to as *Green-Kubo* relations. They can be employed to obtain numerical values for phenomenological transport coefficients (such as the viscosity, diffusion coefficients and conductivity) from microscopic simulations where the current-current correlation functions are measured in equilibrium systems.

One can not rely on Smoluchowski dynamics here, since the current-current correlation functions exhibit contributions from times shorter than the momentum relaxation time scale τ_B . Currents, or equivalently, velocities of colloidal particles relax on a time scale $\tau_B = M/\zeta$ to equilibrium with the heat bath of solvent molecules (see section 4.2), which relaxation process is excluded in Smoluchowski dynamics. A treatment on the diffusive time scale $\tau_D \gg \tau_B$ would not include such short-time contributions to current-current correlation functions. Without these "relaxation contributions", Green-Kubo formulas some times even predict negative values for inherently positive phenomenological coefficients.

7.1 Derivation of the Green-Kubo formula

Consider the linear response of the current \mathbf{j}_A of an observable A . The current is defined as,

$$\mathbf{j}_A(\mathbf{r}|\mathbf{X}) = \sum_{j=1}^N A_j \mathbf{v}_j \delta(\mathbf{r} - \mathbf{r}_j), \quad (132)$$

where, as compared to eq.(110) (with B replaced by A) the velocity \mathbf{v}_j is added here. Ensemble averaging of this current gives the average amount of A that flows through a unit surface area per unit of time. Substitution into the linear response result (113) of the previous section leads to,

$$\langle \mathbf{j}_A \rangle(\mathbf{r}, t) = \beta \int_{-\infty}^t dt' \int d\mathbf{r}' \Xi(\mathbf{r} - \mathbf{r}', t - t') \varphi^{ext}(\mathbf{r}', t'), \quad (133)$$

where it is used that the current is 0 in equilibrium. The response function (117) is now equal to.

$$\Xi(\mathbf{r} - \mathbf{r}', t - t') = \frac{\partial}{\partial t} \langle B(\mathbf{r}', t') \mathbf{j}_A(\mathbf{r}, t) \rangle_0. \quad (134)$$

This correlation function can be rewritten in terms of a current-current correlation function as follows. First let's go back to eq.(116) (where the Liouville operator replaces the Smoluchowski operator),

$$\Xi(\mathbf{r} - \mathbf{r}', t - t') = \int d\mathbf{X} \mathbf{j}_A(\mathbf{r}|\mathbf{X}) \exp\{\hat{\mathcal{L}}_{eq}(t - t')\} \hat{\mathcal{L}}_{eq} [P_{eq}(\mathbf{X}) B(\mathbf{r}'|\mathbf{X})]. \quad (135)$$

Now let us define the conjugate operator $\hat{\mathcal{L}}_{eq}^\dagger$ to the Liouville operator $\hat{\mathcal{L}}_{eq}$ as,

$$\hat{\mathcal{L}}_{eq} [P_{eq}(\mathbf{X}) F(\mathbf{X})] \equiv P_{eq}(\mathbf{X}) \hat{\mathcal{L}}_{eq}^\dagger F(\mathbf{X}), \quad (136)$$

for any phase function F . Since the Liouville operator (46) contains only first order derivatives, and $\hat{\mathcal{L}}_{eq} P_{eq} = 0$, it immediately follows that,

$$\hat{\mathcal{L}}_{eq}^\dagger = \hat{\mathcal{L}}_{eq}. \quad (137)$$

It is furthermore easily verified from the expression (46) that,

$$\hat{\mathcal{L}}_{eq} \delta(\mathbf{r} - \mathbf{r}_n) = \mathbf{v}_n \cdot \nabla \delta(\mathbf{r} - \mathbf{r}_n). \quad (138)$$

Hence, from eqs.(110,132),

$$\hat{\mathcal{L}}_{eq} B(\mathbf{r}'|\mathbf{X}(t')) = \nabla' \cdot \sum_{i=1}^N B_i \mathbf{v}_i(t') \delta(\mathbf{r}' - \mathbf{r}_i(t')) = \nabla' \cdot \mathbf{j}_B(\mathbf{r}'|\mathbf{X}(t')). \quad (139)$$

After a partial spatial integration, the linear response equations can thus be written as,

$$\langle \mathbf{j}_A \rangle(\mathbf{r}, t) = \beta \int_{-\infty}^t dt' \int d\mathbf{r}' \Theta(\mathbf{r} - \mathbf{r}', t - t') \cdot \mathbf{F}^{ext}(\mathbf{r}', t'), \quad (140)$$

where the tensor Θ is equal to,

$$\Theta(\mathbf{r} - \mathbf{r}', t - t') = \langle \mathbf{j}_B(\mathbf{r}', t') \mathbf{j}_A(\mathbf{r}, t) \rangle_0 . \quad (141)$$

The external force in eq.(140) is equal to,

$$\mathbf{F}^{ext}(\mathbf{r}', t') = -\nabla' \varphi^{ext}(\mathbf{r}', t') . \quad (142)$$

That the force instead of the potential as such appears here is intuitively clear since a current is indeed driven by a force rather than the absolute value of the potential itself. When this external force changes slowly in time as compared to the decay time of the current-current correlation function, which is of the order of microstructural relaxation times, and the force changes slowly on the length scale set by the range of the inter-particle interactions, the external force $\mathbf{F}^{ext}(\mathbf{r}', t')$ in eq.(140) may be taken equal to $\mathbf{F}^{ext}(\mathbf{r}, t)$. In addition, in an isotropic, rotationally invariant system, the off-diagonal elements of the current-current correlation function are zero. Also, all diagonal elements are equal, and hence $\Theta \sim \hat{\mathbf{I}}$, where $\hat{\mathbf{I}}$ is the identity tensor. Finally using that,

$$\int d\mathbf{r} \int d\mathbf{r}' \langle \mathbf{j}_B(\mathbf{r}', 0) \mathbf{j}_A(\mathbf{r}, \tau) \rangle_0 = \sum_{i,j=1}^N B_i A_j \int_0^\infty d\tau \langle \mathbf{v}_i(0) \cdot \mathbf{v}_j(\tau) \rangle_0 , \quad (143)$$

we can rewrite the above expressions to arrive at *the Green-Kubo formula*,

$$\begin{aligned} \langle \mathbf{j}_A(\mathbf{r}, t) \rangle &= \beta \Theta \mathbf{F}^{ext}(\mathbf{r}, t) , \\ \Theta &= \frac{1}{3V} \sum_{i,j=1}^N B_i A_j \int_0^\infty d\tau \langle \mathbf{v}_i(0) \cdot \mathbf{v}_j(\tau) \rangle_0 . \end{aligned} \quad (144)$$

It should be noted that the variable B is determined by the way the external potential acts on to the system, as formally described in eq.(109).

These equations are at the basis of many computer-simulation calculations of linear phenomenological transport coefficients. Expressions for the self-diffusion coefficient and the sedimentation coefficient are derived in the following two subsections on the basis of the Green-Kubo formula.

7.2 Self-diffusion

Consider a single colloidal sphere (*the tracer particle*) in a possibly concentrated dispersion of other spheres (*the host particles*). The host spheres are assumed to be identical to the tracer sphere. An external force \mathbf{F}^{ext} is applied that acts only on the single tracer particle, not on the host particles. The thermally averaged velocity that the tracer particles attains in the stationary state can be written as,

$$\langle \mathbf{v} \rangle = \frac{1}{\zeta_s} \mathbf{F}^{ext} , \quad (145)$$

where ζ_s is the *self-friction coefficient*. This friction coefficient includes both friction with the solvent and interactions with the force-free host particles. The analysis in section 4 to arrive at the Smoluchowski equation (68) can be repeated for a subset of tracer particles which are so

dilute that they do not interact with each other. The derivation of the Smoluchowski equation can be done from the start with the neglect of interactions between the tracer particles. The only forces acting on a tracer sphere are now the Brownian force and the hydrodynamic force $\mathbf{F}^h = -\zeta_s \mathbf{v}^{cg}$ where ζ is the same friction coefficient that appears in eq.(145). Hence,

$$\frac{\partial}{\partial t} P(\mathbf{r}, t) = D_s \nabla^2 P(\mathbf{r}, t), \quad (146)$$

where $P(\mathbf{r}, t)$ is the (non-equilibrium) pdf for the position coordinate of the tracer sphere. The same expression (67) for the diffusion coefficient is found, where now the friction coefficient includes interactions of the tracer sphere with the host spheres. The diffusion coefficient,

$$D_s = \frac{k_B T}{\zeta_s}, \quad (147)$$

is referred to as *the self-diffusion coefficient*. It is a long-time diffusion coefficient in the sense that it contains the friction coefficient of the stationary translating tracer sphere, long after the external force has been switched on. This diffusion coefficient describes the dynamics of a single sphere in a matrix of other spheres. It is related to the *mean-squared displacement*,

$$W(t) \equiv \langle |\mathbf{r}(t) - \mathbf{r}(t=0)|^2 \rangle. \quad (148)$$

of the tracer sphere. The connection between the mean-squared displacement and the self-diffusion coefficient can be obtained from the Smoluchowski equation. Multiplying both sides of eq.(146) with r^2 and integration gives (with $\mathbf{r}(t=0)$ taken equal to 0),

$$\begin{aligned} \frac{d}{dt} W(t) &= D_s \int d\mathbf{r} r^2 \nabla^2 P(\mathbf{r}, t) \\ &= D_s \int d\mathbf{r} P(\mathbf{r}, t) \nabla^2 r^2 = 6 D_s, \end{aligned} \quad (149)$$

where in the second line, two partial integrations have been performed. Since $W(t=0) = 1$, it follows that,

$$W(t) = 6 D_s t. \quad (150)$$

This specifies how the self-diffusion coefficient characterizes the dynamics of the tracer sphere. A Green-Kubo formula for the self-diffusion coefficient can be obtained from a comparison of the Green-Kubo formula (144) and eq.(145) in the form,

$$\langle \mathbf{j} \rangle = \rho \langle \mathbf{v} \rangle = \beta D_s \rho \mathbf{F}^{ext}, \quad (151)$$

with ρ the number density of tracer spheres (which should be small enough to prevent tracer spheres to interact with each other). Since the external potential couples to the density of the tracer particles, both A_i and B_j in the Green-Kubo formula (144) are equal to 1. Furthermore, since the tracer spheres do not interact with each other, $\langle \mathbf{v}_i(0) \cdot \mathbf{v}_j(\tau) \rangle_0 = 0$ when $i \neq j$. The Green-Kubo formula (144) thus leads to,

$$D_s = \frac{1}{3} \int_0^\infty d\tau \langle \mathbf{v}(0) \cdot \mathbf{v}(\tau) \rangle_0, \quad (152)$$

where \mathbf{v} is the velocity of a tracer sphere. In a simulation, tracing the velocities of the particles thus allows to compute the self-diffusion coefficient for any concentration of host particles and arbitrary interaction potentials

For non-interacting colloidal spheres, eq.(50) can be used in combination with eq.(152) to obtain $D_s = k_B T / \zeta$, where it is used that $\langle v^2 \rangle_0 = 3k_B T / M$, which follows from the equi-partition theorem. This reproduces Einstein's expression for the single-particle diffusion coefficient. Note that this value for the diffusion coefficient is determined entirely from dynamics for times shorter than the momentum relaxation time scale. A treatment on the diffusive time scale would have given the wrong answer.

7.3 Sedimentation

Instead of a force on a single particle, now consider the case where the same force acts on all particles. This force may be thought of as the earth gravitational force, due to which colloidal particles slowly sediment to the bottom of the container. Similar to eq.(145) we have,

$$\langle \mathbf{j} \rangle = \rho \langle \mathbf{v} \rangle = \rho \frac{1}{\zeta_c} \mathbf{F}^{ext}, \quad (153)$$

where now ρ is the total number density of colloidal particles and ζ_c is a *collective-friction coefficient*. This friction coefficient differs from the "self-friction coefficient" in the previous subsection, due to the fact that each given particle interacts with other particles that move on average along with the given particle. Both direct interactions and hydrodynamic interactions differ on average in both cases. Comparing eq.(153) with the Green-Kubo formula (144) immediately gives,

$$\frac{1}{\zeta_c} = \frac{\beta}{3N} \sum_{i,j=1}^N \int_0^\infty d\tau \langle \mathbf{v}_i(0) \cdot \mathbf{v}_j(\tau) \rangle_0, \quad (154)$$

since, as before, both A_i and B_j are unity. This result can be reformulated in terms of *the sedimentation coefficient* S , which is defined as the ratio of the velocity of a colloidal particle and the velocity v_0 of a colloidal sphere in pure solvent. Since $v_0 = \beta D_0 F^{ext}$, where D_0 is the Einstein diffusion coefficient (67), the sedimentation coefficient follows from eq.(154) as,

$$S = \frac{1}{3N D_0} \sum_{i,j=1}^N \int_0^\infty d\tau \langle \mathbf{v}_i(0) \cdot \mathbf{v}_j(\tau) \rangle_0. \quad (155)$$

Contrary to self-diffusion, cross terms where $i \neq j$ are non-zero, since the particles under consideration now interact with each other.

In the next section it will be shown on the basis of the Green-Kubo formula that there is a connection between the sedimentation coefficient and the collective diffusion coefficient.

8 Onsager's Regression Hypothesis

The Green-Kubo formula derived in the previous section allows for the calculation of transport coefficients that relate to a conservative external field, that is, an external field for which a potential can be defined (see eq.(105)). This excludes transport coefficients such as the shear viscosity and thermal conductivity. It also excludes transport coefficients which connect a flux with spatial gradients of an observable, like for collective diffusion. For non-thermodynamic

transport coefficients such as the shear viscosity, the above analysis can be repeated with a different form for the operator due to the external field as compared to eq.(105), which is beyond the scope of this chapter. For thermodynamic transport coefficients such as the thermal conductivity, and for example collective diffusion, a different approach must be taken. In all cases, Onsager's regression hypothesis can be employed to obtain the relevant Green-Kubo formula.

8.1 Formulation of Onsager's regression hypothesis

Onsager's regression hypothesis states that equilibrium fluctuations of a phase variable relax on average in the same way as the corresponding macroscopic variable. Suppose, as a simple example, that a macroscopic variable A obeys a linear kinetic, phenomenological equation of motion of the form,

$$\frac{\partial A(\mathbf{r}, t)}{\partial t} = M \nabla^2 A(\mathbf{r}, t), \quad (156)$$

where M is a linear transport coefficient. Onsager's regression hypothesis implies that the phase function $A(\mathbf{X})$ that complies with the macroscopic variable A , that is $\langle A(\mathbf{X}) \rangle = A(\mathbf{r}, t)$, obeys the same equation of motion on average. When $\langle A \rangle$ at time $t = 0$ is specified to be equal to A_0 , this implies that,

$$\frac{\partial \langle A \rangle_0(\mathbf{r}, t)}{\partial t} = M \nabla^2 \langle A \rangle_0(\mathbf{r}, t), \quad (157)$$

where the subscript "0" refers to the initial condition for $\langle A \rangle$. The initial condition for $\langle A \rangle$ resembles a typical fluctuation of the equilibrium system. The time derivative in this equation should be interpreted as,

$$\frac{\partial \langle A \rangle_0(\mathbf{r}, t)}{\partial t} \equiv \frac{\langle A \rangle_0(\mathbf{r}, t + \tau) - \langle A \rangle_0(\mathbf{r}, t)}{\tau}, \quad (158)$$

where τ is much larger than the time τ_{coll} between collisions of particles and much smaller than the relaxation time τ_{relax} of fluctuations,

$$\tau_{coll} \ll \tau \ll \tau_{relax}. \quad (159)$$

When fluctuations decay within a few particle collision times, macroscopic equations of motion can not describe the decay of such fluctuations. It takes a large number of collisions before the decay of a quantity obeys macroscopic equations of motion.

In the following two subsections, Green-Kubo formula for the collective-diffusion coefficient and the shear viscosity of a molecular fluid will be derived from Onsager's regression hypothesis.

8.2 Collective-diffusion

In a phenomenological approach to describe diffusion, the particle current is assumed to be proportional to the gradient of the particle number density. This is a good approximation for small gradients of the concentration. Hence,

$$\langle \mathbf{j}_\rho \rangle = -D_c \nabla \rho, \quad (160)$$

where the transport coefficient D_c is referred to as *Fick's diffusion coefficient*. Contrary to the self-diffusion coefficient, Fick's diffusion coefficient describes the collective motion of many particles simultaneously. It is therefore alternatively referred to as *the collective diffusion coefficient*. The minus sign is introduced here to render D_c positive. This Ansatz is known as *Fick's first law*. The continuity equation (73) (applied to colloidal particles instead of fluid molecules) leads to *Fick's second law*, also referred to as *Fick's diffusion equation*,

$$\frac{\partial}{\partial t} \rho(\mathbf{r}, t) = D_c \nabla^2 \rho(\mathbf{r}, t) . \quad (161)$$

From Onsager's regression hypothesis (157) and eq.(32) it thus follows that,

$$\frac{\partial}{\partial t} \langle \rho(\mathbf{r}, t) \rho(\mathbf{r}', t') \rangle_0 = D_c \nabla^2 \langle \rho(\mathbf{r}, t) \rho(\mathbf{r}', t') \rangle_0 . \quad (162)$$

Fourier transformation with respect to $\mathbf{r} - \mathbf{r}'$ gives,

$$\frac{\partial}{\partial t} \langle \rho(\mathbf{k}, t) \rho(-\mathbf{k}, t') \rangle_0 = -D_c k^2 \langle \rho(\mathbf{k}, t) \rho(-\mathbf{k}, t') \rangle_0 , \quad (163)$$

the solution of which reads,

$$\langle \rho(\mathbf{k}, t) \rho(-\mathbf{k}, t') \rangle_0 = \langle \rho(\mathbf{k}, 0) \rho(-\mathbf{k}, 0) \rangle_0 \exp\{-D_c k^2 (t - t')\} . \quad (164)$$

An expression for the current-current correlation function can be obtained as follows. Consider the time-derivative,

$$\begin{aligned} \frac{\partial^2}{\partial t^2} \langle \rho(\mathbf{k}, t) \rho(-\mathbf{k}, t') \rangle_0 &= \frac{\partial^2}{\partial t^2} \langle \rho(\mathbf{k} | \mathbf{X}) \exp\{\hat{\mathcal{L}}_{eq}(t - t')\} [P_{eq}(\mathbf{X}) \rho(-\mathbf{k} | \mathbf{X})] \rangle_0 \\ &= \langle \rho(\mathbf{k} | \mathbf{X}) \exp\{\hat{\mathcal{L}}_{eq}(t - t')\} \hat{\mathcal{L}}_{eq}^2 [P_{eq}(\mathbf{X}) \rho(-\mathbf{k} | \mathbf{X})] \rangle_0 . \end{aligned} \quad (165)$$

By partial integration, it is easily shown from the expression (46) for the Liouville operator that for any two phase functions F and G ,

$$\langle F(\mathbf{X}) \hat{\mathcal{L}}_{eq} G(\mathbf{X}) \rangle_0 = - \langle G(\mathbf{X}) \hat{\mathcal{L}}_{eq} F(\mathbf{X}) \rangle_0 . \quad (166)$$

Hence, using eqs.(136,137),

$$\frac{\partial^2}{\partial t^2} \langle \rho(\mathbf{k}, t) \rho(-\mathbf{k}, t') \rangle_0 = - \langle [\hat{\mathcal{L}}_{eq} \rho(\mathbf{k} | \mathbf{R})] \exp\{\hat{\mathcal{L}}_{eq}(t - t')\} P_{eq}(\mathbf{R}) [\hat{\mathcal{L}}_{eq} \rho(-\mathbf{k} | \mathbf{R})] \rangle_0 . \quad (167)$$

From the Fourier transformed version of eq.(138),

$$\hat{\mathcal{L}}_{eq} \exp\{-i\mathbf{k} \cdot \mathbf{r}_n\} = -i\mathbf{k} \cdot \mathbf{v}_n \exp\{-i\mathbf{k} \cdot \mathbf{r}_n\} , \quad (168)$$

it thus follows that,

$$\frac{\partial^2}{\partial t^2} \langle \rho(\mathbf{k}, t) \rho(-\mathbf{k}, t') \rangle_0 = -\mathbf{k}\mathbf{k} : \langle \mathbf{j}(\mathbf{k}, t) \mathbf{j}(-\mathbf{k}, t') \rangle_0 = -\frac{1}{3} k^2 \langle \mathbf{j}(\mathbf{k}, t) \cdot \mathbf{j}(-\mathbf{k}, t') \rangle_0 , \quad (169)$$

where in the last line it is used, as before, that the off-diagonal of the current-current correlation function are zero and the diagonal elements are equal. Substitution into eq.(164) and time-integrating leads to,

$$D_c = \frac{1}{3} \frac{1}{\langle \rho(\mathbf{k}, 0) \rho(-\mathbf{k}, 0) \rangle_0} \int_0^\infty d\tau \langle \mathbf{j}(\mathbf{k}, \tau) \cdot \mathbf{j}(-\mathbf{k}, 0) \rangle_0 . \quad (170)$$

Note that,

$$\frac{1}{N} \langle \rho(\mathbf{k}, 0) \rho(-\mathbf{k}, 0) \rangle_0 = \frac{1}{N} \sum_{i,j=1}^N \langle \exp\{-i\mathbf{k} \cdot (\mathbf{r}_i(0) - \mathbf{r}_j(0))\} \rangle_0, \quad (171)$$

is the static structure factor $S(k)$ (see eqs.(125,130)), which can be measured by means of scattering experiments. Substitution of the definition of the particle current (the Fourier transform of eq.(132) with $A_j = 1$) and the expression (131) for the zero wave vector limit of the static structure factor in terms of the osmotic compressibility into eq.(170) finally gives the Green-Kubo formula for the collective-diffusion coefficient,

$$D_c = \frac{\beta}{3N} \frac{\partial \Pi(\bar{\rho}, T, \mu_s)}{\partial \bar{\rho}} \sum_{i,j=1}^N \int_0^\infty d\tau \langle \mathbf{v}_i(0) \cdot \mathbf{v}_j(\tau) \rangle_0. \quad (172)$$

The zero wave vector limit is taken here, since the phenomenological theory that is at the basis of the derivation is valid only in that limit.

Comparing the Green-Kubo formula for sedimentation (155) and collective diffusion (172) shows that,

$$D_c = D_0 \beta \frac{\partial \Pi(\bar{\rho}, T, \mu_s)}{\partial \bar{\rho}} S. \quad (173)$$

The interpretation of this relation is as follows. One can ask for the force experienced by a colloidal particle embedded in a concentration gradient. Assume that it is actually the gradient in osmotic pressure Π that drives the colloidal particles, that is, the force per unit volume equal to $\mathbf{F} = -\nabla \Pi$. The force on a single colloidal particle is then equal to $-\rho^{-1} \nabla \Pi$. When there are only gradients in the density, this is the same as $\mathbf{F} = -\rho^{-1} \frac{\partial \Pi}{\partial \rho} \nabla \rho$. The flux of colloidal particles is, according to eq.(153), equal to $\rho \langle \mathbf{v} \rangle = -\frac{1}{\zeta_c} \frac{\partial \Pi}{\partial \rho} \nabla \rho$. Fick's diffusion coefficient would then be equal to $D_c = \frac{1}{\zeta_c} \frac{\partial \Pi}{\partial \rho} = D_0 \beta \frac{\partial \Pi}{\partial \rho} S$, which reproduces eq.(173). The osmotic compressibility is thus indeed the driving force for collective diffusion. The sedimentation coefficient describes the friction as an assembly of spheres that move simultaneously. The result (173) for the collective diffusion coefficient can thus be interpreted as the ratio of a driving force and a friction. This is qualitatively the same as in eq.(147) for the self-diffusion coefficient, where $k_B T$ is the thermal driving force for Brownian motion and ζ_s is the friction factor.

This intuition reveals why the Green-Kubo formula (144) can not be used directly for collective diffusion. The driving force for collective diffusion is inherently related to properties of the system itself, and is not simply determined by an external force.

8.3 The shear viscosity

In this section we shall derive the Green-Kubo formula for the shear viscosity η_0 of a fluid. For low Reynolds numbers (see section 5.3) and in the absence of an external body force, the Navier-Stokes equation (78) for an incompressible fluid reduces to,

$$\rho \frac{\partial}{\partial t} \mathbf{v}(\mathbf{r}, t) = \nabla \cdot \boldsymbol{\Sigma}(\mathbf{r}, t) = \eta_0 \nabla^2 \mathbf{v}(\mathbf{r}, t) - \nabla p(\mathbf{r}, t), \quad (174)$$

where ρ the mass density of the fluid, \mathbf{v} is the fluid flow velocity, $\boldsymbol{\Sigma}$ is the stress tensor and p is the pressure. We shall consider a laminar flow in the x -direction, that is, $\mathbf{v} = (v_x(y, t), 0, 0)$,

with y the gradient direction, which is the direction along which the velocity varies. Since there is only a force in the x -direction on surfaces orientated with their surface normal in the y -direction, it follows from the definition of the stress tensor (see section 5.2) that only the yx -component Σ_{yx} of the stress tensor is non-zero. Furthermore, the pressure can only vary in the y -direction in this case, so that eq.(174) simplifies to,

$$\rho \frac{\partial}{\partial t} v_x(y, t) = \frac{\partial}{\partial y} \Sigma_{yx}(y, t) = \eta_0 \frac{\partial^2}{\partial y^2} v_x(y, t), \quad (175)$$

Note the similarity of this equation of motion and the equation of motion (161) for the number density ρ of colloidal spheres (not to be confused with the ρ in the above equation, which is the mass density of the fluid). Fourier transformation with respect to y gives,

$$\rho \frac{\partial}{\partial t} v_x(k, t) = i k \Sigma_{yx}(y, t) = -\eta_0 k^2 v_x(k, t). \quad (176)$$

According to Onsager's regression hypothesis we thus have,

$$\rho \frac{\partial}{\partial t} \langle v_x(k, t) v_x(-k, t') \rangle_0 = -\eta_0 k^2 \langle v_x(k, t) v_x(-k, t') \rangle_0. \quad (177)$$

with the solution,

$$\langle v_x(k, t) v_x(-k, t') \rangle_0 = \langle v_x(k, 0) v_x(-k, 0) \rangle_0 \exp \left\{ -\frac{\eta_0}{\rho} k^2 (t - t') \right\}. \quad (178)$$

Since the equilibrium pdf is $\sim \exp\{-\beta[\Phi + \frac{1}{2}m \sum_j v_j^2]\}$, where the interaction potential Φ is independent of velocities, position coordinates and velocities are statistically independent variables, the velocities of different particles are independent, and the average velocities are 0. Here, m is the mass of a fluid molecule. Hence, (with $v_{i,x}$ the x -component of the velocity and y_i the y -component of the position coordinate of particle i),

$$\begin{aligned} \langle v_x(k, 0) v_x(-k, 0) \rangle_0 &= \int dy \int dy' \exp\{-ik(y - y')\} \sum_{i,j=1}^N \langle v_{i,x} v_{j,x} \delta(y - y_i) \delta(y' - y_j) \rangle_0 \\ &= \sum_{i,j=1}^N \langle \exp\{-ik(y_i - y_j)\} \rangle_0 \langle v_{i,x} v_{j,x} \rangle_0 = N \langle v_x v_x \rangle_0, \end{aligned}$$

where v_x is the transversal velocity of a single particle. According to the equipartition theorem, $\langle v_x v_x \rangle_0 = k_B T / m$. Substitution into eq.(178) gives,

$$\langle v_x(k, t) v_x(-k, t') \rangle_0 = \frac{N k_B T}{m} \exp \left\{ -\frac{\eta_0}{\rho} k^2 (t - t') \right\}. \quad (179)$$

Consider the second order time-derivative of the left hand-side,

$$\frac{\partial^2}{\partial t^2} \langle v_x(k, t) v_x(-k, t') \rangle_0 = \langle v_x(k | \mathbf{X}) \exp\{\hat{\mathcal{L}}_{eq}(t - t')\} \hat{\mathcal{L}}_{eq}^2 [P_{eq}(\mathbf{X}) v_x(-k | \mathbf{X})] \rangle_0. \quad (180)$$

From eqs.(136,137,166) this can be rewritten as,

$$\begin{aligned} \frac{\partial^2}{\partial t^2} \langle v_x(k, t) v_x(-k, t') \rangle_0 &= - \langle [\hat{\mathcal{L}}_{eq} v_x(k | \mathbf{X})] \exp\{\hat{\mathcal{L}}_{eq}(t-t')\} P_{eq}(\mathbf{X}) [\hat{\mathcal{L}}_{eq} v_x(-k | \mathbf{X})] \rangle_0 \\ &\equiv - \frac{1}{m^2} \langle j_x(k, t) j_x(-k, t) \rangle_0, \end{aligned} \quad (181)$$

where the "current" j is defined as,

$$\begin{aligned} j_x(k | \mathbf{X}) &\equiv m \hat{\mathcal{L}}_{eq} v_x(k | \mathbf{X}) \\ &= m \frac{d}{dt} v_x(k | \mathbf{X}(t)) = \sum_{j=1}^N \left\{ ik \frac{p_{j,y} p_{j,x}}{m} - F_{j,x} \right\} \exp\{-iky_j\}. \end{aligned} \quad (182)$$

The second equation follows from,

$$\frac{d}{dt} F(\mathbf{X}(t)) = \hat{\mathcal{L}}_{eq} F(\mathbf{X}), \quad (183)$$

for any phase function F , which is consequence of Newton's equation of motion. The second part of these equations follows from explicit differentiation with respect to t and using the expression (46) for the Liouville operator. This equation shows that j_x is the momentum current. Since this current is in the x -direction and k is the magnitude of the wave vector that points in the y -direction, it is commonly referred to as *the transversal current*. Differentiating eq.(179) twice, a subsequent time-integration and using that the mass density ρ is equal to mN/V leads to the Green-Kubo formula for the viscosity,

$$\eta_0 = \frac{1}{V k_B T} \lim_{k \rightarrow 0} \frac{1}{k^2} \int_0^\infty d\tau \langle j_x(k, \tau) j_x(-k, 0) \rangle_0, \quad (184)$$

where the zero wave vector limit has been taken, since the phenomenological theory is only valid in that limit.

The Green-Kubo formula can be written in terms of a stress-stress correlation function. In order to obtain a microscopic expression for the stress tensor, we should find the tensor σ such that $j_x = ik\sigma_{yx}$, in analogy with its macroscopic counter part in eq.(175) in Fourier transformed form. According to eq.(182) the microscopic stress tensor should obey the relation,

$$ik \sigma_{yx}(k | \mathbf{X}) = j_x(k | \mathbf{X}) = ik \sum_{j=1}^N \left\{ \frac{p_{j,y} p_{j,x}}{m} - \frac{1}{ik} F_{j,x} \right\} \exp\{-iky_j\}. \quad (185)$$

In the small wave vector limit we have,

$$\frac{1}{ik} \exp\{-iky_j\} = \frac{1}{i} \frac{\partial}{\partial k} \exp\{-iky_j\} = -y_j \exp\{-iky_j\}. \quad (186)$$

Hence, combining eqs.(185,186), the following expression for (the small wave vector limit) of the microscopic stress tensor is obtained,

$$\sigma_{yx}(k | \mathbf{X}) = \sum_{j=1}^N \left\{ \frac{p_{j,y} p_{j,x}}{m} + y_j F_{j,x} \right\} \exp\{-iky_j\}. \quad (187)$$

Generalizing this to more general flows, the position dependent microscopic stress tensor is given by,

$$\sigma(\mathbf{r}|\mathbf{X}) = \sum_{j=1}^N \left\{ \frac{\mathbf{p}_j \mathbf{p}_j}{m} + \mathbf{r}_j \mathbf{F}_j \right\} \delta(\mathbf{r} - \mathbf{r}_j) . \quad (188)$$

From eq.(185) and the Green-Kubo formula (184) in terms of the current-current correlation function we thus arrive at the following formula in terms of the stress tensor correlation function,

$$\eta_0 = \frac{1}{V k_B T} \lim_{k \rightarrow 0} \int_0^\infty d\tau \langle \sigma_{yx}(k, \tau) \sigma_{yx}(-k, 0) \rangle_0 , \quad (189)$$

Together with the microscopic expression (187) for the stress tensor, this formula enables to obtain the shear viscosity by means of simulations where particle coordinates and velocities are tracked.

8.4 Some remarks on the Onsager approach

Phenomenological equations of motion in combination with Onsager's regression hypothesis predict an exponential time dependence of time-correlation functions. Such an exponential dependence is also predicted from linear response theory when non-local effects and memory effects in response equations like (133) are neglected, that is, when the response function $\Xi(\mathbf{r} - \mathbf{r}', t - t')$ is assumed to be only non-zero for $\mathbf{r} = \mathbf{r}'$ and $t = t'$. There may be non-exponential time dependencies like long-time tails. The analysis is valid more generally, also for non-single exponential decay. The generalization of, for example eq.(161) to include memory and non-local effects is,

$$\frac{\partial}{\partial t} \rho(\mathbf{r}, t) = \int d\mathbf{r}' \int_{-\infty}^t dt' D_c(\mathbf{r} - \mathbf{r}', t - t') \nabla'^2 \rho(\mathbf{r}', t') . \quad (190)$$

where the kernel D_c is the generalized collective diffusion coefficient. The analysis can now be repeated after Fourier transformation both with respect to \mathbf{r} and t , which gives,

$$i \omega \rho(\mathbf{k}, \omega) = - D_c(\mathbf{k}, \omega) k^2 \rho(\mathbf{k}, \omega) . \quad (191)$$

Onsager's regression hypothesis can be applied here to obtain eq.(164) in time-Fourier transformed form. The entire analysis can be copied to obtain the Green-Kubo formula (172), again in time-Fourier transformed form. Now the limit where $\omega \rightarrow 0$ of the resulting Green-Kubo formula must be taken, since the phenomenological coefficient in the original Fick's law (161) is only valid for slowly varying fields, such that memory effects can be neglected. The Green-Kubo formulas obtained in the previous two subsections are therefore more generally valid, also when the correlation functions are not single-exponential in time.

Two important theories are not addressed here : the Mori-Zwanzig formalism to derive from the Liouville equation, without any assumptions, equations of motion for time-correlation functions, and Einstein's theory where probability density functions for fluctuations of thermodynamic variables are defined. The treatment of these theories is beyond the scope of the present chapter.

9 Additional Reading

Much of the above treated material can be found in textbooks. Linear response theory and Green-Kubo formulas are treated in the book of Kubo [6] and, for example Reichl [7]. Computer simulations techniques to obtain transport coefficients based on Green-Kubo formulas are treated in ref.[8]. The books of Russel [9] and Dhont [10] are specialized to colloidal systems.

References

- [1] J.M. Deutsch, I.J. Oppenheim, J. Chem. Phys. **54**, 3547 (1971).
- [2] T.J. Murphy, J.L. Aguirre, J. Chem. Phys. **57**, 2098 (1972).
- [3] C.W. Oseen, *Neuere Methoden und Ergebnisse in der Hydrodynamik*. Akademische Verlagsgesellschaft, Leipzig, 1927.
- [4] J. Vogel, B.U. Felderhof, J. Chem. Phys. **97**, 6744 (1992).
- [5] S. Kim, S.J. Karrila, *Microhydrodynamics*, Butterworth-Heinemann, 1991.
- [6] R. Kubo, M. Toda, N. Hashisume, *Statistical Physics II : Nonequilibrium Statistical Mechanics*, Springer-Verlag, Berlin, 1978.
- [7] L.E. Reichl, *A Modern Course in Statistical Physics*, Edwards Arnold Publishers, 1980.
- [8] D.J. Evans, G.P. Morriss, *Statistical Mechanics of Nonequilibrium Liquids*, Academic Press, London, 1990.
- [9] W.B. Russel, D.A. Saville, W.R. Schowalter, *Colloidal Dispersions*, Cambridge University Press, Cambridge, 1991.
- [10] J.K.G. Dhont, *An Introduction to Dynamics of Colloids*, Elsevier, Amsterdam, 1996.