Theor Chim Acta (1992) 82: 75–91

Theoretica
Chimica Acta

The time evolution of the pair distribution function of polymeric systems

C. F. Curtiss

Theoretical Chemistry Institute, Department of Chemistry, University of Wisconsin, Madison, WI 53706, USA

Received December 28, 1990/Accepted May 20, 1991

Summary. The stress tensor of a polymeric system, solution or melt, is the sum of "single molecule" terms which may be expressed as integrals involving the distribution function in the phase space of a single molecule and "intermolecular" terms which involve the distribution function in the configuration space of pairs of molecules. The evaluation of the single molecule terms is usually based on the solution of the "diffusion" equation in the configuration space of a single molecule. In the present development, an analogous "diffusion" equation in the configuration space of a pair of molecules is developed. The development is based on a generalization of the "time-smoothing" ideas introduced by Kirkwood. Expressions are obtained for the various friction coefficients as time correlation functions.

Key words: Polymeric systems – Pair distribution function – Stress tensor – Distribution function

1. Introduction

The theory of the rheological behavior of polymeric systems involves a statistical study of the behavior of the polymeric molecules and that of the solvent molecules, if any. Most of the developments of these theories are "mean field" theories in which the environment of a particular polymeric molecule, which is made up of all the other polymeric molecules and the solvent molecules, is idealized as a continuous background, usually a continuous Newtonian fluid. An essential problem is then the determination of the distribution functions in the configuration spaces of the single polymeric molecules.

The statistical expression for the stress tensor is an ensemble average. If the forces are derivable from potentials of the form described in the following, a portion of this term, the "single molecule term" may be written in terms of a distribution function in the phase space of a single molecule; the remaining terms involve the distribution functions in the configuration spaces of pairs of molecules of the same or different species. In most treatments, only the single molecule terms are considered. In the present discussion, we develop an equation for the time evolution of the pair configuration space distribution functions.

Approximations to these functions will lead to more accurate expressions for the stress tensor and thus for the various rheological properties. In general, the notation of Ref. [1] is used.

2. The system

Let $\mathbf{r}^{\alpha i}$ be the vector to the center of mass of molecule, i, of species, α. The configuration coordinates of the system are taken to be the set of vectors, $\mathbf{r}^{\alpha i}$, and the sets of generalized coordinates, $Q_s^{\alpha i}$, associated with each of the molecules. The conjugate momenta are denoted $\mathbf{p}^{\alpha i}$ and $P_s^{\alpha i}$. These coordinates denoted collectively as $x^{\alpha i}$ represent the subset of the phase space coordinates of the entire system which describe the dynamical state of molecule i of species α. It is also convenient to let x_α represent the coordinates of a phase space of a single molecule of species α.

The distribution function in the phase space of the full system, indicated simply by x is denoted by $f(x, t)$ and is normalized to unity:

$$\int f(x, t)\, dx = 1 \tag{2.1}$$

We then define a dynamical variable, $B(x)$, in the full space as:

$$B(x) = \sum_{ij} \delta(x^{\alpha i} - x_\alpha)\delta(x^{\beta i} - x_\beta) \tag{2.2}$$

where $\delta(x^{\alpha i} - x_\alpha)$ represents a product of δ-functions in the variables indicated.

The average of a dynamical variable, such as $B(x)$, over the ensemble described by the distribution function $f(x, t)$ is denoted by:

$$\langle B(x) \rangle = \int B(x) f(x, t)\, dx \tag{2.3}$$

It follows directly from the definition (see Eq. (17.3-3) of Ref. [1]), that the average the dynamical variable defined by Eq. (2.2):

$$\langle B(x) \rangle = f^{(2)}_{\alpha\beta}(x_\alpha, x_\beta, t) \tag{2.4}$$

is the distribution function in the phase space of a pair of molecules of species α and β.

The distribution function in the configuration space of a pair of molecules is the integral of this function over all the conjugate momenta:

$$\Psi^{(2)}_{\alpha\beta}(\mathbf{r}^\alpha, Q^\alpha, \mathbf{r}^\beta, Q^\beta, t) = \int f^{(2)}_{\alpha\beta}(x_\alpha, x_\beta, t)\, d\mathbf{p}^\alpha\, dP^\alpha\, d\mathbf{p}^\beta\, dP^\beta \tag{2.5}$$

It is frequently convenient to change variables from the pair $\mathbf{r}^\alpha$ and $\mathbf{r}^\beta$ to the pair $\mathbf{R}^{\alpha\beta}$ and $\mathbf{r}$. The vector:

$$\mathbf{R}^{\alpha\beta} = \mathbf{r}^\beta - \mathbf{r}^\alpha \tag{2.6}$$

is the vector from the center of mass of a molecule of species α to that of a molecule of species β, and $\mathbf{r}$ is the vector to the center of mass of the two molecule system. The pair phase space distribution function expressed in terms of these variables is denoted $\tilde{f}^{(2)}_{\alpha\beta}(\mathbf{r}, \mathbf{R}, Q^\alpha, Q^\beta, \mathbf{p}^\alpha, P^\alpha, \mathbf{p}^\beta, P^\beta, t)$, and the corresponding configuration space distribution function is denoted $\tilde{\Psi}^{(2)}_{\alpha\beta}(\mathbf{r}, \mathbf{R}, Q^\alpha, Q^\beta, t)$.

The distribution function in the phase space of a single molecule is:

$$f_\alpha(x_\alpha, t) = \sum_i \langle \delta(x^{\alpha i} - x_\alpha) \rangle \tag{2.7}$$

and the distribution function in the configuration space of a single molecule is:

$$\Psi_\alpha(x_\alpha, t) = \int f_\alpha(x_\alpha, t)\, d\boldsymbol{p}^\alpha\, d\boldsymbol{P}^\alpha \tag{2.8}$$

As in the usual treatments [1], we take the total potential energy of the system, $\Phi^{(T)}$, to be the sum of contributions from intermolecular effects, Φ, from intramolecular effects, the $\phi^{\alpha i}$, and external effects, the $\phi^{(e)\alpha i}$:

$$\Phi^{(T)} = \Phi + \sum_{\alpha i} (\phi^{\alpha i} + \phi^{(e)\alpha i}) \tag{2.9}$$

The total intermolecular potential energy of the full system is taken to be the sum of terms associated with all pairs of molecules:

$$\Phi = (1/2) \sum_{\alpha i, \beta j} \Phi^{\alpha i, \beta j} \tag{2.10}$$

We then take the potential energy associated with a pair of molecules of species α and β to be the sum of terms associated with interactions between all pairs of "beads" making up the two molecules:

$$\Phi^{\alpha\beta} = \sum_{\mu\nu} \Phi_{\nu\mu}^{\alpha\beta} \tag{2.11}$$

The potential, $\Phi_{\nu\mu}^{\alpha\beta}$, which describes the force acting between bead ν of a molecule of species α and bead μ of a molecules of species β is assumed to depend only on the distance between the particular pair of beads:

$$R_{\nu\mu}^{\alpha\beta} = |\boldsymbol{R}_{\nu\mu}^{\alpha\beta}| \tag{2.12}$$

where

$$\boldsymbol{R}_{\nu\mu}^{\alpha\beta} = \boldsymbol{r}_\mu^\beta - \boldsymbol{r}_\nu^\alpha \tag{2.13}$$

is the vector from bead $\alpha\nu$ to bead $\beta\mu$.

The intramolecular potential associated with a molecule of species α, ϕ^α, is taken to be a function of the internal coordinates, Q_s^α, only, and the potential associated with external forces, $\phi^{(e)\alpha}$, is taken to be a function the Q_s^α and the position of center of mass, $\boldsymbol{r}^\alpha$.

The force on the center of mass of a molecule of species α due to the interaction of bead $\alpha\nu$ and bead $\beta\mu$ is then:

$$\boldsymbol{F}_{\nu\mu}^{\alpha\beta} = -\frac{\partial}{\partial \boldsymbol{r}^\alpha} \Phi_{\nu\mu}^{\alpha\beta} \tag{2.14}$$

and the total force on the center of mass due to the interactions of bead $\alpha\nu$ with the beads of a molecule of species β is:

$$\boldsymbol{F}_\nu^{\alpha\beta} = \sum_\mu \boldsymbol{F}_{\nu\mu}^{\alpha\beta} \tag{2.15}$$

Then the total force on a molecule of species α due to the beads of a molecule of species β is:

$$\boldsymbol{F}^{\alpha\beta} = \sum_\nu \boldsymbol{F}_\nu^{\alpha\beta} \tag{2.16}$$

Finally, the total force on molecule αi is:

$$\boldsymbol{F}^{(T)\alpha i} = \boldsymbol{F}^{(e)\alpha i} + \sum_{\beta j} \boldsymbol{F}^{\alpha i, \beta j} \tag{2.17}$$

where

$$\boldsymbol{F}^{(e)\alpha i} = -\frac{\partial}{\partial \boldsymbol{r}^{\alpha i}} \phi^{(e)\alpha i} \tag{2.18}$$

is the external force on the molecule.

It is also convenient to define a set of generalized forces (which lead to changes in the orientations and internal configurations of the molecules). First, we have the intermolecular contribution:

$$\mathscr{F}_s^{\alpha\beta} = -\frac{\partial}{\partial Q_s^\alpha} \sum_{\mu\nu} \Phi_{\nu\mu}^{\alpha\beta} \tag{2.19}$$

The intramolecular term is:

$$\mathscr{F}_s^{\alpha} = -\frac{\partial}{\partial Q_s^\alpha} \phi^{\alpha} \tag{2.20}$$

and the effects of external potentials are given by:

$$\mathscr{F}_s^{(e)\alpha} = -\frac{\partial}{\partial Q_s^\alpha} \phi^{(e)\alpha} \tag{2.21}$$

The total generalized force on molecule αi is then:

$$\mathscr{F}_s^{(T)\alpha i} = \mathscr{F}_s^{\alpha i} + \mathscr{F}_s^{(e)\alpha i} + \sum_{\beta j} \mathscr{F}_s^{\alpha i, \beta j} \tag{2.22}$$

Next, we define a "hydrodynamic force", in the phase space of a single molecule, on bead ν of a molecule of species α by the relation:

$$\boldsymbol{F}_\nu^{(\eta)\alpha} f_\alpha(x_\alpha, t) = \sum_\beta \iiiint \boldsymbol{F}_\nu^{\alpha\beta} \tilde{f}_{\alpha\beta}^{(2)}(\boldsymbol{r}, \boldsymbol{R}, Q^\alpha, Q^\beta, \boldsymbol{p}^\alpha, P^\alpha, \boldsymbol{p}^\beta, P^\beta, t)\, d\boldsymbol{R}\, dQ^\beta\, d\boldsymbol{p}^\beta\, dP^\beta \tag{2.23}$$

An integration of this equation over the momentum coordinates leads to:

$$\boldsymbol{F}_\nu^{(h)\alpha} \Psi_\alpha(\boldsymbol{r}^\alpha, Q^\alpha, t) = \sum_\beta \iiint \boldsymbol{F}_\nu^{\alpha\beta} \tilde{\Psi}_{\alpha\beta}^{(2)}(\boldsymbol{r}, \boldsymbol{R}, Q^\alpha, Q^\beta, t)\, dQ^\beta\, d\boldsymbol{R} \tag{2.24}$$

where $\boldsymbol{F}_\nu^{(h)\alpha}$ is the hydrodynamic force, in the configuration space, on bead ν of a molecule of species α, defined by Eq. (18.1-18) of Ref. [1].

In the present treatment, it is convenient to define a similar average force, the "coupling force", as an average force, in the phase space of a pair of molecules of species α and β, on bead ν of a molecule of species α, due to all of the molecules other than the particular pair. Explicitly, this force is defined by the relation:

$$\boldsymbol{F}_\nu^{(\eta)\alpha\beta} f_{\alpha\beta}^{(2)}(x_\alpha, x_\beta, t) = \sum_\gamma \int \boldsymbol{F}_\nu^{\alpha\gamma} f_{\alpha\beta\gamma}^{(3)}(x_\alpha, x_\beta, x_\gamma, t)\, dx_\gamma \tag{2.25}$$

where $f_{\alpha\beta\gamma}^{(3)}(x_\alpha, x_\beta, x_\gamma, t)$ is the contracted distribution function in the phase space of three molecules defined in a manner similar to that of $f_{\alpha\beta}^{(2)}(x_\alpha, x_\beta, t)$ by Eq. (2.4). From this definition, it follows that:

$$\boldsymbol{F}_\nu^{(\eta)\alpha\beta} f_{\alpha\beta}^{(2)}(x_\alpha, x_\beta, t) = \sum_{ij} \int \boldsymbol{F}_\nu^{\alpha i} \delta(x^{\alpha i} - x_\alpha)\delta(x^{\beta j} - x_\beta) f(x, t)\, dx \tag{2.26}$$

This force arises in the following developments.

We note that in the limit that the molecules α and β are far separated, that is that $|\boldsymbol{r}^{\beta} - \boldsymbol{r}^{\alpha}| \rightarrow \infty$, the coordinates of the molecules are uncorrelated so that:

$$f_{\alpha\beta}^{(2)}(x_\alpha, x_\beta, t) = f_\alpha(x_\alpha, t) f_\beta(x_\beta, t) \tag{2.27}$$

Furthermore, if this is true and if the forces are of sufficiently short range, contributions to the integral on the right of Eq. (2.25) arise only when β is also far from γ and thus we may replace $f_{\alpha\beta\gamma}^{(3)}(x_\alpha, x_\beta, x_\gamma, t)$ in the integrand on the right of Eq. (2.25) by the product $f_{\alpha\gamma}^{(2)}(x_\alpha, x_\gamma, t) f_\beta(x_\beta, t)$. Thus, in the limit, that $|\boldsymbol{r}^{\beta} - \boldsymbol{r}^{\alpha}| \rightarrow \infty$:

$$\boldsymbol{F}_\nu^{(\eta)\alpha\beta} f_\alpha(x_\alpha, t) f_\beta(x_\beta, t) \rightarrow \sum_\gamma \int \boldsymbol{F}_\nu^{\alpha\gamma} f_{\alpha\gamma}^{(2)}(x_\alpha, x_\gamma, t) f_\beta(x_\beta, t)\, dx_\gamma \tag{2.28}$$

It then follows from Eq. (2.23) that in this limit:

$$\boldsymbol{F}_\nu^{(\eta)\alpha\beta} \rightarrow \boldsymbol{F}_\nu^{(\eta)\alpha} \tag{2.29}$$

that is, the dynamical state of the molecule of species β affects this coupling force on the molecule of species α only if it is sufficiently close the molecule of species α.

3. The pair distribution function

To develop an equation for the time evolution of the pair distribution function, we follow a development similar to that of section 17.5 of Ref. [1]. It follows directly from the Liouville equation that, in general:

$$\frac{\partial}{\partial t} \langle B(x) \rangle = \langle \mathscr{L} B(x) \rangle \tag{3.1}$$

where $B(x)$ is an arbitrary dynamical variable in the phase space of the full system and $\mathscr{L}$ is the Liouville operator of the system. We then find that using the dynamical variable, B, defined by Eq. (2.2), this general equation of change, becomes:

$$\left(\frac{\partial}{\partial t} + \mathscr{L}_{\alpha\beta}^{(2)}\right) f_{\alpha\beta}^{(2)}(x_\alpha, x_\beta, t) = -\sum_\nu \mathscr{P}_\nu^\alpha \cdot \boldsymbol{F}_\nu^{(\eta)\alpha\beta} f_{\alpha\beta}^{(2)}(x_\alpha, x_\beta, t) - \sum_\nu \mathscr{P}_\nu^\beta \cdot \boldsymbol{F}_\nu^{(\eta)\beta\alpha} f_{\alpha\beta}^{(2)}(x_\alpha, x_\beta, t) \tag{3.2}$$

where $\boldsymbol{F}_\nu^{(\eta)\alpha\beta}$ is the coupling force defined by Eq. (2.25), $\mathscr{L}_{\alpha\beta}^{(2)}$ is the Liouville operator of an isolated pair of molecules of species, α and β:

$$\mathscr{L}_{\alpha\beta}^{(2)} = \mathscr{L}_\alpha^{(1)} + \mathscr{L}_\beta^{(1)} + \sum_\nu \boldsymbol{F}_\nu^{\alpha\beta} \cdot \mathscr{P}_\nu^\alpha + \sum_\nu \boldsymbol{F}_\nu^{\beta\alpha} \cdot \mathscr{P}_\nu^\beta \tag{3.3}$$

and $\mathscr{L}_\alpha^{(1)}$ is the Liouville operator of an isolated molecule of species, α, including the effects of the intramolecular and external potentials. The $\mathscr{P}_\nu^\alpha$ are vector operators defined as:

$$\mathscr{P}_\nu^\alpha = \frac{\partial}{\partial \boldsymbol{p}^\alpha} + \frac{1}{(m_\nu^\alpha)^{1/2}} \sum_s \boldsymbol{b}_{\nu s}^\alpha \frac{\partial}{\partial P_s^\alpha} \tag{3.4}$$

where the $\boldsymbol{b}_{vs}^{\alpha}$ are the base vectors defined as:

$$\boldsymbol{b}_{vs}^{\alpha} = (m_v^{\alpha})^{1/2} \frac{\partial}{\partial Q_s^{\alpha}} \boldsymbol{R}_v^{\alpha} \tag{3.5}$$

and m_v^{α} is the mass of bead v of a molecule of species α. Equation (3.2) with $\boldsymbol{F}_v^{(\eta)\alpha\beta}$ and $\boldsymbol{F}_v^{(\eta)\beta\alpha}$ set to zero is the Liouville equation of an isolated pair of molecules of species α and β. The forces, $\boldsymbol{F}_v^{(\eta)\alpha\beta}$ and $\boldsymbol{F}_v^{(\eta)\beta\alpha}$, describe the coupling of a typical pair of such molecules with the remaining portion of the system, that is, with the environment. Equation (3.2) is simply an integral of the Liouville equation of the system and thus is exact. The "truncation problem" which is discussed in the following is that of obtaining approximate expressions for the coupling forces, and the method used is a generalization of that which leads to the usual "diffusion" equation for the distribution function in the configuration space of a single polymeric molecule.

In an important series of papers, Kirkwood [2] developed a basic approach to the statistical mechanical theory of the nonequilibrium behavior of fluids. Kirkwood considered primarily systems made up of molecules idealized as mass points and obtained explicit expressions for the stress tensor and other statistical quantities as integrals involving contracted distribution functions. Our previous development [1] of the expression for the stress tensor of a system containing polymeric molecules is largely an extension to systems of more complex molecules of the approach used by Irving and Kirkwood [3]. The integral expressions are exact, within the limitations of the molecular models. The essential problem which introduces irreversibility, is that of obtaining a "closed" equation for the time evolution of the pertinent distribution functions.

Kirkwood [2] introduced arguments which led to the conclusion that irreversibility enters the equations through a "time-smoothing". This time-smoothing is over a time interval, τ, which is small on a macroscopic time scale but long on the scale of molecular events. This time-smoothing leads to equations for the hydrodynamic forces which are similar in form to those which are usually introduced through a "Stokes' law" type of empricism. In an earlier paper [4], these ideas were used to develop the usual [1] "diffusion equation" in the configuration space of a single molecule and expressions for the "friction coefficients". Here we generalize these ideas to the configuration spaces of pairs of molecules.

Introducing the time-smoothing ideas, we average Eq. (3.2) over a previous time interval of duration, τ, starting at the "present" time. The result is an equation of very similar form:

$$\left(\frac{\partial}{\partial t} + \mathscr{L}_{\alpha\beta}^{(2)}\right)\bar{f}_{\alpha\beta}^{(2)}(x_\alpha, x_\beta, t) = -\sum_{v} \mathscr{P}_v^{\alpha} \cdot \bar{\boldsymbol{F}}_v^{(\eta)\alpha\beta}\bar{f}_{\alpha\beta}^{(2)}(x_\alpha, x_\beta, t) - \sum_{v} \mathscr{P}_v^{\beta} \cdot \bar{\boldsymbol{F}}_v^{(\eta)\beta\alpha}\bar{f}_{\alpha\beta}^{(2)}(x_\alpha, x_\beta, t) \tag{3.6}$$

in which the pair distribution function, $f_{\alpha\beta}^{(2)}(x_\alpha, x_\beta, t)$, is replaced by the time-smoothed function:

$$\bar{f}_{\alpha\beta}^{(2)}(x_\alpha, x_\beta, t) = \frac{1}{\tau} \int_0^{\tau} f_{\alpha\beta}^{(2)}(x_\alpha, x_\beta, t - t')\, dt' \tag{3.7}$$

and the coupling force is replaced by the time-smoothed force defined by:

$$\bar{\boldsymbol{F}}_v^{(\eta)\alpha\beta}\bar{f}_{\alpha\beta}^{(2)}(x_\alpha, x_\beta, t) = \frac{1}{\tau} \int_0^{\tau} \boldsymbol{F}_v^{(\eta)\alpha\beta} f_{\alpha\beta}^{(2)}(x_\alpha, x_\beta, t - t')\, dt' \tag{3.8}$$

It follows from the definition, Eq. (2.25), that this force may also be written in the form:

$$\bar{\boldsymbol{F}}_\nu^{(\eta)\alpha\beta}\bar{f}^{(2)}_{\alpha\beta}(x_\alpha, x_\beta, t) = \frac{1}{\tau}\sum_\gamma \int_0^\tau \int \boldsymbol{F}_\nu^{\alpha\beta} f^{(3)}_{\alpha\beta\gamma}(x_\alpha, x_\beta, x_\gamma, t-t')\, dx_\gamma\, dt' \tag{3.9}$$

or in terms of the distribution function in the phase space of the full system, as:

$$\bar{\boldsymbol{F}}_\nu^{(\eta)\alpha\beta}\bar{f}^{(2)}_{\alpha\beta}(x_\alpha, x_\beta, t) = \frac{1}{\tau}\sum_{ij} \int_0^\tau \int \boldsymbol{F}_\nu^{\alpha i}\delta(x^{\alpha i} - x_\alpha)\delta(x^{\beta j} - x_\beta) f(x, t-t')\, dx\, dt' \tag{3.10}$$

where $\boldsymbol{F}_\nu^{\alpha i}$ is the intermolecular force on bead ν of molecule αi.

The essential approximation which leads to the decoupling of the equation for the pair distribution function from that of the higher order distribution functions is an approximation for the ensemble distribution function. In the present development, we again [4] generalize the ideas introduced by Kirkwood [2]. In evaluating the term in the sum of the right of Eq. (3.10) associated with a particular pair of values of i and j, we take as an approximation to the ensemble distribution function:

$$f(x, t) = f^{(2)}_{\alpha\beta}(x^{\alpha i}, x^{\beta j}, t)\frac{f_{\mathrm{eq}}(x, t)}{f^{(2)}_{\alpha\beta,\mathrm{eq}}(x^{\alpha i}, x^{\beta j}, t)} \tag{3.11}$$

where $f_{\mathrm{eq}}(x, t)$ and $f^{(2)}_{\alpha\beta,\mathrm{eq}}(x^{\alpha i}, x^{\beta j}, t)$ are the equilibrium ensemble and pair distribution functions characteristic of the local macroscopic conditions. In this approximation, the dependence of the ensemble distribution on the coordinates of molecules, αi and βj is exact but the dependence on the coordinates of the remaining molecules in the system is that determined by local equilibrium conditions. This approximation is analogous to the mean field ideas which are usually used in the developments of theories of polymeric systems as indicated in the previous development [4], but now it is a pair of molecules (rather than a single molecule) in the "mean field" of the remaining molecules.

Since

$$f(x, t-t') = f(x_0, t) \tag{3.12}$$

where

$$x_0 = e^{t'\mathscr{L}}x \tag{3.13}$$

and

$$f_{\mathrm{eq}}(x_0, t) = f_{\mathrm{eq}}(x, t) \tag{3.14}$$

we find on expansion, that, to terms of first order in the time displacements:

$$f(x, t-t') = f(x, t)\left\{1 + \left[(x_0^{\alpha i} - x^{\alpha i})\frac{\partial}{\partial x^{\alpha i}} + (x_0^{\beta j} - x^{\beta j})\frac{\partial}{\partial x^{\beta j}}\right] + \cdots\right\}$$
$$\times \ln\frac{f^{(2)}_{\alpha\beta}(x^{\alpha i}, x^{\beta j}, t)}{f^{(2)}_{\alpha\beta,\mathrm{eq}}(x^{\alpha i}, x^{\beta j}, t)} \tag{3.15}$$

where sums over the coordinates $x^{\alpha i}$ and $x^{\beta j}$ are implied.

Next, we define the time averages associated with the various coordinates and momenta, collectively, as:

$$\zeta_{\nu}^{\alpha i,\beta j} = \frac{1}{\tau k T} \int_0^{\tau} \boldsymbol{F}_{\nu}^{\alpha i}(x_0^{\beta j} - x^{\beta j})\, dt' \tag{3.16}$$

where T is the local temperature. These quantities are functions in the phase space of the complete system.

It follows from Eq. (3.13) that:

$$(x_0^{\beta j} - x^{\beta j}) = (e^{t'\mathscr{L}} - 1)x^{\beta j} \tag{3.17}$$

which may be rewritten in the integral form:

$$(x_0^{\beta j} - x^{\beta j}) = \int_0^{t'} e^{t''\mathscr{L}}(\mathscr{L}x^{\beta j})\, dt'' \tag{3.18}$$

When this integral form is used in the definition of the $\zeta_{\nu}^{\alpha i,\beta j}$, Eq. (3.16), and the order of the time integrals interchanged, one finds that:

$$\zeta_{\nu}^{\alpha i,\beta j} = \frac{1}{kT} \int_0^{\tau} \left(1 - \frac{t}{\tau}\right) \boldsymbol{F}_{\nu}^{\alpha i}(e^{t\mathscr{L}} x^{\beta j})\, dt \tag{3.19}$$

One may now take the limit that $\tau \to \infty$. We thus find that the $\zeta_{\nu}^{\alpha i,\beta j}$ are the time correlation functions:

$$\zeta_{\nu}^{\alpha i,\beta j} = \frac{1}{kT} \int_0^{\infty} \boldsymbol{F}_{\nu}^{\alpha i}(e^{t\mathscr{L}} x^{\beta j})\, dt \tag{3.20}$$

We next define an average friction coefficient, as a function in the phase space of a pair of molecules of species α and β by relation:

$$\begin{aligned} \zeta_{\nu}^{(\eta)\alpha\beta} \bar{f}_{\alpha\beta}^{(2)}(x_\alpha, x_\beta, t) &= \sum_{ij} \int \zeta_{\nu}^{\alpha i,\beta j} \delta(x^{\alpha i} - x_\alpha)\delta(x^{\beta j} - x_\beta) f(x, t)\, dx \\ &= \frac{1}{kT} \sum_{ij} \left\langle \int_0^{\infty} [\boldsymbol{F}_{\nu}^{\alpha i}\, e^{t\mathscr{L}} \mathscr{L} x^{\beta j}] \delta(x^{\alpha i} - x_\alpha)\delta(x^{\beta j} - x_\beta)\, dt \right\rangle \end{aligned} \tag{3.21}$$

where the angular brackets, $\langle \cdots \rangle$, indicate an average over the ensemble distribution function. The superscripts are the species indices of the two factors in the definition of the $\zeta_{\nu}^{\alpha i,\beta j}$, Eq. (3.16). This definition is similar to the definition of the force $\boldsymbol{F}_{\nu}^{(\eta)\alpha\beta}$ by Eq. (2.25). The factors, $\mathscr{L}x^{\beta j}$, in the integrand of this expression are specifically:

$$\mathscr{L}\boldsymbol{r}^{\beta j} = \boldsymbol{p}^{\beta j}/m^{\beta} \tag{3.22}$$

$$\mathscr{L}Q_s^{\beta j} = \sum_t G_{st}^{\beta} P_t^{\beta j} \tag{3.23}$$

$$\mathscr{L}\boldsymbol{p}^{\beta j} = \boldsymbol{F}^{(T)\beta j} \tag{3.24}$$

$$\mathscr{L}P_s^{\beta j} = \mathscr{F}_s^{(T)\beta j} - \tfrac{1}{2} \sum_{\mathrm{tu}} P_t^{\beta j} P_u^{\beta j} \frac{\partial}{\partial Q_s^{\beta j}} G_{\mathrm{tu}}^{\beta j} \tag{3.25}$$

where $\boldsymbol{F}^{(T)\beta j}$ and the $\mathscr{F}_s^{(T)\beta j}$ are the total force and total generalized forces defined by Eqs. (2.17) and (2.22), respectively. It is to be expected that little correlation occurs between the forces and the momenta and hence in the following we neglect the $\zeta_{\nu}^{(\eta)\alpha\beta}$ associated with the configuration coordinates.

When the expression for the distribution function, $f(x, t - t')$, Eq. (3.15), is used in the expression for $\bar{\boldsymbol{F}}_{\nu}^{(\eta)\alpha\beta}$, Eq. (3.10), one finds that:

$$\bar{\boldsymbol{F}}_{\nu}^{(\eta)\alpha\beta} \bar{f}_{\alpha\beta}^{(2)}(x_\alpha, x_\beta, t) = \boldsymbol{F}_{\nu}^{(\eta)\alpha\beta} \bar{f}_{\alpha\beta}^{(2)}(x_\alpha, x_\beta, t) + \boldsymbol{F}_{\nu}^{(\eta,1)\alpha\beta} \bar{f}_{\alpha\beta}^{(2)}(x_\alpha, x_\beta, t) + \cdots$$

where

$$\boldsymbol{F}_\nu^{(\eta,1)\alpha\beta} = kT\left[\zeta_\nu^{(\eta)\alpha\alpha}\frac{\partial}{\partial x_\alpha} + \zeta_\nu^{(\eta)\alpha\beta}\frac{\partial}{\partial x_\beta}\right]\ln\frac{f_{\alpha\beta}^{(2)}(x_\alpha, x_\beta, t)}{f_{\alpha\beta,\mathrm{eq}}^{(2)}(x_\alpha, x_\beta, t)} \tag{3.26}$$

and the sums on the right implied by the notation, x_α, involve only the momentum coordinates. The term, $\boldsymbol{F}_\nu^{(\eta,1)\alpha\beta}$ is the "hydrodynamic force" on bead ν of a molecule of species α as a function in the phase space of a pair of molecules. One thus sees that the effect of the time smoothing is to add this hydrodynamic term.

The equation for the time evolution of the time-smoothed pair distribution function, Eq. (3.6), then becomes:

$$\begin{aligned}\left(\frac{\partial}{\partial t} + \mathscr{L}_{\alpha\beta}^{(2)}\right)\bar{f}_{\alpha\beta}^{(2)}(x_\alpha, x_\beta, t) + \sum_\nu \mathscr{P}_\nu^\alpha \cdot \boldsymbol{F}_\nu^{(\eta)\alpha\beta}\bar{f}_{\alpha\beta}^{(2)}(x_\alpha, x_\beta, t) + \sum_\nu \mathscr{P}_\nu^\beta \cdot \boldsymbol{F}_\nu^{(\eta)\beta\alpha}\bar{f}_{\alpha\beta}^{(2)}(x_\alpha, x_\beta, t)\\ = -\sum_\nu \mathscr{P}_\nu^\alpha \cdot \boldsymbol{F}_\nu^{(\eta,1)\alpha\beta}\bar{f}_{\alpha\beta}^{(2)}(x_\alpha, x_\beta, t) - \sum_\nu \mathscr{P}_\nu^\beta \cdot \boldsymbol{F}_\nu^{(\eta,1)\beta\alpha}\bar{f}_{\alpha\beta}^{(2)}(x_\alpha, x_\beta, t)\end{aligned} \tag{3.27}$$

On comparing this with Eq. (3.2), one sees that the effect of the time-smoothing is essentially that of adding the terms involving the "hydrodynamic forces" $\boldsymbol{F}_\nu^{(\eta,1)\alpha\beta}$ and $\boldsymbol{F}_\nu^{(\eta,1)\beta\alpha}$. The problem of obtaining a closed equation for the pair distribution function then becomes that of evaluating the friction coefficients, the $\zeta_\nu^{(\eta)\alpha\beta}$.

4. The "diffusion" equation

We next consider the contraction of the problem to the configuration spaces of pairs of molecules. First, the time-smoothed configuration distribution function is defined as:

$$\bar{\Psi}_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t) = \int \bar{f}_{\alpha\beta}^{(2)}(x_\alpha, x_\beta, t)\, d\boldsymbol{p}^\alpha\, dP^\alpha\, d\boldsymbol{p}^\beta\, dP^\beta \tag{4.1}$$

We then define averages in the configuration space of pairs by:

$$[\![\cdots]\!]^{\alpha\beta}\bar{\Psi}_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t) = \int (\cdots)\bar{f}_{\alpha\beta}^{(2)}(x_\alpha, x_\beta, t)\, d\boldsymbol{p}^\alpha\, dP^\alpha\, d\boldsymbol{p}^\beta\, dP^\beta \tag{4.2}$$

Then on integrating the equation for the time evolution of the time-smoothed pair distribution, Eq. (3.27), over all the momentum coordinates, one obtains the equation of continuity:

$$\begin{aligned}&\frac{\partial}{\partial t}\bar{\Psi}_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t) + \frac{1}{m^\alpha}\frac{\partial}{\partial \boldsymbol{r}^\alpha}\cdot[\![\boldsymbol{p}^\alpha]\!]^{\alpha\beta}\bar{\Psi}_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t)\\ &+\frac{1}{m^\beta}\frac{\partial}{\partial \boldsymbol{r}^\beta}\cdot[\![\boldsymbol{p}^\beta]\!]^{\alpha\beta}\bar{\Psi}_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t)\\ &+\sum_{\mathrm{st}}\frac{\partial}{\partial Q_s^\alpha}G_{\mathrm{st}}^\alpha[\![P_t^\alpha]\!]^{\alpha\beta}\bar{\Psi}_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t)\\ &+\sum_{\mathrm{st}}\frac{\partial}{\partial Q_s^\beta}G_{\mathrm{st}}^\beta[\![P_t^\beta]\!]^{\alpha\beta}\bar{\Psi}_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t) = 0\end{aligned} \tag{4.3}$$

Next, we multiply the same equation successively by the various momentum coordinates and again integrate over all the momenta to obtain two sets of equations, which may be interpreted as equations of motion in the configuration space of pairs of molecules. First, we define a "generalized Brownian" force, $\mathscr{F}_s^{(b)\alpha\beta}$, by the relation:

$$\begin{aligned}
-\mathscr{F}_s^{(b)\alpha\beta}\bar{\Psi}_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t) = {} & \frac{\partial}{\partial t}\llbracket P_s^\alpha\rrbracket^{\alpha\beta}\bar{\Psi}_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t) \\
& + \frac{1}{m^\alpha}\frac{\partial}{\partial \boldsymbol{r}^\alpha}\cdot\llbracket \boldsymbol{p}^\alpha P_s^\alpha\rrbracket^{\alpha\beta}\bar{\Psi}_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t) \\
& + \frac{1}{m^\beta}\frac{\partial}{\partial \boldsymbol{r}^\beta}\cdot\llbracket \boldsymbol{p}^\beta P_s^\alpha\rrbracket^{\alpha\beta}\bar{\Psi}_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t) \\
& + \sum_{\mathrm{tu}}\frac{\partial}{\partial Q_t^\alpha}G_{\mathrm{tu}}^\alpha\llbracket P_u^\alpha P_s^\alpha\rrbracket^{\alpha\beta}\bar{\Psi}_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t) \\
& + \sum_{\mathrm{tu}}\frac{\partial}{\partial Q_t^\beta}G_{\mathrm{tu}}^\beta\llbracket P_u^\beta P_s^\alpha\rrbracket^{\alpha\beta}\bar{\Psi}_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t) \\
& + \tfrac{1}{2}\sum_{\mathrm{tu}}\left(\frac{\partial}{\partial Q_s^\alpha}G_{\mathrm{tu}}^\alpha\right)\llbracket P_t^\alpha P_u^\alpha\rrbracket^{\alpha\beta}\bar{\Psi}_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t)
\end{aligned} \tag{4.4}$$

Then, on multiplying Eq. (3.27) by P_s^α and integrating, we find that:

$$\mathscr{F}_s^{(b)\alpha\beta} + \mathscr{F}_s^{(\phi)\alpha} + \mathscr{F}_s^{(e)\alpha} + \mathscr{F}_s^{(a)\alpha\beta} + \mathscr{F}_s^{(h)\alpha\beta} = 0 \tag{4.5}$$

where

$$\mathscr{F}_s^{(a)\alpha\beta} = \mathscr{F}_s^{\alpha\beta} + \sum_\nu \frac{1}{(m_\nu^\alpha)^{1/2}}\boldsymbol{b}_{\nu s}^\alpha \cdot \llbracket \boldsymbol{F}_\nu^{(\eta)\alpha\beta}\rrbracket \tag{4.6}$$

and

$$\mathscr{F}_s^{(h)\alpha\beta} = \sum_\nu \frac{1}{(m_\nu^\alpha)^{1/2}}\boldsymbol{b}_{\nu s}^\alpha \cdot \boldsymbol{F}_\nu^{(h)\alpha\beta} \tag{4.7}$$

where

$$\boldsymbol{F}_\nu^{(h)\alpha\beta}\Psi_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t) = \iiiint \boldsymbol{F}_\nu^{(\eta,1)\alpha\beta}f_{\alpha\beta}^{(2)}(x_\alpha, x_\beta, t)\, d\boldsymbol{p}^\alpha\, dP^\alpha\, d\boldsymbol{p}^\beta\, dP^\beta \tag{4.8}$$

Equation (4.5) is an effective force balance in the configuration space of a pair of molecules of species α and β associated with coordinate Q_s^α. The term $\mathscr{F}_s^{(a)\alpha\beta}$ is the sum of an effective force associated with the direct interaction with a molecule of species β and a term associated with the interaction with all the other molecules of species β. The last term on the left of Eq. (4.5) is the "hydrodynamic force", which arises from the terms on the right of Eq. (3.27). If we assume, as an approximation, that the $\zeta_\nu^{(a)\alpha\beta}$ are independent of the momentum coordinates, we find that:

$$\begin{aligned}
\boldsymbol{F}_\nu^{(h)\alpha\beta} = {} & kT\zeta_\nu^{(a)\alpha\alpha}\cdot\left[\!\!\left[\frac{\partial}{\partial \boldsymbol{p}^\alpha}\ln f_{\alpha\beta,\mathrm{eq}}^{(2)}(x_\alpha, x_\beta, t)\right]\!\!\right]^{\alpha\beta} + kT\zeta_\nu^{(a)\alpha\beta}\cdot\left[\!\!\left[\frac{\partial}{\partial \boldsymbol{p}^\beta}\ln f_{\alpha\beta,\mathrm{eq}}^{(2)}(x_\alpha, x_\beta, t)\right]\!\!\right]^{\alpha\beta} \\
& + kT\sum_s \zeta_{\nu s}^{(a)\alpha\alpha}\left[\!\!\left[\frac{\partial}{\partial P_s^\alpha}\ln f_{\alpha\beta,\mathrm{eq}}^{(2)}(x_\alpha, x_\beta, t)\right]\!\!\right]^{\alpha\beta} + kT\sum_s \zeta_{\nu s}^{(a)\alpha\beta}\left[\!\!\left[\frac{\partial}{\partial P_s^\beta}\ln f_{\alpha\beta,\mathrm{eq}}^{(2)}(x_\alpha, x_\beta, t)\right]\!\!\right]^{\alpha\beta}
\end{aligned} \tag{4.9}$$

where

$$\zeta_{v}^{(a)\alpha\beta} = (1/kT)\sum_{ij}\left\langle \int_0^\infty \boldsymbol{F}_v^{\alpha i}\, e^{t\mathscr{L}}\boldsymbol{F}^{\beta j}\, dt\, \delta(x^{\alpha i}-x_\alpha)\delta(x^{\beta j}-x_\beta)\right\rangle_{\text{eq}} \tag{4.10}$$

$$\zeta_{vs}^{(a)\alpha\beta} = (1/kT)\sum_{ij}\left\langle \int_0^\infty \boldsymbol{F}_v^{\alpha i}\, e^{t\mathscr{L}}(\mathscr{L}P_s^{\beta j}\, dt\, \delta(x^{\alpha i}-x_\alpha)\delta(x^{\beta j}-x_\beta)\right\rangle_{\text{eq}} \tag{4.11}$$

The friction tensors, $\zeta_{v}^{(a)\alpha\alpha}$, and the vectors, $\zeta_{vs}^{(a)\alpha\alpha}$, are functions in same space, given by similar expression, with $\boldsymbol{F}^{\beta j}$ replaced by $\boldsymbol{F}^{\alpha i}$ and $P_s^{\beta j}$ replaced by $P_s^{\alpha j}$.

Next, we define the total Brownian force, $\boldsymbol{F}^{(b)\alpha\beta}$, on a molecule of species α by:

$$\begin{aligned}
-\boldsymbol{F}^{(b)\alpha\beta}\bar{\Psi}_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t) &= \frac{\partial}{\partial t}\llbracket \boldsymbol{p}^\alpha \rrbracket^{\alpha\beta}\bar{\Psi}_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t)\\
&+\frac{1}{m^\alpha}\frac{\partial}{\partial \boldsymbol{r}^\alpha}\cdot \llbracket \boldsymbol{p}^\alpha\boldsymbol{p}^\alpha \rrbracket^{\alpha\beta}\bar{\Psi}_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t)\\
&+\frac{1}{m^\beta}\frac{\partial}{\partial \boldsymbol{r}^\beta}\cdot \llbracket \boldsymbol{p}^\beta\boldsymbol{p}^\alpha \rrbracket^{\alpha\beta}\bar{\Psi}_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t)\\
&+\sum_{\text{st}}\frac{\partial}{\partial Q_s^\alpha}G_{\text{st}}^\alpha\llbracket P_t^\alpha\boldsymbol{p}^\alpha \rrbracket^{\alpha\beta}\bar{\Psi}_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t)\\
&+\sum_{\text{st}}\frac{\partial}{\partial Q_s^\beta}G_{\text{st}}^\beta\llbracket P_t^\beta\boldsymbol{p}^\alpha \rrbracket^{\alpha\beta}\bar{\Psi}_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t)
\end{aligned} \tag{4.12}$$

Then in an analogous fashion, on multiplying Eq. (3.27) by $\boldsymbol{p}^\alpha$ and integrating we find that:

$$\boldsymbol{F}^{(b)\alpha\beta} + \boldsymbol{F}^{(e)\alpha\beta} + \boldsymbol{F}^{(a)\alpha\beta} + \boldsymbol{F}^{(h)\alpha\beta} = 0 \tag{4.13}$$

where

$$\boldsymbol{F}^{(a)\alpha\beta} = \boldsymbol{F}^{\alpha\beta} + \sum_{v}\llbracket \boldsymbol{F}_v^{(\eta)\alpha\beta}\rrbracket \tag{4.14}$$

and

$$\boldsymbol{F}^{(h)\alpha\beta} = \sum_{v}\boldsymbol{F}_v^{(h)\alpha\beta} \tag{4.15}$$

Equation (4.13) is a force balance, similar to Eq. (4.5), involving total forces on the center of mass of the molecule of species α.

The equilibrium distribution function in the phase space of pairs is well-known to be of the form:

$$f_{\alpha\beta,\text{eq}}^{(2)}(x_\alpha, x_\beta, t) = f_{\alpha,\text{eq}}(x_\alpha, t) f_{\beta,\text{eq}}(x_\beta, t)\exp(-\Phi^{(a)\alpha\beta}/kT) \tag{4.16}$$

where $\Phi^{(a)\alpha\beta}$, the potential of average force between the molecules, is a function in the configuration space only. Since the dynamical states of two molecules which are far apart are uncorrelated, this function has the property that:

$$\Phi^{(a)\alpha\beta} \to 0 \tag{4.17}$$

as $|\boldsymbol{R}| \to \infty$. The function $f_{\alpha,\text{eq}}(x_\alpha, t)$ is the equilibrium distribution function in the phase space of single molecule of species α. This function is of the form:

$$f_{\alpha,\text{eq}}(x_\alpha, t) = (1/J_{\alpha,\text{eq}})\Xi_{\alpha,\text{eq}}\exp[-(\phi^\alpha + \phi^{(e)\alpha})/kT] \tag{4.18}$$

where $J_{\alpha,\mathrm{eq}}$ is the normalization constant, which is fixed by the condition that:

$$\int f_{\alpha,\mathrm{eq}}(x_\alpha, t)\, dQ^\alpha\, d\boldsymbol{p}^\alpha\, dP^\alpha = n_\alpha \tag{4.19}$$

the number density of molecules of species, α. For simplicity, we assume that the temperature, T, of the system is uniform in space, but we will assume that the stream velocity, $\boldsymbol{v}(\boldsymbol{r}, t)$, is a function of both space and time. We then take the momentum factor, $\Xi_{\alpha,\mathrm{eq}}$, to be:

$$\Xi_{\alpha,\mathrm{eq}} = \exp\left[-\frac{1}{2kT}\sum_\nu m_\nu^\alpha(\dot{\boldsymbol{r}}_\nu^\alpha - \boldsymbol{v}_\nu^\alpha)^2\right] \tag{4.20}$$

where

$$\boldsymbol{v}_\nu^\alpha = \boldsymbol{v}(\boldsymbol{r}_\nu^\alpha, t) \tag{4.21}$$

is the stream velocity at bead ν of a molecule of species α.

Next, let us consider the expression for $\boldsymbol{F}_\nu^{(\eta)\alpha\beta}$ given by Eq. (2.25), evaluated at equilibrium. First, we find from that relation and Eq. (4.15) that:

$$\begin{aligned}\boldsymbol{F}^{(a)\alpha\beta} f_{\alpha\beta,\mathrm{eq}}^{(2)}(x_\alpha, x_\beta, t) = \boldsymbol{F}^{\alpha\beta} f_{\alpha\beta,\mathrm{eq}}^{(2)}(x_\alpha, x_\beta, t) - \sum_{ij}\int\left[\frac{\partial}{\partial \boldsymbol{r}^{\alpha i}}\Phi\right] \\ \times \delta(x^{\alpha i} - x_\alpha)\delta(x^{\beta j} - x_\beta) f(x, t)_{\mathrm{eq}}\, dx\end{aligned} \tag{4.22}$$

It then follows from the form of the equilibrium distribution function in the full phase space that:

$$\begin{aligned}&kT\sum_{ij}\int \delta(x^{\alpha i} - x_\alpha)\delta(x^{\beta j} - x_\beta)\left(\frac{\partial}{\partial \boldsymbol{r}^{\alpha i}} f(x, t)_{\mathrm{eq}}\right) dx \\ &= \left[-\frac{\partial}{\partial \boldsymbol{r}^\alpha}(\phi^\alpha + \phi^{(e)\alpha}) + \boldsymbol{F}^{(a)\alpha\beta}\right] f_{\alpha\beta,\mathrm{eq}}^{(2)}(x_\alpha, x_\beta, t)\end{aligned} \tag{4.23}$$

From this it follows that:

$$\begin{aligned}&\left[-\frac{\partial}{\partial \boldsymbol{r}^\alpha}(\phi^\alpha + \phi^{(e)\alpha}) + \boldsymbol{F}^{(a)\alpha\beta}\right] f_{\alpha\beta,\mathrm{eq}}^{(2)}(x_\alpha, x_\beta, t) \\ &= -kT\sum_{ij}\left(\frac{\partial}{\partial \boldsymbol{r}^{\alpha i}}\delta(x^{\alpha i} - x_\alpha)\right)\delta(x^{\beta j} - x_\beta) f(x, t)_{\mathrm{eq}}\, dx \\ &= kT\frac{\partial}{\partial \boldsymbol{r}^\alpha}\sum_{ij}\int \delta(x^{\alpha i} - x_\alpha)\delta(x^{\beta j} - x_\beta) f(x, t)_{\mathrm{eq}}\, dx \\ &= kT\frac{\partial}{\partial \boldsymbol{r}^\alpha} f_{\alpha\beta,\mathrm{eq}}^{(2)}(x_\alpha, x_\beta, t)\end{aligned} \tag{4.24}$$

One then finds from the expression for $f_{\alpha\beta,\mathrm{eq}}^{(2)}(x_\alpha, x_\beta, t)$, Eq. (4.16), that:

$$\boldsymbol{F}^{(a)\alpha\beta} = -\frac{\partial}{\partial \boldsymbol{r}^\alpha}\Phi^{(a)\alpha\beta} \tag{4.25}$$

In a similar manner, it may be shown from Eq. (4.6) that:

$$\mathscr{F}_s^{(a)\alpha\beta} = -\frac{\partial}{\partial Q_s^\alpha}\Phi^{(a)\alpha\beta} \tag{4.26}$$

That is, at equilibrium, the potential $\Phi^{(a)\alpha\beta}$, defined by Eq. (4.16), leads to the average forces $\boldsymbol{F}^{(a)\alpha\beta}$ and $\mathscr{F}_s^{(a)\alpha\beta}$ defined by Eqs. (4.6) and (4.14).

Using the form of the equilibrium pair distribution function given by Eq. (4.16), the expression for the hydrodynamic force, Eq. (4.9), becomes:

$$\begin{aligned}\boldsymbol{F}_\nu^{(h)\alpha\beta} = &-\sum_\mu (m_\mu^\alpha/m^\alpha)\zeta_\nu^{(a)\alpha\alpha}\cdot([\![\dot{\boldsymbol{r}}_\mu^\alpha]\!]^{\alpha\beta}-\boldsymbol{v}_\mu^\alpha)-\sum_\mu (m_\mu^\beta/m^\beta)\zeta_\nu^{(a)\alpha\beta}\cdot([\![\dot{\boldsymbol{r}}_\mu^\beta]\!]^{\alpha\beta}-\boldsymbol{v}_\mu^\beta)\\ &-\sum_{\mu\mathrm{st}}(m_\mu^\alpha)^{1/2}G_{\mathrm{st}}^\alpha\zeta_{\nu s}^{(a)\alpha\alpha}\boldsymbol{b}_{\mu t}^\alpha\cdot([\![\dot{\boldsymbol{r}}_\mu^\alpha]\!]^{\alpha\beta}-\boldsymbol{v}_\mu^\alpha)\\ &-\sum_{\mu\mathrm{st}}(m_\mu^\beta)^{1/2}G_{\mathrm{st}}^\beta\zeta_{\nu s}^{(a)\alpha\beta}\boldsymbol{b}_{\mu t}^\alpha\cdot([\![\dot{\boldsymbol{r}}_\mu^\beta]\!]^{\alpha\beta}-\boldsymbol{v}_\mu^\beta)\end{aligned}\tag{4.27}$$

If the flow field is homogenious, that is, if:

$$\left(\frac{\partial}{\partial\boldsymbol{r}}\boldsymbol{v}\right)^\dagger=\kappa\tag{4.28}$$

where κ is independent of the space coordinate, $\boldsymbol{r}$, the last expression for the hydrodynamic force reduces to:

$$\begin{aligned}\boldsymbol{F}_\nu^{(h)\alpha\beta} = &-\zeta_\nu^{(a)\alpha\alpha}\cdot[[\![\dot{\boldsymbol{r}}^\alpha]\!]^{\alpha\beta}-\boldsymbol{v}(\boldsymbol{r}^\alpha,t)]-\zeta_\nu^{(a)\alpha\beta}\cdot[[\![\dot{\boldsymbol{r}}^\beta]\!]^{\alpha\beta}-\boldsymbol{v}(\boldsymbol{r}^\beta,t)]\\ &-\sum_{\mu\mathrm{st}}(m_\mu^\alpha)^{1/2}G_{\mathrm{st}}^\alpha\zeta_{\nu s}^{(a)\alpha\alpha}\boldsymbol{b}_{\mu t}^\alpha\cdot[[\![\dot{\boldsymbol{R}}_\mu^\alpha]\!]^{\alpha\beta}-\kappa\cdot\boldsymbol{R}_\mu^\alpha]\\ &-\sum_{\mu\mathrm{st}}(m_\mu^\beta)^{1/2}G_{\mathrm{st}}^\beta\zeta_{\nu s}^{(a)\alpha\beta}\boldsymbol{b}_{\mu t}^\beta\cdot[[\![\dot{\boldsymbol{R}}_\mu^\beta]\!]^{\alpha\beta}-\kappa\cdot\boldsymbol{R}_\mu^\beta]\end{aligned}\tag{4.29}$$

It is now convenient to change variables from the coordinates of the centers of mass of the two molecules, $\boldsymbol{r}^\alpha$ and $\boldsymbol{r}^\beta$, to the center of mass of the two molecule system:

$$\boldsymbol{r}=(m^\alpha\boldsymbol{r}^\alpha+m^\beta\boldsymbol{r}^\beta)/m\tag{4.30}$$

where

$$m=m^\alpha+m^\beta\tag{4.31}$$

is total mass of the pair, and the vector between the centers of mass, $\boldsymbol{R}$, defined by Eq. (2.6) (to simplify the notation we no longer introduce the superscripts).

The equation of continuity, Eq. (4.3), then becomes:

$$\begin{aligned}&\frac{\partial}{\partial t}\bar{\Psi}_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha,Q^\alpha,\boldsymbol{r}^\beta,Q^\beta,t)+\frac{\partial}{\partial\boldsymbol{r}}\cdot[\![\dot{\boldsymbol{r}}]\!]^{\alpha\beta}\bar{\Psi}_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha,Q^\alpha,\boldsymbol{r}^\beta,Q^\beta,t)\\ &+\frac{\partial}{\partial\boldsymbol{R}}\cdot[\![\dot{\boldsymbol{R}}]\!]^{\alpha\beta}\bar{\Psi}_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha,Q^\alpha,\boldsymbol{r}^\beta,Q^\beta,t)\\ &+\sum_s\frac{\partial}{\partial Q_s^\alpha}[\![\dot{Q}_s^\alpha]\!]^{\alpha\beta}\bar{\Psi}_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha,Q^\alpha,\boldsymbol{r}^\beta,Q^\beta,t)\\ &+\sum_s\frac{\partial}{\partial Q_s^\beta}[\![\dot{Q}_s^\beta]\!]^{\alpha\beta}\bar{\Psi}_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha,Q^\alpha,\boldsymbol{r}^\beta,Q^\beta,t)=0\end{aligned}\tag{4.32}$$

and the expression for the hydrodynamic force, Eq. (4.27), becomes:

and the expression for the hydrodynamic force, Eq. (4.27), becomes:

$$\boldsymbol{F}_\nu^{(h)\alpha\beta} = -(\zeta_\nu^{(a)\alpha\alpha} + \zeta_\nu^{(a)\alpha\beta}) \cdot ([\![\dot{\boldsymbol{r}}]\!]^{\alpha\beta} - \boldsymbol{v}(\boldsymbol{r}, t)) + \left(\frac{m^\beta}{m}\zeta_\nu^{(a)\alpha\alpha} - \frac{m^\alpha}{m}\zeta_\nu^{(a)\alpha\beta}\right) \cdot ([\![\dot{\boldsymbol{R}}]\!]^{\alpha\beta} - \kappa \cdot \boldsymbol{R})$$
$$- \sum_s \zeta_{\nu s}^{(a)\alpha\alpha}([\![\dot{Q}_s^\alpha]\!]^{\alpha\beta} - \kappa : \boldsymbol{M}_s^\alpha) - \sum_s \zeta_{\nu s}^{(a)\alpha\beta}([\![\dot{Q}_s^\beta]\!]^{\alpha\beta} - \kappa : \boldsymbol{M}_s^\beta) \tag{4.33}$$

where

$$\boldsymbol{M}_s^\alpha = \sum_{\mu t} (m_\mu^\alpha)^{1/2} G_{\mathrm{st}}^\alpha \boldsymbol{R}_\mu^\alpha \boldsymbol{b}_{\mu t}^\alpha \tag{4.34}$$

The last result may be used in the expression for the generalized hydrodynamic forces, $\mathscr{F}_s^{(h)\alpha\beta}$, Eq. (4.7), and the total hydrodynamic forces, $\boldsymbol{F}^{(h)\alpha\beta}$, Eq. (4.15) to obtain a set of linear equations which determine the momentum averages, $[\![\dot{\boldsymbol{r}}]\!]^{\alpha\beta}$, $[\![\dot{\boldsymbol{R}}]\!]^{\alpha\beta}$, and $[\![\dot{Q}_s^\alpha]\!]^{\alpha\beta}$. These may then be solved for the momentum averages and the force balances, Eqs. (4.5) and (4.13) then used in the resulting expressions. The result is a set of expressions which may be used in the equation of continuity, Eq. (4.3), to obtain a closed equation for the time evolution of the distribution function, $\bar{\Psi}_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t)$. In the following, we develop these ideas in a particular limiting approximation which will appear to be analogous to that of neglecting "hydrodynamic interaction effects".

5. Scalar friction coefficients

It follows from Eq. (4.10) that:

$$\zeta_\nu^{(a)\alpha\beta} = \sum_\mu \zeta_{\nu\mu}^{(a)\alpha\beta} \tag{5.1}$$

where

$$\zeta_{\nu\mu}^{(a)\alpha\beta} = \frac{1}{kT}\sum_{ij}\left\langle \int_0^\infty \boldsymbol{F}_\nu^{\alpha i} e^{t\mathscr{L}} \boldsymbol{F}_\mu^{\beta j}\, dt\, \delta(x^{\alpha i} - x_\alpha)\delta(x^{\beta j} - x_\beta)\right\rangle_{\mathrm{eq}} \tag{5.2}$$

We next consider the expression for $\zeta_{\nu s}^{(a)\alpha\beta}$, Eq. (4.11). The expression for $\mathscr{L}P_s^{\beta j}$ is given by Eq. (3.25). If we again neglect the correlations between the forces and momenta, we may neglect the terms in the sum. Then if we take the base vectors, $\boldsymbol{b}_{\mu s}^\beta$, to be constant or neglect the effect of the Liouville operator, $\mathscr{L}$, on these vectors, we find that:

$$\zeta_{\nu s}^{(a)\alpha\beta} = \sum_\mu (m_\mu^\beta)^{-1/2} \zeta_{\nu\mu}^{(a)\alpha\beta} \cdot \boldsymbol{b}_{\mu s}^\beta \tag{5.3}$$

Then to illustrate the development of a closed equation for $\bar{\Psi}_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t)$ we will take:

$$\zeta_{\nu\mu}^{(a)\alpha\beta} = \delta_{\alpha\beta}\delta_{\nu\mu}\zeta^\alpha\delta \tag{5.4}$$

where ζ^α is a constant. It will appear, later, that this approximation is equivalent to neglecting hydrodynamic interaction among beads on the same molecule, the $\delta_{\nu\mu}$ factor, and among beads of different molecules, the $\delta_{\alpha\beta}$ factor. We will also assume that all the beads of a particular species of molecules are of the same mass.

$$m_\nu^\alpha = m^{(b)\alpha} \tag{5.5}$$

We then find from Eqs. (4.7) and (4.33) that:

$$\mathscr{F}_s^{(h)\alpha\beta} = -\delta_{\alpha\beta}(\zeta^\alpha/m^{(b)\alpha}) \sum_t g_{\mathrm{st}}^\alpha([\![\dot{Q}_t^\beta]\!]^{\alpha\beta} - \kappa : \boldsymbol{M}_t^\alpha) \tag{5.6}$$

and Eqs. (4.15) and (4.33) that:

$$\boldsymbol{F}^{(h)\alpha\beta} = -N_\alpha \zeta^\alpha([\![\dot{\boldsymbol{r}}]\!]^{\alpha\beta} - \boldsymbol{v}(\boldsymbol{r}, t)) + N_\alpha(m^\beta/m)\zeta^\alpha([\![\dot{\boldsymbol{R}}]\!]^{\alpha\beta} - \kappa \cdot \boldsymbol{R}) \tag{5.7}$$

where N_α is the number of beads making up a molecule of species α. With these approximations, the equations may readily be solved and one finds that:

$$[\![\dot{\boldsymbol{r}}]\!]^{\alpha\beta} = \boldsymbol{v}(\boldsymbol{r}, t) - (N_\beta\zeta^\beta m^\alpha \boldsymbol{F}^{(h)\alpha\beta} + N_\alpha\zeta^\alpha m^\beta \boldsymbol{F}^{(h)\beta\alpha})/(N_\alpha N_\beta \zeta^\alpha\zeta^\beta m) \tag{5.8}$$

$$[\![\dot{\boldsymbol{R}}]\!]^{\alpha\beta} = \kappa \cdot \boldsymbol{R} + (N_\beta\zeta^\beta \boldsymbol{F}^{(h)\alpha\beta} - N_\alpha\zeta^\alpha \boldsymbol{F}^{(h)\beta\alpha})/(N_\alpha N_\beta \zeta^\alpha\zeta^\beta) \tag{5.9}$$

$$[\![\dot{Q}_s^\alpha]\!]^{\alpha\beta} = \kappa \cdot \boldsymbol{M}_s^\alpha - (m^{(b)\alpha}/\zeta^\alpha) \sum_t G_{\mathrm{st}}^\alpha \mathscr{F}_s^{(h)\alpha\alpha} \tag{5.10}$$

The Brownian forces are given by Eqs. (4.4) and (4.12). If one uses Eqs. (4.18) and (4.20) with the $\boldsymbol{v}_v^\alpha$ set to a constant value to evaluate these expressions, one finds that:

$$\mathscr{F}_s^{(b)\alpha\beta} = -kT \frac{\partial}{\partial Q_s} \ln[(g^\alpha)^{-1/2} \Psi_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t)] \tag{5.11}$$

$$\boldsymbol{F}^{(b)\alpha\beta} = -kT\left(\frac{m^\alpha}{m}\frac{\partial}{\partial \boldsymbol{r}} - \frac{\partial}{\partial \boldsymbol{R}}\right) \ln \Psi_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t) \tag{5.12}$$

$$\boldsymbol{F}^{(b)\beta\alpha} = -kT\left(\frac{m^\beta}{m}\frac{\partial}{\partial \boldsymbol{r}} + \frac{\partial}{\partial \boldsymbol{R}}\right) \ln \Psi_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t) \tag{5.13}$$

It then follows from the force balances, Eqs. (4.5) and (4.13), that:

$$\begin{aligned}[\![\dot{\boldsymbol{r}}]\!]^{\alpha\beta} = {} & \boldsymbol{v}(\boldsymbol{r}, t) - (N_\beta\zeta^\beta m^\alpha \boldsymbol{F}^{(a)\alpha\beta} + N_\alpha\zeta^\alpha m^\beta \boldsymbol{F}^{(a)\beta\alpha})/(N_\alpha N_\beta \zeta^\alpha\zeta^\beta m) \\ & -kT \frac{N_\beta\zeta^\beta(m^\alpha)^2 + N_\alpha\zeta^\alpha(m^\beta)^2}{N_\alpha N_\beta \zeta^\alpha\zeta^\beta m^2} \frac{\partial}{\partial \boldsymbol{r}} \ln \Psi_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t) \\ & +kT \frac{N_\beta\zeta^\beta m^\alpha - N_\alpha\zeta^\alpha m^\beta}{N_\alpha N_\beta \zeta^\alpha\zeta^\beta m} \frac{\partial}{\partial \boldsymbol{R}} \ln \Psi_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t)\end{aligned} \tag{5.14}$$

$$\begin{aligned}[\![\dot{\boldsymbol{R}}]\!]^{\alpha\beta} = {} & \kappa \cdot \boldsymbol{R} - (N_\beta\zeta^\beta \boldsymbol{F}^{(a)\alpha\beta} - N_\alpha\zeta^\alpha \boldsymbol{F}^{(a)\beta\alpha})/(N_\alpha N_\beta \zeta^\alpha\zeta^\beta) \\ & +kT \frac{N_\beta\zeta^\beta m^\alpha - N_\alpha\zeta^\alpha m^\beta}{N_\alpha N_\beta \zeta^\alpha\zeta^\beta m} \frac{\partial}{\partial \boldsymbol{r}} \ln \Psi_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t) \\ & -kT \frac{N_\beta\zeta^\beta + N_\alpha\zeta^\alpha}{N_\alpha N_\beta \zeta^\alpha\zeta^\beta} \frac{\partial}{\partial \boldsymbol{R}} \ln \Psi_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t)\end{aligned} \tag{5.15}$$

$$\begin{aligned}[\![\dot{Q}_s^\alpha]\!]^{\alpha\beta} = {} & \kappa : \boldsymbol{M}_s^\alpha + (m^{(b)\alpha}/\zeta^\alpha) \sum_t G_{\mathrm{st}}^\alpha \\ & \times \left[\mathscr{F}_s^{(a)\alpha\beta} - kT \frac{\partial}{\partial Q_s^\alpha} \ln(g^\alpha)^{1/2} \Psi_{\alpha\beta}^{(2)}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t)\right]\end{aligned} \tag{5.16}$$

To avoid undue, but interesting, complications associated with "drift" of pairs, we will restrict the discussion to the simple case which leads to $[\![\dot{\boldsymbol{r}}]\!]^{\alpha\beta} = \boldsymbol{v}(\boldsymbol{r}, t)$. For this purpose we will assume that the number densities of the various species, the n_α, and the external potentials, the $\phi^{(e)}$, are independent of the position coordinate and time. The third term on the left of Eq. (5.14) is then zero. We will then assume that:

$$N_\alpha \zeta^\alpha / m^\alpha = N_\beta \zeta^\beta / m^\beta \tag{5.17}$$

so that the second and last terms are zero.

When the last set of equations is used in the equation of continuity, Eq. (4.32), one finds that:

$$\begin{aligned}
&\frac{\partial}{\partial t} \bar{\Psi}^{(2)}_{\alpha\beta}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t) \\
&\quad + \frac{\partial}{\partial \boldsymbol{R}} \cdot \left[\kappa \cdot \boldsymbol{R} \bar{\Psi}^{(2)}_{\alpha\beta}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t) + \frac{1}{\zeta} \left(\boldsymbol{F} - kT \frac{\partial}{\partial \boldsymbol{R}} \right) \bar{\Psi}^{(2)}_{\alpha\beta}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t) \right] \\
&\quad + \sum_s \frac{\partial}{\partial Q^\alpha_s} \Bigg[\kappa : \boldsymbol{M}^\alpha_s \bar{\Psi}^{(2)}_{\alpha\beta}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t) \\
&\quad + \frac{m^{(b)\alpha}}{\zeta^\alpha} \sum_t G^\alpha_{\mathrm{st}} \left(\mathscr{F}^{(a)\alpha\beta}_t - kT (g^\alpha)^{1/2} \frac{\partial}{\partial Q^\alpha_t} (g^\alpha)^{-1/2} \right) \bar{\Psi}^{(2)}_{\alpha\beta}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t) \Bigg] \\
&\quad + \sum_s \frac{\partial}{\partial Q^\beta_s} \Bigg[\kappa : \boldsymbol{M}^\beta_s \bar{\Psi}^{(2)}_{\alpha\beta}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t) \\
&\quad + \frac{m^{(b)\beta}}{\zeta^\alpha} \sum_t G^\beta_{\mathrm{st}} \left(\mathscr{F}^{(a)\beta\alpha}_t - kT (g^\beta)^{1/2} \frac{\partial}{\partial Q^\beta_t} (g^\beta)^{-1/2} \right) \bar{\Psi}^{(2)}_{\alpha\beta}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t) \Bigg]
\end{aligned} \tag{5.18}$$

where

$$\zeta = \frac{N_\alpha N_\beta \zeta^\alpha \zeta^\beta}{N_\beta \zeta^\beta + N_\alpha \zeta^\alpha} \tag{5.19}$$

and

$$\boldsymbol{F} = \frac{N_\alpha \zeta^\alpha \boldsymbol{F}^{(a)\beta\alpha} - N_\beta \zeta^\beta \boldsymbol{F}^{(a)\alpha\beta}}{N_\beta \zeta^\beta + N_\alpha \zeta^\alpha} = -\frac{\partial}{\partial \boldsymbol{R}} \Phi^{(a)} \tag{5.20}$$

Equation (5.18) is a generalization of the usual "diffusion equation" for the distribution function in the configuration space of a single molecule to an analogous equation for the pair configurational distribution function. The usual equation for the time evolution of $\bar{\Psi}_\alpha(\boldsymbol{r}^\alpha, Q^\alpha, t)$ may be obtained from a limiting form of the present equation.

In the limit that the two molecules are far separated, that is, in the limit that $|\boldsymbol{R}| \to \infty$:

$$\bar{\Psi}^{(2)}_{\alpha\beta}(\boldsymbol{r}^\alpha, Q^\alpha, \boldsymbol{r}^\beta, Q^\beta, t) \to \bar{\Psi}_\alpha(\boldsymbol{r}^\alpha, Q^\alpha, t) \bar{\Psi}_\beta(\boldsymbol{r}^\alpha, Q^\alpha, t) \tag{5.21}$$

and

$$\mathscr{F}^{\alpha\beta}_s \to \mathscr{F}^\alpha_s + \mathscr{F}^{(e)\alpha}_s \tag{5.22}$$

From these limits, it follows from Eq. (5.18) that:

$$\begin{aligned}
&\frac{\partial}{\partial t}\bar{\Psi}_\alpha(\boldsymbol{r}^\alpha, Q^\alpha, t) + \sum_s \frac{\partial}{\partial Q_s^\alpha}\Bigg\{\kappa : \boldsymbol{M}_s^\alpha \bar{\Psi}_\alpha(\boldsymbol{r}^\alpha, Q^\alpha, t) \\
&\quad + \frac{m^{(b)\alpha}}{\zeta^\alpha}\sum_t G_{\mathrm{st}}^\alpha\Bigg[(\mathscr{F}_s^\alpha + \mathscr{F}_s^{(e)\alpha})\bar{\Psi}_\alpha(\boldsymbol{r}^\alpha, Q^\alpha, t) \\
&\quad - kT(g^\alpha)^{1/2}\frac{\partial}{\partial Q_t^\alpha}(g^\alpha)^{-1/2}\bar{\Psi}_\alpha(\boldsymbol{r}^\alpha, Q^\alpha, t)\Bigg]\Bigg\} = 0 \qquad (5.23)
\end{aligned}$$

where $\mathscr{F}_s^\alpha$ and $\mathscr{F}_s^{(e)\alpha}$ are defined by Eqs. (2.20) and (2.21). This is the usual "diffusion equation" in the configuration space of a single molecule (see Eq. (16.2-6) of Ref. [1]).

References

1. Bird RB, Curtiss CF, Armstrong RC, Hassager O (1987) Dynamics of polymeric liquids, Vol 2 kinetic theory. Wiley, New York
2. Kirkwood JG (1946) J Chem Phys 14:180; (1947) 15:72
3. Irving JH, Kirkwood JG (1950) J Chem Phys 18:817
4. Curtiss CF (1988) J Reol 32:403