# Stress and heat flux in a dumbbell solution(*)

## I. MÜLLER (PADERBORN)

IN THE KINETIC theory of macromolecular solutions the macromolecules are modelled as dumbbells whose dimensions exceed the dimensions of the fluid particles of the solvent and therefore the interaction between the different parts of the dumbbells contributes to the stress in the solution. The present paper has been motivated by the idea that, if the macromolecules contribute to the stress because of their nonlocal interaction, they should also contribute to the internal energy and the flux of internal energy. It is therefore the objective of this paper to identify the macromolecular contribution to stress, internal energy and heat flux and to point out the means by which these quantities can be related to the fields of continuum mechanics.

W teorii kinetycznej roztworów makromolekularnych makrocząsteczki modelowane są „dwubiegunami” o wymiarach przekraczających wymiary cząsteczek cieczy rozpuszczalnika; w związku z tym oddziaływanie między poszczególnymi częściami „biegunami” wpływa na stan naprężenia w roztworach. U podstaw pracy leży pogląd, że w sytuacji, gdy makrocząsteczki wpływają na naprężenie, z uwagi na ich nielokalne oddziaływania, powinny one również wpływać na energię wewnętrzną i jej strumień. Celem pracy jest zatem identyfikacja makromolekularnego wkładu do stanu naprężenia, energii wewnętrznej i strumienia ciepła oraz wskazanie sposobu w jaki wielkości te związać można z polami mechaniki ośrodków ciągłych.

В кинетической теории макромолекулярных растворов макромолекулы моделируются „биполюсами” о размерах превышающих размеры молекул жидкости растворителя, в связи с этим взаимодействие между отдельными „полюсами” влияет на напряженное состояние в растворах. В основах работы лежит мнение, что в ситуации, когда макромолекулы влияют на напряжение, из-за нелокального взаимодействия, они тоже должны влиять на внутреннюю энергию и ее поток. Целью работы следовательно является идентификация макромолекулярного вклада в напряженное состояние, внутреннюю энергию и поток тепла, а также указание, каким образом эти величины можно связать с полями механики сплошных сред.

## 1. Introduction

MANY solutions of macromolecular substances exhibit normal stress effects and secondary flows which a continuum theory can describe by assuming non-Newtonian constitutive equations. Such equations are nonlocal and non-instantaneous in the sense that they relate the stress not only to first spatial derivatives of the velocity — as in a newtonian fluid — but to space and space-time derivates of higher order of the velocity.

In the kinetic theory of macromolecular solutios the macromolecules are modelled as dumbbells whose dimensions exceed the dimensions of the fluid particles of the solvent and therefore the interaction between the different parts of the dumbbells contributes to the stress in the solution. That contribution has often been derived and a particularly suggestive derivation can be found in the article [1] by BIRD, WARNER and EVANS. Recently, this subject has been systematized and considerably generalized in [2] by BIRD, CURTISS and HASSAGER who have also treated molecular models different from the dumbbell model.

---

## 2. Basic concepts

### 2.1. The model

For the purpose of the formulation of the statistical theory we represent a polymer solution as a mixture of two constituents:

Constituent 0, the solvent has molecules which we consider as point particles of mass $m_0$. The state of the molecule $i$ is therefore characterized by the position $r_{0i}$ and the velocity $\dot{r}_{0i}$, and the index $i$ runs over all values from 1 to $N_0$, the number of molecules of constituent 0.

Constituent 1, the solute, consists of macromolecules whose structure we considerably simplify in that we consider them as dumbbell molecules of mass $m_1$ whose two partial masses are equal. The state of molecule $\alpha$ is characterized by the position $r_{1\alpha}$ and the velocity $\dot{r}_{1\alpha}$ of the center of mass $S$ and by the distance vector $R_\alpha$ between the two masses and its rate of change (see the Fig. 1). The index $\alpha$ runs from 1 to $N_1$ where $N_1$ is the total number of dumbbells.
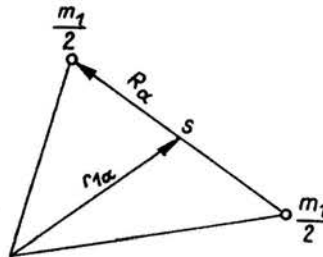


FIG. 1.

In a dilute polymer solution the interaction between different dumbbells may be ignored. The two partial masses of the dumbbell molecule $\alpha$ interact with each other and the interaction force on the mass at $r_{1\alpha} \mp \frac{1}{2} R_\alpha$ will be denoted by $\pm I^\alpha$. These two masses also interact with the solvent molecules and we write $\sum\limits_{i=1}^{N_0} F_\pm^{\alpha i}$ for that interaction force on the mass at $r_{1\alpha} \mp \frac{1}{2} R_\alpha$. The equations of motion for the two masses thus read in the absence of external forces

$$(2.1) \qquad \ddot{r}_{1\alpha} \mp \frac{1}{2} \ddot{R}_\alpha = \frac{2}{m_1} \sum_{i=1}^{N_0} F_\mp^{\alpha i} \pm \frac{2}{m_1} I^\alpha.$$

We assume that $F_\mp^{\alpha i}$ depends on $r_{1\alpha} \mp \frac{1}{2} R_\alpha - r_0$ and that $I^\alpha$ depends on $R^\alpha$. It is then useful to introduce the fields $F$ and $I$, such that

$$(2.2) \qquad F_\mp^{\alpha i} = F(r_{1\alpha} \mp \frac{1}{2} R_\alpha - r_{0i}) \quad \text{and} \quad I_\alpha = I(R_\alpha).$$

Summation and subtraction of the two equations for $\ddot{\mathbf{r}}_{1\alpha} \mp \frac{1}{2} \ddot{\mathbf{R}}_\alpha$ leads to equations for the motion of the center of mass and of the relative motion respectively, viz.

(2.3)

$$\ddot{\mathbf{r}}_{1\alpha} = \frac{1}{m_1} \sum_{i=1}^{N_0} \left[ \mathbf{F}\left(\mathbf{r}_{1\alpha} + \frac{1}{2}\mathbf{R}_\alpha - \mathbf{r}_{0i}\right) + \mathbf{F}\left(\mathbf{r}_{1\alpha} - \frac{1}{2}\mathbf{R}_\alpha - \mathbf{r}_{0i}\right) \right],$$

$$\ddot{\mathbf{R}}_\alpha = \frac{2}{m_1} \sum_{i=1}^{N_0} \left[ \mathbf{F}\left(\mathbf{r}_{1\alpha} + \frac{1}{2}\mathbf{R}_\alpha - \mathbf{r}_{0i}\right) - \mathbf{F}\left(\mathbf{r}_{1\alpha} - \frac{1}{2}\mathbf{R}_\alpha - \mathbf{r}_{0i}\right) \right] - \frac{4}{m_1} \mathbf{I}(\mathbf{R}_\alpha).$$

### 2.2. Probability densities

The state of a mixture is in this model fully characterized by the prescription of the values

$$\mathbf{r}_{0i}, \dot{\mathbf{r}}_{0i}, \mathbf{r}_{1\alpha}, \dot{\mathbf{r}}_{1\alpha}, \mathbf{R}_\alpha, \dot{\mathbf{R}}_\alpha \quad \text{for all} \quad \begin{array}{l} i = 1, 2, ..., N_0, \\ \alpha = 1, 2, ..., N_1. \end{array}$$

The state of an ensemble of such mixtures is therefore characterized by the density function

$$f = f(\mathbf{r}_{01} ... \mathbf{r}_{0N_0} ... \dot{\mathbf{r}}_{01}, \dot{\mathbf{r}}_{0N_0}, \mathbf{r}_{11} ... \mathbf{r}_{1N_1}, \dot{\mathbf{r}}_{11} ... \dot{\mathbf{r}}_{1N_1}, \mathbf{R}_1 ... \mathbf{R}_{N_1}, \dot{\mathbf{R}}_1 ... \mathbf{R}_{N_1}, t)$$

which is normalized by the requirement

$$\int f d\chi = 1,$$

where $d\chi$ stands for the integration element $\prod_{i=1}^{N_1} d^3 r_{0i} d^3 r_{0i} \prod_{\alpha=1}^{N_1} d^3 r_{1\alpha} d^3 \dot{r}_{1\alpha} d^3 R_\alpha d^3 \dot{R}_\alpha$. With this normalization we may interpret $f$ as the probability density for the state $\mathbf{r}_{0i}, \dot{\mathbf{r}}_{0i}, \mathbf{r}_{1\alpha}, \dot{\mathbf{r}}_{1\alpha}, \mathbf{R}_\alpha, \dot{\mathbf{R}}_\alpha$ in a single mixture. This interpretation of $f$ implies that

(2.4) $f_{01}^{i\beta}(\mathbf{r}', \dot{\mathbf{r}}', \mathbf{r}, \dot{\mathbf{r}}, \mathbf{R}, \dot{\mathbf{R}}, t) =$

$$= \int \delta(\mathbf{r}_{0i} - \mathbf{r}') \delta(\dot{\mathbf{r}}_{0i} - \dot{\mathbf{r}}') \delta(\mathbf{r}_{1\beta} - \mathbf{r}) \delta(\dot{\mathbf{r}}_{1\beta} - \dot{\mathbf{r}}) \delta(\mathbf{R}_\beta - \mathbf{R}) \delta(\dot{\mathbf{R}}_\beta - \dot{\mathbf{R}}) f d\chi$$

is the probability density of finding the molecule $i$ of constituent 0 in the state $\mathbf{r}', \dot{\mathbf{r}}'$ and the molecule $\beta$ of constituent 1 in the state $\mathbf{r}, \dot{\mathbf{r}}, \mathbf{R}, \dot{\mathbf{R}}$.

Integration of $f_{01}^{i\beta}$ over all $\mathbf{r}', \dot{\mathbf{r}}'$ leads to the probability density $f_1^\beta(\mathbf{r}, \dot{\mathbf{r}}, \mathbf{R}, \dot{\mathbf{R}}, t)$ of finding the molecule $\beta$ of constituent 1 in the state $\mathbf{r}, \dot{\mathbf{r}}, \mathbf{R}, \dot{\mathbf{R}}$ and we have

(2.5) $$f_1^\beta(\mathbf{r}, \dot{\mathbf{r}}, \mathbf{R}, \dot{\mathbf{R}}, t) = \int \delta(\mathbf{r}_{1\beta} - \mathbf{r}) \delta(\dot{\mathbf{r}}_{1\beta} - \dot{\mathbf{r}}) \delta(\mathbf{R}_\beta - \mathbf{R}) \delta(\dot{\mathbf{R}}_\beta - \dot{\mathbf{R}}) f d\chi.$$

We define

(2.6) $$f_1(\mathbf{r}, \dot{\mathbf{r}}, \mathbf{R}, \dot{\mathbf{R}}) = \frac{\sum_{\beta=1}^{N_1} f_1^\beta(\mathbf{r}, \dot{\mathbf{r}}, \mathbf{R}, \dot{\mathbf{R}}, t)}{N_1}$$

and this is the probability density of finding any molecule of constituent 1 in the state $\mathbf{r}, \dot{\mathbf{r}}, \mathbf{R}, \dot{\mathbf{R}}$.

In particular, $f_1\left(\mathbf{r}\pm\dfrac{1}{2}\mathbf{R},\ \dot{\mathbf{r}}\pm\dfrac{1}{2}\dot{\mathbf{R}},\ \mathbf{R},\ \dot{\mathbf{R}},\ t\right)$ is therefore the probability density of finding a partial mass $m_1/2$ of a dumbbell with $\mathbf{R}$, $\dot{\mathbf{R}}$ at the position $\mathbf{r}$ and with a velocity $\dot{\mathbf{r}}$ when the center of mass lies at $\mathbf{r}\pm\dfrac{1}{2}\mathbf{R}$ and has the velocity $\dot{\mathbf{r}}\pm\dfrac{1}{2}\dot{\mathbf{R}}$.

### 2.3. Expectation values

With the probability densities $f_1\left(\mathbf{r}\pm\dfrac{1}{2}\mathbf{R},\ \dot{\mathbf{r}}\pm\dfrac{1}{2}\dot{\mathbf{R}},\ \mathbf{R},\ \dot{\mathbf{R}},\ t\right)$ one can now define the expectation values at the point $\mathbf{r}$ of the mass density $\varrho_1$, the momentum density $\varrho_1\mathbf{u}_1$, the momentum flux tensor $\mathbf{P}_1$, the kinetic energy density $\varrho_1 e_1^k$, and the flux of kinetic energy $J_1^k$ as follows:

$$\varrho_1 = \frac{m_1}{2}N_1\int \quad [f_1(+,+)+f_1(-,-)]d^3\dot{r}\,d^3R\,d^3\dot{R},$$

$$\varrho_1\mathbf{u}_1 = \frac{m_1}{2}N_1\int \dot{\mathbf{r}} \quad [\qquad\qquad]d^3\dot{r}\,d^3R\,d^3\dot{R},$$

(2.7)
$$\mathbf{P}_1 = \frac{m_1}{2}N_1\int \dot{\mathbf{r}}\dot{\mathbf{r}} \quad [\qquad\qquad]d^3\dot{r}\,d^3R\,d^3\dot{R},$$

$$\varrho_1 e_1^k = \frac{m_1}{2}N_1\int \frac{\dot{\mathbf{r}}\cdot\dot{\mathbf{r}}}{2} \quad [\qquad\qquad]d^3\dot{r}\,d^3R\,d^3\dot{R},$$

$$J_1^k = \frac{m_1}{2}N_1\int \frac{\dot{\mathbf{r}}\cdot\dot{\mathbf{r}}}{2}\dot{\mathbf{r}} \quad [\qquad\qquad]d^3\dot{r}\,d^3R\,d^3\dot{R},$$

where the index 1 throughout stands for constituent 1 and where $f_1(\pm,\pm)$ stands for $f_1\left(\mathbf{r}\pm\dfrac{1}{2}\mathbf{R},\ \dot{\mathbf{r}}\pm\dfrac{1}{2}\mathbf{R},\ \mathbf{R},\ \dot{\mathbf{R}},\ t\right)$. All expressions on the left hand side are functions of $\mathbf{r}$ and $t$.

### 3. Equations of transfer

The continuity equation for the probability density $f$ expresses the fact that the number of mixtures in the ensemble is constant and it reads

(3.1)
$$\frac{\partial f}{\partial t} + \sum_{i=1}^{N_0}\left(\frac{\partial\dot{\mathbf{r}}_{0i}f}{\partial\mathbf{r}_{0i}} + \frac{\partial\ddot{\mathbf{r}}_{0i}f}{\partial\dot{\mathbf{r}}_{0i}}\right) + \sum_{\alpha=1}^{N_1}\left(\frac{\partial\dot{\mathbf{r}}_{1\alpha}f}{\partial\mathbf{r}_{1\alpha}} + \frac{\partial\dot{\mathbf{R}}_\alpha f}{\partial\mathbf{R}_\alpha} + \frac{\partial\ddot{\mathbf{r}}_{1\alpha}f}{\partial\dot{\mathbf{r}}_{1\alpha}} + \frac{\partial\ddot{\mathbf{R}}_\alpha f}{\partial\dot{\mathbf{R}}_\alpha}\right) = 0.$$

We shall assume that $f$ tends to zero rapidly for great values of $\dot{\mathbf{r}}_{0i}$, $\dot{\mathbf{r}}_{1\alpha}$, $\mathbf{R}_\alpha$, $\dot{\mathbf{R}}_\alpha$ and that the expectation values of the normal velocity of both constituents vanish at the wall. Under

these assumptions the integration of the continuity equation (3.1) over all variables $r_{0l}, \dot{r}_{0l}, r_{1\alpha}, \dot{r}_{1\alpha}, R_{\alpha}, \dot{R}_{\alpha}$ except $r_{1\beta}, \dot{r}_{1\beta}, R_{\beta}, \dot{R}_{\beta}$ and subsequent summation over all $\beta$ results in the equation of transfer for the probability density $f_1$:

$$(3.2) \quad \frac{\partial f_1}{\partial t} + \dot{r}\frac{\partial f_1}{\partial r} + \dot{R}\frac{\partial f_1}{\partial R} + \frac{\partial}{\partial \dot{r}}\left(\frac{1}{m_1}(F_+ + F_-)f_1\right) +$$

$$+ \frac{\partial}{\partial \dot{R}}\left(\left[\frac{2}{m_1}(F_+ - F_-) - \frac{4}{m_1}I(R)\right]f_1\right) = 0.$$

Here $F_{\pm}$ denote the expectation values of the force which the particles of constituent 0 exert on the partial masses at $r \pm \frac{1}{2}R$, respectively, of a dumbbell whose state is characterized by $r, \dot{r}, R, \dot{R}$. More explicitly, we have

$$(3.3) \quad F_{\pm} = \frac{\sum_{i,\beta}\int F\left(r \pm \frac{1}{2}R - r_{0l}\right)f_{01}^{i\beta}(r_0, \dot{r}_{0l}, r, \dot{r}, R, \dot{R}, t)d^3 r_{0l}d^3\dot{r}_{0l}}{N_1 f_1(r, \dot{r}, R, \dot{R})}.$$

A special assumption is made regarding the expectation values of the forces between the partial masses of a dumbbell molecule and the solvent molecules: It is assumed that $F_{\pm}$ is proportional to the velocity difference

$$\dot{r} \pm \frac{1}{2}\dot{R} - u_0\left(r \pm \frac{1}{2}R\right)$$

between the partial mass and the solvent. Therefore we write

$$(3.4) \quad F_{\pm} = -\zeta\left[\dot{r} \pm \frac{1}{2}\dot{R} - u_0\left(r \pm \frac{1}{2}R\right)\right]$$

and obtain as the equation of transfer for $f_1$

$$(3.5) \quad \frac{\partial f_1}{\partial t} + \dot{r}\frac{\partial f_1}{\partial r} + \dot{R}\frac{\partial f_1}{\partial R} - \frac{2\zeta}{m_1}\frac{\partial}{\partial \dot{r}}\left[\left(\left(\dot{r} - \frac{u_0\left(r + \frac{1}{2}R\right) + u_0\left(r - \frac{1}{2}R\right)}{2}\right)f_1\right)\right]$$

$$- \frac{2\zeta}{m_1}\frac{\partial}{\partial \dot{R}}\left[\left(\dot{R} - \left(u_0\left(r + \frac{1}{2}R\right) - u_0\left(r - \frac{1}{2}R\right)\right)\right)f_1\right] - \frac{4}{m_1}\frac{\partial}{\partial \dot{R}}(I(R)f_1) = 0.$$

The relation (3.4) is known as the assumption of the Stokes drag law and the coefficient of propartionality $\zeta$ in that law is related to the viscosity of the solvent.

Integration of Eq. (3.5) over all $\dot{r}$ and $\dot{R}$ leads to

$$(3.6) \quad \frac{\partial}{\partial t}\int f_1 d\dot{r} d\dot{R} + \frac{\partial}{\partial r}\int \dot{r}f_1 d\dot{r} d\dot{R} + \int \frac{\partial \dot{R}f_1}{\partial R} d\dot{r} d\dot{R} = 0,$$

if $f_1$ tends to zero fast enough with increasing $\dot{r}, \dot{R}$ so that integrals over distant surfaces in the $(\dot{r}, \dot{R})$-space can be neglected.

The definitions (2.7) for density $\varrho$, velocity $\mathbf{u}_1$, etc. of constituent 1 suggest that we are particularly interested in the values of $f_1$ that belong to the arguments $\mathbf{r} \pm \frac{1}{2} \mathbf{R}, \dot{\mathbf{r}} \pm \frac{1}{2} \dot{\mathbf{R}}, \mathbf{R},$ $\dot{\mathbf{R}}$. Obviously we can write

$$\left. \frac{\partial f_1(\mathbf{r}, \dot{\mathbf{r}}, \mathbf{R}, \dot{\mathbf{R}}, t)}{\partial r} \right|_{\mathbf{r} \pm \frac{1}{2}\mathbf{R}, \dot{\mathbf{r}} \pm \frac{1}{2}\dot{\mathbf{R}}, \mathbf{R}, \dot{\mathbf{R}}} = \frac{\partial f_1 \left( \mathbf{r} \pm \frac{1}{2}\mathbf{R}, \dot{\mathbf{r}} \pm \frac{1}{2}\dot{\mathbf{R}}, \mathbf{R}, \dot{\mathbf{R}}, t \right)}{\partial r},$$

$$\left. \frac{\partial f_1(\mathbf{r}, \dot{\mathbf{r}}, \mathbf{R}, \dot{\mathbf{R}}, t)}{\partial R} \right|_{\mathbf{r} \pm \frac{1}{2}\mathbf{R}, \dot{\mathbf{r}} \pm \frac{1}{2}\dot{\mathbf{R}}, \mathbf{R}, \dot{\mathbf{R}}}$$

$$= \frac{\partial f_1 \left( \mathbf{r} \pm \frac{1}{2}\mathbf{R}, \dot{\mathbf{r}} \pm \frac{1}{2}\dot{\mathbf{R}}, \mathbf{R}, \dot{\mathbf{R}}, t \right)}{\partial R} \mp \frac{1}{2} \frac{\partial f_1 \left( \mathbf{r} \pm \frac{1}{2}\mathbf{R}, \dot{\mathbf{r}} \pm \frac{1}{2}\dot{\mathbf{R}}, \mathbf{R}, \dot{\mathbf{R}}, t \right)}{\partial r},$$

and similar expressions hold for the derivatives of $f_1$ with respect to $\dot{r}$ and $\dot{R}$. It is then easy to show that Eq. (3.5) is equivalent to the following equation of transfer for

(3.7) $\quad f_1 \left( \mathbf{r} \pm \frac{1}{2} \mathbf{R}, \dot{\mathbf{r}} \pm \frac{1}{2} \dot{\mathbf{R}}, \mathbf{R}, \dot{\mathbf{R}}, t \right)$:

$$\frac{\partial f_1(\pm\pm)}{\partial f} + \frac{\partial \dot{r} f_1(\pm\pm)}{\partial r} \frac{\partial R f_1(\pm\pm)}{\partial R} - \frac{2\zeta}{m_1} \frac{\partial}{\partial r} \left[ \left( \dot{\mathbf{r}} - \left( \pm\frac{1}{2} + \frac{1}{2} \right) \mathbf{u}_0 \left( \mathbf{r} \right. \right. \right.$$

$$\left. \left. \left. + \left( \pm\frac{1}{2} - \frac{1}{2} \right) \mathbf{R} \right) + \left( \pm\frac{1}{2} - \frac{1}{2} \right) \mathbf{u}_0 \left( \mathbf{r} + \left( \pm\frac{1}{2} + \frac{1}{2} \right) \mathbf{R} \right) \right] f_1(\pm\pm) \right.$$

$$- \frac{2\zeta}{m_1} \frac{\partial}{\partial \dot{R}} \left( \left[ \dot{\mathbf{R}} - \mathbf{u}_0 \left( \mathbf{r} + \left( \pm\frac{1}{2} + \frac{1}{2} \right) \mathbf{R} \right) + \mathbf{u}_0 \left( \mathbf{r} + \left( \pm\frac{1}{2} - \frac{1}{2} \right) \mathbf{R} \right) \right] f_1(\pm\pm) \right)$$

$$+ \frac{4\left( \pm\frac{1}{2} \right)}{m_1} \frac{\partial}{\partial \dot{r}} \left( \mathbf{I}(\mathbf{R}) f_1(\pm\pm) \right) - \frac{4}{m_1} \frac{\partial}{\partial \dot{R}} \left( \mathbf{I}(\mathbf{R}) f_1(\pm\pm) \right) = 0.$$

When the two equations implied by Eq. (3.7) are added, one obtains

(3.8) $\quad \dfrac{\partial f_1(++) + f_1(--)}{\partial t} + \dfrac{\partial \dot{r}(f_1(++) + f_1(--))}{\partial r} + \dfrac{\partial \dot{R}(f_1(++) + f_1(--))}{\partial R}$

$$- \frac{2\zeta}{m_1} \frac{\partial}{\partial \dot{r}} \left( [\dot{\mathbf{r}} - \mathbf{u}_0(\mathbf{r})] \left( f_1(++) - f_1(--) \right) \right)$$

$$- \frac{2\zeta}{m_1} \frac{\partial}{\partial \dot{R}} \left( [\dot{\mathbf{R}} - \mathbf{u}_0(\mathbf{r}+\mathbf{R}) + \mathbf{u}_0(\mathbf{r})] f_1(++) + [\dot{\mathbf{R}} - \mathbf{u}_0(\mathbf{r}) + \mathbf{u}_0(\mathbf{r}-\mathbf{R})] f_1(--) \right)$$

$$+ \frac{2}{m_1} \frac{\partial}{\partial \dot{r}} \left( \mathbf{I}(\mathbf{R}) \left( f_1(++) - f_1(--) \right) \right) - \frac{4}{m_1} \frac{\partial}{\partial \dot{R}} \left( \mathbf{I}(\mathbf{R}) \left( f_1(++) + f_1(--) \right) \right) = 0.$$

## 4. Equations of balance

### 4.1. General equations of balance

Multiplication of the equation of transfer (3.8) by a function $g(\mathbf{r}, \dot{\mathbf{r}}, \mathbf{R}, \dot{\mathbf{R}})$ and integration over all $\dot{\mathbf{r}}, \dot{\mathbf{R}}$ leads to the general equation of balance[1]

$$(4.1) \quad \frac{\partial}{\partial t} \int g \left( f_1(++) + f_1(--) \right) d\dot{\mathbf{r}} \, d\dot{\mathbf{R}} + \frac{\partial}{\partial \mathbf{r}} \int \dot{\mathbf{r}} g (f_1(++) + f_1(--)) d\dot{\mathbf{r}} \, d\dot{\mathbf{R}}$$

$$+ \frac{\partial}{\partial \mathbf{R}} \int \dot{\mathbf{R}} g (f_1(++) + f_1(--)) d\dot{\mathbf{r}} \, d\dot{\mathbf{R}} - \int \left[ \frac{\partial g}{\partial t} + \dot{\mathbf{r}} \frac{\partial g}{\partial \mathbf{r}} + \dot{\mathbf{R}} \frac{\partial g}{\partial \mathbf{R}} \right] (f_1(++)$$

$$+ f_1(--)) d\dot{\mathbf{r}} \, d\dot{\mathbf{R}} + \frac{2\zeta}{m_1} \int \frac{\partial g}{\partial \dot{\mathbf{r}}} [\dot{\mathbf{r}} - \mathbf{u}_0(\mathbf{r})] (f_1(++) + f_1(--)) d\dot{\mathbf{r}} \, d\dot{\mathbf{R}}$$

$$+ \frac{2\zeta}{m_1} \int \frac{\partial g}{\partial \dot{\mathbf{R}}} \{(\dot{\mathbf{R}} - \mathbf{u}_0(\mathbf{r}+\mathbf{R}) + \mathbf{u}_0(\mathbf{r})) f_1(++) + (\dot{\mathbf{R}} - \mathbf{u}_0(\mathbf{r})$$

$$+ \mathbf{u}_0(\mathbf{r}-\mathbf{R})) f_1(--)\} d\dot{\mathbf{r}} \, d\dot{\mathbf{R}} - \frac{2}{m_1} \int \frac{\partial g}{\partial \dot{\mathbf{r}}} \mathbf{I}(\mathbf{R}) (f_1(++) - f_1(-)) d\dot{\mathbf{r}} \, d\dot{\mathbf{R}}$$

$$+ \frac{4}{m_1} \int \frac{\partial g}{\partial \dot{\mathbf{R}}} \mathbf{I}(\mathbf{R}) (f_1(++) + f_1(--)) d\dot{\mathbf{r}} \, d\dot{\mathbf{R}} = 0.$$

### 4.2. Balance of mass of the dumbbell constituent

With $g = \frac{m_1}{2} N_1$ Eq. (4.1) delivers the balance of mass at the point $\mathbf{r}$ of those dumbbells whose distance vectors are $\mathbf{R}$:

$$(4.2) \quad \frac{\partial}{\partial t} \int \frac{m_1}{2} N_1 (f_1(++) + f_1(--)) d^3 \dot{\mathbf{r}} \, d^3 \dot{\mathbf{R}} + \frac{\partial}{\partial \mathbf{r}} \int \frac{m_1}{2} N_1 \dot{\mathbf{r}} (f_1(++)$$

$$+ f_1(--)) d^3 \dot{\mathbf{r}} \, d^3 R + \frac{\partial}{\partial \mathbf{R}} \int \frac{m_1}{2} N_1 \dot{\mathbf{R}} (f_1(++) + f(--)) d^3 \dot{\mathbf{r}} \, d^3 \dot{\mathbf{R}} = 0.$$

The mass balance of constituent 1 results from Eq. (4.2) by integrating over $\mathbf{R}$ and — by use of the definitions (2.7) — we may write it as

$$(4.3) \qquad\qquad \frac{\partial \varrho_1}{\partial t} + \frac{\partial \varrho_1 \mathbf{u}_1}{\partial \mathbf{r}} = 0.$$

---

[1] Here and in subsequent formulae we assume that $f_1$ tends to zero sufficiently rapidly for great $\dot{\mathbf{r}}, \mathbf{R}, \dot{\mathbf{R}}$, so that integrals over the distant surfaces in the spaces of the variables $\dot{\mathbf{r}}, \mathbf{R}$ and $\dot{\mathbf{R}}$ can be neglected.

### 4.3. Balance of momentum of the dumbbell constituent

We choose $g = \dfrac{m_1}{2} N_1 \dot{\mathbf{r}}$ in Eq. (4.1) and obtain

$$(4.4) \quad \frac{\partial}{\partial t} \int \frac{m_1}{2} N_1 \dot{\mathbf{r}}(f_1(++)+f_1(--))d^3\dot{r}\, d^3\dot{R} + \frac{\partial}{\partial \mathbf{r}} \int \frac{m_1}{2} N_1 \dot{\mathbf{r}}\dot{\mathbf{r}}((f_1(++)$$

$$+f_1(--))d^3\dot{r}\,d^3\dot{R} + \frac{\partial}{\partial \mathbf{R}} \int \frac{m_1}{2} N_1 \dot{\mathbf{r}}\dot{\mathbf{R}}(f_1(++)-f_1(--))d^3\dot{r}\,d^3\dot{R}$$

$$+ \frac{2\zeta}{m_1} \int \frac{m_1}{2} N_1 [\dot{\mathbf{r}}-\mathbf{u}_0(\mathbf{r})](f_1(++)+f_1(--))d^3\dot{r}\,d^3\dot{R}$$

$$- \frac{2}{m_1} \int \frac{m_1}{2} N_1 \mathbf{I}(R)(f_1(++)-f_1(--))d^3\dot{r}\,d^3\dot{R} = 0,$$

which represents the contribution of those dumbbells to the balance of momentum at the point $\mathbf{r}$ whose distance vectors are $\mathbf{R}$. Integration over all $\mathbf{R}$ yields the balance of momentum of constituent 1 which — by use of the definitions (2.7) — can be written as

$$(4.5) \quad \frac{\partial \varrho_1 u_1}{\partial t} + \frac{\partial \mathbf{P}_1}{\partial r} - \int \mathbf{I}(R)N_1(f_1(++)-f_1(--))d^3\dot{r}\,d^3R\,d^3\dot{R} = -\frac{2\zeta}{m_1}\varrho_1(u_1-u_0).$$

The third term in this balance is due to the interaction force between the partial masses of the dumbbell molecules. If $f_1$ varies sufficiently slowly in its first two variables over the ranges of $\mathbf{R}$ and $\dot{\mathbf{R}}$, we may approximate that term by use of a truncated Taylor expansion:

$$(4.6) \quad f_1\left(\mathbf{r}\pm\frac{1}{2}\mathbf{R},\ \dot{\mathbf{r}}\pm\frac{1}{2}\dot{\mathbf{R}},\ \mathbf{R},\ \dot{\mathbf{R}}\right) \approx f_1 \pm \frac{1}{2}\mathbf{R}\frac{\partial f_1}{\partial \mathbf{r}} \pm \frac{1}{2}\dot{\mathbf{R}}\frac{\partial f_1}{\partial \dot{\mathbf{r}}},$$

where the argument of $f_1$ on the right hand side is $\mathbf{r},\ \dot{\mathbf{r}},\ \mathbf{R},\ \dot{\mathbf{R}}$. Thus we obtain the relation

$$(4.7) \quad -\int \mathbf{I}(R)N_1(f_1(++)-f_1(--))d^3\dot{r}\,d^3R\,d^3\dot{R} =$$

$$= \frac{\partial}{\partial r}\left(-\int \mathbf{I}(R)RN_1f_1(\mathbf{r},\dot{\mathbf{r}},\mathbf{R},\dot{\mathbf{R}})d^3\dot{r}\,d^3R\,d^3\dot{R}\right)$$

whence follows the momentum balance in the form

$$(4.8) \quad \frac{\partial \varrho_1 u_1}{\partial t} + \frac{\partial}{\partial r}\left(\mathbf{P}_1 - \int \mathbf{I}(R)RN_1f_1(\mathbf{r}\dot{\mathbf{r}}\mathbf{R}\dot{\mathbf{R}})d^3\dot{r}\,d^3R\,d^3\dot{R}\right) = -\frac{2\zeta}{m_1}\varrho_1(\mathbf{u}_1-\mathbf{u}_0),$$

which suggest the definition of the stress tensor $\mathbf{t}^D$ due to the dumbbell interaction:

$$(4.9) \qquad \mathbf{t}^D = \int \mathbf{I}(R)RN_1f_1(\mathbf{r}\dot{\mathbf{r}}\mathbf{R}\dot{\mathbf{R}})d^3\dot{r}\,d^3R\,d^3\dot{R}.$$

The momentum flux $\mathbf{P}_1$ contains a convective part, viz. $\varrho_1 \mathbf{u}_1 \mathbf{u}_1$, and it is usefull and customary to split that part off and introduce the stress $\mathbf{t}_1^k$, defined as

$$(4.10) \qquad \mathbf{t}_1^k \equiv -\mathbf{P}_1 + \varrho \mathbf{u}_1 \mathbf{u}_1 = \int \frac{m_1}{2}(\dot{\mathbf{r}}-\mathbf{u}_1)(\dot{\mathbf{r}}-\mathbf{u}_1)(f_1(++)+f_1(--))d^3\dot{r}\,d^3R\,d^3\dot{R}.$$

With this definition the momentum balance can be written in the form

$$(4.11) \qquad \varrho_1 \overset{\cdot 1}{\underset{-1}{\mathbf{u}}} - \frac{\partial(\mathbf{t}_1^k + \mathbf{t}^D)}{\partial \mathbf{r}} = -\frac{2\zeta}{m_1} \varrho_1 (\mathbf{u}_1 - \mathbf{u}_0),$$

where $^{\cdot 1}$ denotes the rate of change in the frame that moves with the dumbbell constituent. $\mathbf{t}_1^k + \mathbf{t}_1^D$ is the total stress of that constituent and the term $-\dfrac{2\zeta}{m_1} \varrho_1 (\mathbf{u}_1 - \mathbf{u}_0)$ on the right hand side represents the momentum production of constituent 1 due to the interaction of the two constituents 0 and 1.

#### 4.4. Balance of energy of the dumbbell constituent

We choose $g = \dfrac{m_1}{4} N_1 \dot{\mathbf{r}} \cdot \dot{\mathbf{r}}$ in the general equation of balance (4.1) and obtain

$$(4.12) \qquad \frac{\partial}{\partial t} \int \frac{m_1}{2} N_1 \frac{\dot{\mathbf{r}} \cdot \dot{\mathbf{r}}}{2} (f_1(++) + f_1(--)) d^3 \dot{r} d^3 \dot{R}$$

$$+ \frac{\partial}{\partial \mathbf{r}} \int \frac{m_1}{2} N_1 \frac{\dot{\mathbf{r}} \dot{\mathbf{r}}}{2} \dot{\mathbf{r}} (f_1(++) + f_1(--)) d^3 \dot{r} d^3 \dot{R} + \frac{\partial}{\partial \mathbf{R}} \int \frac{m_1}{2} N_1 \frac{\dot{\mathbf{r}} \dot{\mathbf{r}}}{2} \dot{\mathbf{R}} (f_1(++)$$

$$+ f_1(--)) d^3 \dot{r} d^3 R + \frac{2\zeta}{m_1} \int \frac{m_1}{2} N_1 \dot{\mathbf{r}} [\dot{\mathbf{r}} - u_0(\mathbf{r})] (f_1(++) + f_1(--)) d^3 \dot{r} d^3 \dot{R}$$

$$- \frac{2}{m_1} \int \frac{m_1}{2} N_1 \dot{\mathbf{r}} \mathbf{H}(\mathbf{R}) (f_1(++) - f_1(--)) d^3 \dot{r} d^3 \dot{R} = 0.$$

This equation represents the contribution of the dumbbells with the distance vector $\mathbf{R}$ to the energy balance at $\mathbf{r}$. Upon integration over all $\mathbf{R}$ Eq. (4.12) will deliver the balance of energy of constituent 1 which — with the definitions (2.7) — can be written as

$$(4.13) \qquad \frac{\partial \varrho_1 e_1^k}{\partial t} + \frac{\partial \mathbf{I}_1^k}{\partial \mathbf{r}} - \int \mathbf{I}(\mathbf{R}) \dot{\mathbf{r}} N_1 (f_1(++) - f_1(--)) d^3 \dot{r} d^3 R d^3 \dot{R} =$$

$$= -\frac{2\zeta}{m_1} (Sp\, \mathbf{P}_1 - \varrho_1 \mathbf{u}_1 \cdot \mathbf{u}_0).$$

Here again the third term on the right hand side is due to the interaction between the partial masses of a dumbbell. We transform that term by use of a truncated Taylor expansion (4.6) and obtain

$$- \int \mathbf{I}(R) \dot{\mathbf{r}} N_1 (f_1(++) - f_1(--)) d^3 \dot{r} d^3 R d^3 \dot{R} =$$

$$= \frac{\partial}{\partial \mathbf{r}} \left( - \int \mathbf{I}(\mathbf{R}) \cdot \dot{\mathbf{r}} \mathbf{R} N_1 f_1 d^3 \dot{r} d^3 R d^3 \dot{R} \right) - \int \mathbf{I}(\mathbf{R}) \cdot \dot{\mathbf{r}} \dot{\mathbf{R}} N_1 \frac{\partial f_1}{\partial \dot{\mathbf{r}}} d^3 \dot{r} d^3 R d^3 \dot{R}$$

$$= \frac{\partial}{\partial \mathbf{r}} \left( - \int \mathbf{I}(\mathbf{R}) \cdot \dot{\mathbf{r}} \mathbf{R} N_1 f_1 d^3 \dot{r} d^3 R d^3 \dot{R} \right) + \int \mathbf{I}(\mathbf{R}) \cdot \dot{\mathbf{R}} N_1 f_1 d^3 \dot{r} d^3 R d^3 \dot{R}.$$

For a further transformation of the second integral it is assumed that $I(R)$ is a central force so that

(4.14)
$$I(R) = i(R)\frac{R}{R}$$

holds. Thus $I(R)$ can be written as $\frac{\partial}{\partial R}\left(\int\limits_0^R i(R')dR'\right)$ and we have

$$-\int I(R) \cdot \dot{r}N_1(f_1(++)-f_1(--))d^3\dot{r}\,d^3R\,d^3\dot{R} =$$

$$= \frac{\partial}{\partial r}\left(-\int I(R) \cdot \dot{r}\dot{R}N_1 f_1 d^3\dot{r}\,d^3R\,d^3\dot{R}\right) + \int \frac{\partial}{\partial R}\left(\int\limits_0^R i(R')dR'\right)\dot{R}N_1 f_1 d^3\dot{r}\,d^3R\,d^3\dot{R}$$

$$= \frac{\partial}{\partial r}\left(-\int I(R) \cdot \dot{r}\dot{R}N_1 f_1 d^3\dot{r}\,d^3R\,d^3\dot{R}\right) - \int \left(\int\limits_0^R i(R')dR'\right)N_1 \frac{\partial \dot{R}f_1}{\partial R}d^3\dot{r}\,d^3R\,d^3\dot{R}.$$

By Eq. (3.6) the expression $\int \dfrac{\partial \dot{R}f_1}{dr}\,d\dot{r}\,d\dot{R}$ can be written as $-\dfrac{\partial}{\partial t}\int f_1 d^3\dot{r}\,d^3\dot{R} - \dfrac{\partial}{\partial r}\int \dot{r}f_1 d^3\dot{r}$ $d^3\dot{R}$ and this result leads to

$$-\int I(R) \cdot \dot{r}N_1(f_1(++)-f_1(--))d^3\dot{r}\,d^3\dot{R} =$$

$$= \frac{\partial}{\partial r}\left(-\int \dot{r}\left[I(R)R-1\int\limits_0^R i(R')dR'\right]N_1 f_1 d^3\dot{r}\,d^3R\,d^3\dot{R}\right)$$

$$+ \frac{\partial}{\partial t}\int \left(\int\limits_0^R i(R')dR'\right)N_1 f_1 d^3\dot{r}\,d^3R\,d^3\dot{R}$$

so that balance of energy assumes the following form:

(4.15)
$$\frac{\partial\left(\varrho_1 e_1^k + \int \left(\int\limits_0^R i(R')dR'\right)N_1 f_1 d^3\dot{r}\,d^3R\,d^3\dot{R}\right)}{\partial t} +$$

$$+ \frac{\partial\left(J_1^k - \int \dot{r}\left[I(R)R-1\int\limits_0^R i(R')dR'\right]N_1 f_1 d^3\dot{r}\,d^3R\,d^3\dot{R}\right)}{\partial r} = -\frac{2\zeta}{m_1}(Sp P_1 - \varrho_1 u_1 u_0),$$

**1** denotes the unit tensor.

The form of this balance suggests the definition of the density of potential energy $\varrho_1 \varepsilon^D$ in the dumbbells and of the energy flux $J^D$ due to the dumbbell interaction

(4.16)
$$\varrho_1 \varepsilon^D = \int \left(\int\limits_0^R i(R')dR'\right)N_1 f_1 d^3\dot{r}\,d^3R\,d^3\dot{R},$$

(4.17)
$$J^D = \int \dot{r}\left[I(R)R-1\int\limits_0^R i(R')dR'\right]N_1 f_1 d^3\dot{r}\,d^3R\,d^3\dot{R}.$$

### 4.5. Balance of internal energy

The energy density $\varrho_1 e_1^k$ constains a kinetic energy, viz. $\frac{\varrho_1}{2} u_1^2$. This part is usually split off and we denote the remainder by $\varrho_1 e_1^k$:

$$(4.18) \qquad \varrho_1 \varepsilon_1^k \equiv \varrho_1 e_1^k - \frac{\varrho_1}{2} u_1^2 = \int \frac{m_1}{4} (\dot{\mathbf{r}}-\mathbf{u}_1)(\dot{\mathbf{r}}-\mathbf{u}_1) N_1 f_1(++)+f_1(--) d^3\dot{r} d^3 R d^3 \dot{R}.$$

$\varrho_1(\varepsilon_1^k+\varepsilon^D)$ is called the internal energy and this quantity is assumed to be a scalar under rotations and translations which the total energy is not.

Similarly, the energy flux $\mathbf{J}_1^k + \mathbf{J}^D$ contains convective terms, viz. $\varrho_1\left(\varepsilon_k^1+\frac{1}{2}u_1^2+\varepsilon^D\right)\mathbf{u}_1$ and the power of the stresses $\mathbf{t}_1^k+\mathbf{t}^D$ on the motion of constituent 1, viz. $(\mathbf{t}_1^k+\mathbf{t}^D)\mathbf{u}_1$. The remainder — which is assumed to be a vector under rotations and translations — will be called flux of internal energy of the dumbbell constituent and will be denoted $\mathbf{q}_1^k+\mathbf{q}^D$, where

$$(4.19) \qquad \mathbf{q}_1^k = \int \frac{m_1}{4} (\dot{\mathbf{r}}-\mathbf{u}_1)(\dot{\mathbf{r}}-\mathbf{u}_1)(\dot{\mathbf{r}}-\mathbf{u}_1) N(f_1(++)+f_1(--)) d^3\dot{r} d^3 R d^3 \dot{R}$$

so that $\mathbf{q}^D$ comes out as

$$(4.20) \qquad \mathbf{q}^D = -\int (\dot{\mathbf{r}}-\mathbf{u}_1)\left[\mathbf{I}(\mathbf{R})\mathbf{R}-1\int_0^R i(R')dR'\right] N_1 f_1 d^3\dot{r} d^3 R d^3.$$

$\mathbf{q}^D$ is the contribution of the dumbbells to the flux of internal energy.

The energy balance of the dumbbell constituent can thus be written as

$$(4.21) \qquad \varrho_1\left(\varepsilon_1^k+\frac{1}{2}u_1^2+\varepsilon^D\right)^{'1} + \frac{\partial}{\partial r}(\mathbf{q}_1^k+\mathbf{q}_1^D-(\mathbf{t}_1^k+\mathbf{t}^D)\mathbf{u}_1) = \frac{2\zeta}{m_1}(Sp\,t_1^k-\varrho_1(u_1-u_0)u_1),$$

where again $^{'1}$ denotes the rate of change in the frame that moves with constituent 1.

Multiplication of the momentum balance by $\mathbf{u}_1$ gives the balance of kinetic energy and if we subtract that from the above energy balance we obtain the balance of internal energy of the dumbbell constituent, viz.

$$(4.22) \qquad \varrho_1(\varepsilon_1^k+\varepsilon^D)^{'1} + \frac{\partial}{\partial r}(\mathbf{q}_1^k+\mathbf{q}^D) = (\mathbf{t}_1^k+\mathbf{t}^D)\frac{\partial \mathbf{u}_1}{\partial r} + \frac{2\zeta}{m_1} Sp\,t_1^k.$$

$\frac{2\zeta}{m_1} Sp\,t_1^k$ is the production of internal energy of constituent 1 which is due to the interaction of the constituents 0 and 1.

## 5. On the determination of $\mathbf{t}^D$, $\mathbf{q}^D$ and $\varepsilon^D$

### 5.1. Constitutive equations

So far we have identified the dumbbell contributions to the stress, the specific internal energy and the flux of internal energy in terms of the distribution function $f_1(\mathbf{r}, \dot{\mathbf{r}}, \mathbf{R}, \dot{\mathbf{R}}, t)$. But what we really want of course in continuum mechanics are constitutive equations

which relate $\mathbf{t}^D$, $\mathbf{q}^D$ and $\varepsilon^D$ to the fields of densities and velocities of the constituents. From the solution of similar projects in the kinetic theory of gases we expect that this objective can only be reached approximately and I shall now show how we might proceed in the present case.

First of all, to simplify notation we introduce the expectation value $[\![g]\!]$ by the definition

$$(5.1) \qquad [\![g]\!]\psi_1(\mathbf{r}, \mathbf{R}, t) \equiv \int g(\mathbf{r}, \dot{\mathbf{r}}, \mathbf{R}, \dot{\mathbf{R}}) f_1(r, \dot{r}, R, \dot{R}, t) d^3\dot{r}\, d^3\dot{R}$$

for any function $g(\mathbf{r}, \dot{\mathbf{r}}, \mathbf{R}, \dot{\mathbf{R}})$. Thus we may write $\mathbf{t}^D$, $\mathbf{g}^D$ and $\varepsilon^D$ from Eqs. (4.9), (4.16), and (4.20) in the forms

$$\mathbf{t}^D = \int \mathbf{I}(\mathbf{R})\mathbf{R} N_1\, \psi_1(\mathbf{r}, \mathbf{R}, t) d^3\mathbf{R},$$

$$(5.2) \qquad \varrho_1 \varepsilon^D = \int \left( \int_0^R i(R')dR' \right) N_1 \psi_1(\mathbf{r}, \mathbf{R}, t) d^3\mathbf{R},$$

$$\mathbf{q}^D = - \int ([\![\dot{\mathbf{r}}]\!] - \mathbf{u}_1) \left[ \mathbf{I}(\mathbf{R})\mathbf{R} - 1 \int_0^R i(R')dR' \right] N_1 \psi_1(\mathbf{r}, \mathbf{R}, t) d^3\mathbf{R}.$$

We conclude that in order to obtain constitutive equations for $\mathbf{t}^D$, $\mathbf{q}^D$ and $\varepsilon^D$ we need to know $\psi(r, R, t)$ and $[\![\dot{r}]\!]$ in terms of the fields of continuum mechanics.

### 5.2. Equations of balance

Multiplication of the equations of transfer for $f_1$ (3.5) by a function $g(\mathbf{r}, \dot{\mathbf{r}}, \mathbf{R}, \dot{\mathbf{R}})$ and subsequent integration over all $\dot{\mathbf{r}}$ and $\dot{\mathbf{R}}$ leads to a general balance equation

$$(5.3) \qquad \frac{\partial [\![g]\!]\psi_1}{\partial t} + \frac{\partial [\![g\dot{\mathbf{r}}]\!]\psi_1}{\partial \mathbf{r}} + \frac{\partial [\![g\dot{\mathbf{R}}]\!]\psi_1}{\partial \mathbf{R}} - \left[\!\!\left[ \frac{\partial g}{\partial t} + \dot{\mathbf{r}}\, \frac{\partial g}{\partial \mathbf{r}} + \dot{\mathbf{R}}\, \frac{\partial g}{\partial \mathbf{R}} \right]\!\!\right] \psi_1$$

$$+ \frac{2\zeta}{m_1} \left[\!\!\left[ \left( \dot{\mathbf{r}} - \frac{\mathbf{u}_0\left(\mathbf{r}+\frac{1}{2}\mathbf{R}\right) + \mathbf{u}_0\left(\mathbf{r}-\frac{1}{2}\mathbf{R}\right)}{2} \right) \frac{\partial g}{\partial \dot{\mathbf{r}}} + \left( \dot{\mathbf{R}} - \left(\mathbf{u}_0\left(\mathbf{r}+\frac{1}{2}\mathbf{R}\right)\right.\right.\right.$$

$$\left.\left.\left. - \mathbf{u}_0\left(\mathbf{r}-\frac{1}{2}\mathbf{R}\right)\right) \right) \frac{\partial g}{\partial \dot{\mathbf{R}}} \right]\!\!\right] \psi_1 + \frac{4}{m_1} \mathbf{I}(\mathbf{R}) \left[\!\!\left[ \frac{\partial g}{\partial \dot{\mathbf{R}}} \right]\!\!\right] \psi_1 = 0.$$

We assume that the relations

$$\frac{\mathbf{u}_0\left(\mathbf{r}+\frac{1}{2}\mathbf{R}\right) + \mathbf{u}_0\left(\mathbf{r}-\frac{1}{2}\mathbf{R}\right)}{2} \approx \mathbf{u}_0(\mathbf{r}) \quad \text{and} \quad \mathbf{u}_0\left(\mathbf{r}+\frac{1}{2}\mathbf{R}\right) - \mathbf{u}_0\left(\mathbf{r}-\frac{1}{2}\mathbf{R}\right) \approx \frac{\partial \mathbf{u}_0}{\partial \mathbf{r}} \mathbf{R}$$

are approximately valid. Furthermore we set

$$\mathbf{a} = \dot{\mathbf{r}} - \mathbf{u}_0 \quad \text{and} \quad \mathbf{A} = \dot{\mathbf{R}} - \frac{\partial \mathbf{u}_0}{\partial \mathbf{r}} \mathbf{R}$$

and we write down particular cases of Eq. (5.3) by choosing $g$ as $1$, $A$, $a$, $AA - \frac{1}{3} A \cdot A1$, $Aa$, $aA$, $aa - \frac{1}{3} a \cdot a1$:

$$(5.4) \qquad \frac{\partial \psi_1}{\partial t} + \frac{\partial [\dot{r}]\psi_1}{\partial r} + \frac{\partial [\dot{R}]\psi_1}{\partial R} = 0,$$

$$(5.5) \qquad \frac{\partial [A]\psi_1}{\partial t} + \frac{\partial [A\dot{r}]\psi_1}{\partial r} + \frac{\partial [A\dot{R}]\psi_1}{\partial R} + \frac{4}{m_1} I \psi_1$$

$$- \left\| \left( \frac{\partial}{\partial t} + \dot{r} \frac{\partial}{\partial r} + \dot{R} \frac{\partial}{\partial R} \right) A \right\| \psi_1 = - \frac{2\zeta}{m_1} [A]\psi_1,$$

$$\frac{\partial [a]\psi_1}{\partial t} + \frac{\partial [a\dot{r}]\psi_1}{\partial r} + \frac{\partial [a\dot{R}]\psi_1}{\partial R} - \left\| \left( \frac{\partial}{\partial t} + \dot{r} \frac{\partial}{\partial r} + \dot{R} \frac{\partial}{\partial R} \right) a \right\| \psi_1 = - \frac{2\zeta}{m_1} [a]\psi_1,$$

$$\frac{\partial \left\| AA - \frac{1}{3} A \cdot A1 \right\| \psi_1}{\partial t} + \frac{\partial \left\| \left( AA - \frac{1}{3} A \cdot A1 \right) \dot{r} \right\| \psi_1}{\partial r} + \frac{\partial \left\| \left( AA - \frac{1}{3} A \cdot A1 \right) \dot{R} \right\| \psi_1}{\partial R}$$

$$+ \frac{4}{m_1} \left( I[A] + [A]I - \frac{2}{3} I \cdot [A]1 \right) \psi_1 - \left\| \left( \frac{\partial}{\partial t} + \dot{r} \frac{\partial}{\partial \dot{r}} + \dot{R} \frac{\partial}{\partial R} \right) \left( AA - \frac{1}{3} A \cdot A1 \right) \right\| \psi_1$$

$$= - \frac{2\zeta}{m_1} 2 \left\| AA - \frac{1}{3} A \cdot A1 \right\|,$$

$$\frac{\partial [Aa]\psi_1}{\partial t} + \frac{\partial [Aa\dot{r}]\psi_1}{\partial r} + \frac{\partial [Aa\dot{R}]\psi_1}{\partial R} + \frac{4}{m_1} I[a]\psi_1$$

$$- \left\| \left( \frac{\partial}{\partial t} + \dot{r} \frac{\partial}{\partial r} + \dot{R} \frac{\partial}{\partial R} \right) Aa \right\| \psi_1 = - \frac{2\zeta}{m_1} 2[Aa]\psi_1,$$

$$\frac{\partial [aA]\psi_1}{\partial t} + \frac{\partial [aA\dot{r}]\psi_1}{\partial r} + \frac{\partial [aA\dot{R}]\psi_1}{\partial R} + \frac{4}{m_1} [a]I\psi_1$$

$$- \left\| \left( \frac{\partial}{\partial t} + \dot{r} \frac{\partial}{\partial r} + \dot{R} \frac{\partial}{\partial R} \right) aA \right\| \psi_1 = - \frac{2\zeta}{m_1} 2[aA]\psi_1,$$

$$\frac{\partial \left\| aa - \frac{1}{3} a \cdot a1 \right\| \psi_1}{\partial t} + \frac{\partial \left\| \left( aa - \frac{1}{3} a \cdot a1 \right) \dot{r} \right\| \psi_1}{\partial r} + \frac{\partial \left\| \left( aa - \frac{1}{3} a \cdot a1 \right) \dot{R} \right\| \psi_1}{\partial R}$$

$$- \left\| \left( \frac{\partial}{\partial t} + \dot{r} \frac{\partial}{\partial r} + \dot{R} \frac{\partial}{\partial R} \right) \left( aa - \frac{1}{3} a \cdot a1 \right) \right\| \psi_1 = - \frac{2\zeta}{m_1} 2 \left\| aa - \frac{1}{3} a \cdot a1 \right\| \psi_1.$$

The most important one of these equations is (5.4), the one corresponding to $g = 1$, because we shall rely upon it to determine the function $\psi_1$. However, before Eq. (5.4) can be of any use, we have to know the fields $[\dot{r}]$ and $[\dot{R}]$ that occur in it. I shall now proceed to show how Eqs (5.5) lend themselves to the formulation of an iterative scheme by which approximate expressions for $[\dot{r}]$ and $[\dot{R}]$ can be found.

http://rcin.org.pl

**5.3. An iteration for the determination of $[\dot{\mathbf{R}}]$ and $[\dot{\mathbf{r}}]$**

As the initiation agreement of the proposed iterative scheme we shall assume that $f_1(\mathbf{r}, \dot{\mathbf{r}}, \mathbf{R}, \dot{\mathbf{R}}, t)$ is of the form

(5.6)    $f_1(\mathbf{r}, \dot{\mathbf{r}}, \mathbf{R}, \dot{\mathbf{R}}, t) = \psi_1(\mathbf{r}, \mathbf{R}, t)$

$$\times \sqrt{\frac{m_1}{2\pi kT}}^3 \sqrt{\frac{m_1}{8\pi kT}} e^{-\frac{m_1}{4kT}\left\{\left(\dot{\mathbf{r}}-\frac{1}{2}\dot{\mathbf{R}}-\mathbf{u}_0\left(\mathbf{r}-\frac{1}{2}\mathbf{R}\right)\right)^2+\left(\dot{\mathbf{r}}+\frac{1}{2}\dot{\mathbf{R}}-\mathbf{u}_0\left(\mathbf{r}+\frac{1}{2}\mathbf{R}\right)\right)^2\right\}}$$

This is the Maxwellian distribution function corresponding to the situation that the two partial masses of a dumbbell molecule are in equilibrium with the solvent at their respective positions. Here and in the sequel the field of temperature is assumed to be uniform. One can easily re-write the distribution function in the form

(5.7)    $f_1(\mathbf{r}, \dot{\mathbf{r}}, \mathbf{R}, \dot{\mathbf{R}}, t) = \psi_1(\mathbf{r}, \mathbf{R}, t)$

$$\times \sqrt{\frac{m_1}{2\pi kT}}^3 \sqrt{\frac{m_1}{8\pi kT}} e^{-\frac{m_1}{2kT}(\dot{\mathbf{r}}-\mathbf{u}_0(\mathbf{r}))^2-\frac{m_1}{8kT}\left(\dot{\mathbf{R}}-\frac{\partial \mathbf{u}_0}{\partial \mathbf{R}}\mathbf{R}\right)^2}$$

By use of Eq. (5.7) one may calculate expressions for the expectation values $[g]$ that occur in Eqs. (5.4) and (5.5) and these will be considered as *zero-th iterates* and will be denoted by $[g]^\circ$. We have

$$[\mathbf{a}]^\circ = 0, \quad [\mathbf{A}]^\circ = 0, \quad [\mathbf{a}\cdot\mathbf{a}]^\circ = 3\frac{k}{m_1}T, \quad [\mathbf{A}\mathbf{A}]^\circ = 12\frac{k}{m_1}T,$$

(5.8)    $$\left[\!\left[\mathbf{a}\mathbf{a}-\frac{1}{3}\mathbf{a}\cdot\mathbf{a}\mathbf{1}\right]\!\right]^\circ = 0, \quad \left[\!\left[\mathbf{A}\mathbf{A}-\frac{1}{3}\mathbf{A}\cdot\mathbf{A}\mathbf{1}\right]\!\right]^\circ = 0, \quad [\mathbf{a}\mathbf{A}]^\circ = 0,$$

$$[\mathbf{a}\mathbf{a}\mathbf{a}]^\circ = 0, \quad [\mathbf{a}\mathbf{a}\mathbf{A}]^\circ = 0, \quad [\mathbf{a}\mathbf{A}\mathbf{A}]^\circ = 0, \quad [\mathbf{A}\mathbf{A}\mathbf{A}]^\circ = 0.$$

We assume that the two relations $[\mathbf{a}\cdot\mathbf{a}] = 3\frac{k}{m_1}T$ and $[\mathbf{A}\cdot\mathbf{A}] = 12\frac{k}{m_1}T$ are generally valid—not only in equilibrium; these relations define temperature in non-equilibrium. $[\mathbf{a}\cdot\mathbf{a}]$ determines the expectation value of the kinetic energy of the centers of mass of the dumbbells and $[\mathbf{A}\cdot\mathbf{A}]$ determines the expectation value of the kinetic energy of the relative motion within a dumbbell. Clearly, those two expectation values might be different in general in non-equilibrium. This would lead us to two different temperatures which presents a complication that should be avoided at this stage.

The first step in the iteration is now taken as follows: We introduce the zero-th iterates on the left hand side of Eqs. (5.5) and calculate *first iterates* by solving these equations for the quantities $[\mathbf{A}]$, $[\mathbf{a}]$, $\left[\!\left[\mathbf{A}\mathbf{A}-\frac{1}{3}\mathbf{A}\cdot\mathbf{A}\mathbf{1}\right]\!\right]$, $[\mathbf{A}\mathbf{a}]$, $[\mathbf{a}\mathbf{A}]$, $\left[\!\left[\mathbf{a}\mathbf{a}-\frac{1}{3}\mathbf{a}\cdot\mathbf{a}\mathbf{1}\right]\!\right]$ on their right hand sides. In this manner we obtain

(5.9)
$$[\dot{\mathbf{R}}]^1 = \frac{\partial\left(\mathbf{u}^0-\frac{m_1}{2\zeta}\overset{\circ 0}{\mathbf{u}}\right)}{\partial \mathbf{r}}\mathbf{R}-\frac{2}{\zeta}\mathbf{I}(\mathbf{R})-\frac{2kT}{\zeta}\frac{\varkappa_n\psi_1}{\partial \mathbf{R}},$$

$$[\dot{\mathbf{r}}]^1 = \left(\mathbf{u}^0-\frac{m_1}{2\zeta}\overset{\circ 0}{\mathbf{u}}\right)-\frac{kT}{2\zeta}\frac{\varkappa_n\psi_1}{\partial \mathbf{r}},$$

where $\overset{\circ}{u}_0$ is the rate of change of $u_0$ for the observer who moves with the constituent 0. The superscript 1 in $[\dot{R}]^1$ and $[\dot{r}]^1$ refers to the first iterative step. It is a simple matter to derive Eqs. (5.9) from Eq. (5.5)$_{1,2}$ according to the above prescription; it is equally

easy, and quite straight-forward to calculate $\left\| AA - \dfrac{1}{3} A \cdot A1 \right\|^1$; $[Aa]^1$, $[aA]^1$ and

$\left\| aa - \dfrac{1}{3} a \cdot a1 \right\|^1$ but the results are not given here beceause they are little suggestive and

because we shall not need them.

The iteration proceeds to the second step by insertion of the first iterates — whose calculation was just indicated — into the left hand side of Eqs. (5.5). The second iterates for $[\dot{R}]$ and $[\dot{r}]$ are then calculated by solving Eqs. (5.5)$_{1,2}$ for $[\dot{R}]$ and $[\dot{r}]$ on their right hand sides.

If we wish to calculate third iterates for $[\dot{R}]$ and $[\dot{r}]$, we need more equations than

those given in Eqs. (5.5) because we need second iterates to $\left\| AA - \dfrac{1}{3} A \cdot A1 \right\|$, $[Aa]$, $[aA]$

and $\left\| aa - \dfrac{1}{3} a \cdot a1 \right\|$. It is easily observed that with increasing order of iteration the

necessary number of equations of balance increases and so does the amount of labour involved.

What we get in the $n$th iterative step is a correction of order $\left(\dfrac{m_1}{\zeta}\right)^n$ to the result of

the $(n-1)^{\text{st}}$ step and since $\left(\dfrac{m_1}{\zeta}\right)$ typically is a time of the order of magnitude of $10^{-12}$ s,

we see that corrections are very small indeed. Because of this, one is usually content with the first iterates and this is all we shall consider here from now on.

### 5.4. The diffusion equation for $\psi_1$

Insertion of the first iterates (5.9) for $[\dot{r}]$ and $[\dot{R}]$ in Eq. (5.4) gives rise to the equation

$$(5.10) \quad \frac{\partial \psi_1}{\partial t} + \frac{\partial \overset{\Delta}{u}_0 \psi_1}{\partial r} - \frac{kT}{2\zeta} \frac{\partial^2 \psi_1}{\partial r^2} + \frac{\partial \left( \dfrac{\partial \overset{\Delta}{u}_0}{\partial r} R - \dfrac{2}{\zeta} I(R) \right) \psi_1}{\partial R} - \frac{2kT}{\zeta} \frac{\partial^2 \psi_1}{\partial R^2} = 0,$$

where the abbreviation $\overset{\Delta}{u}_0$ has been introduced for $u_0 - \dfrac{m_1}{2\zeta} \overset{\circ}{u}_0$.

This equation—or a simplified version of it—is called the *diffusion equation* in the literature, e.g. see the review paper [1] by BIRD, WARNER and EVANS. These authors assume that $\overset{\circ}{u}_0 = 0$, $\dfrac{\partial \psi_1}{\partial r} = 0$ and $Sp\left(\dfrac{\partial u_0}{\partial r}\right) = 0$ so that the solvent motion is isochoric, further-

more the authors assume that $\dfrac{\partial u_0}{\partial r}$ is constant. Thus they have the simpler equation

$$(5.11) \quad \frac{\partial \psi_1}{\partial t} + \frac{\partial}{\partial R} \left\{ \frac{\partial u^0}{\partial r} R \psi_1 - \frac{2kT}{\zeta} \frac{\partial \psi_1}{\partial R} - \frac{2}{\zeta} I(R) \psi_1 \right\} = 0.$$

7*

They derive this equation by assuming that the relative motion of the partial masses in a dumbbell is governed by the difference of the Stokes drag force on the masses and by a "Brownian motion force" $kT \dfrac{\partial \ln \psi_1}{\partial \mathbf{R}}$ that gives rise to the term with the temperature.

One advantage of the present treatment is that the Brownian motion force arises naturally in the first step of the iterative scheme described before. Another advantage is that Eq. (5.10) exhibits the effects of accelerated and non-isochoric motion, in which $\dfrac{\partial \mathbf{u}_0}{\partial \mathbf{r}}$ and $\psi_1$ may also depend on $\mathbf{r}$.

The disadvantage of Eq. (5.10) is of course its complexity. Indeed, while it is possible to find interesting approximate solutions of Eq. (5.11) — at least upon a further simplification of that equation (e.g. see [1] § 6) — no solution of Eq. (5.10) has yet been found which reflects the complications of that equation as compared with Eq. (5.11).

If we had such a solution, it would be in terms of the velocity $\mathbf{u}^0$ and its derivatives; the desired constitutive equations for $\mathbf{t}^D$, $\mathbf{q}^D$ and $\varepsilon^D$ would then result from the insertion of the solution $\psi_1$ into the relations (5.2).

### 5.5. Flux of internal energy

Indeed, after the interaction force $\mathbf{I}(\mathbf{R})$ within the dumbbell has been chosen, the only unknown in the expressions $(5.2)_{1,2}$ for $\mathbf{t}^D$ and $\varepsilon^D$ is the function $\psi_1(\mathbf{r}, \mathbf{R}, t)$ and in the first step in our iteration this function has to be calculated as the solution of the differential equation (5.10). The determination of $\mathbf{q}^D$, however, according to Eqs. $(5.2)_3$ requires the knowledge of $\psi_1 - [\![\dot{\mathbf{r}}]\!]$. Now the first iterate of $[\![\dot{\mathbf{r}}]\!]$ is given by Eq. $(5.9)_1$ and, if that is inserted into Eq. $(5.2)_3$ we obtain

$$\mathbf{q}^D = -(\mathbf{u}_1 - \overset{\triangle}{\mathbf{u}}_0) \int \left( \mathbf{I}(\mathbf{R})\mathbf{R} - \mathbf{1} \int_0^R i(R')dR' \right) N_1 \psi_1(\mathbf{r}, \mathbf{R}, t) d^3R$$

$$+ \frac{kT}{2\zeta} \frac{\partial}{\partial \mathbf{r}} \int \left( \mathbf{I}(\mathbf{R})\mathbf{R} - \mathbf{1} \int_0^R i(R')dR' \right) N_1 \psi_1(r, R, t) d^3R$$

or, by use of Eq. $(5.2)_{1,2}$:

(5.12)                     $\mathbf{q}^D = -(\mathbf{u}_1 - \overset{\triangle}{\mathbf{u}}_0)(\mathbf{t}^D - \varrho_1 \varepsilon^D \mathbf{1}) + \dfrac{kT}{2\zeta} \dfrac{\partial(\mathbf{t}^D - \varrho_1 \varepsilon^D \mathbf{1})}{\partial \mathbf{r}}.$

Thus we conclude that in the present case of constant temperature the dumbbell contribution to the flux of internal energy can be determined from the contributions of the dumbbells to stress and internal energy. Note that $\mathbf{q}^D$ vanishes, when $\psi_1$ is independent of $\mathbf{r}$, when the acceleration $\overset{\circ}{\mathbf{u}}_0$ is zero and when $\mathbf{u}^1 = \mathbf{u}_0$, so that the dumbbells do not drift with respect to the solvent molecules. In particular, therefore, we have $\mathbf{q}^D = 0$ in the case in which the differential equations (5.10) has reduced to Eq. (5.11).

## References

1. R. B. BIRD, H. R. WARNER, D. C. EVANS, *Kinetic theory and rheology of dumbbell suspensions with Brownian motion*, Advances in Polymer Science, **8**, p. 1, Springer Berlin, Heidelberg, New York 1971.
2. C. F. CURTISS, R. B. BIRD, O. HASSAGER, *Kinetic theory and rheology of macromolecular solutions*, Adv. in Chem. Physics, **35**, p. 31, John Wiley and Sons, Inc. 1976.

GESAMTHOCHSCHULE PADERBORN, BRD.