Mesoscopic thermodynamics of stationary non-equilibrium states

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Abstract. Thermodynamics for systems at non-equilibrium stationary states have been formulated, based on the assumption of the existence of a local equilibrium in phase space which enables one to interpret the probability density and its conjugated non-equilibrium chemical potential as mesoscopic thermodynamic variables. The probability current is obtained from the entropy production related to the probability diffusion process and leads to the formulation of the Fokker–Planck equation. For the case of a gas of Brownian particles under steady flow in the dilute and concentrated regimes, we derive non-equilibrium equations of state.

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Systems driven outside equilibrium by the intervention of an external driving force frequently show a peculiar behaviour related to their relevant quantities not observed when they are close to equilibrium. The dependence of thermodynamic quantities on external gradients [1]–[3] and the long-range [4, 5] and ageing [6] behaviours of the correlation functions are examples illustrating this very common characteristic [7]–[12]. To explain those peculiarities has been the subject of intense research in recent years [13, 14]. A common feature observed is that a description performed by simply proceeding through the extension of equilibrium concepts to an out-of-equilibrium situation does not always lead to a correct characterization of the state of the system [15, 16].

Such an approach can be justified when the system is in a local equilibrium state in which the relevant variables are the locally conserved hydrodynamic fields [17]. In any other circumstance taking place when other variables become relevant, one has to propose a more general scenario capable of providing a complete description of the system.

Our purpose in this paper is precisely to analyse one case presenting those typical features: a ‘gas’ of Brownian particles under a shear flow [18]. We will propose a new thermodynamic theory aimed at the characterization of the system at a stationary state. The theory is based upon a broader interpretation of the concept of local equilibrium at the mesoscale, in which the probability density and its conjugated chemical potential are interpreted as mesoscopic thermodynamic variables. This interpretation enables one to analyse irreversible processes taking place in time scales where fluctuations become manifest [19]–[21]. We will derive the non-equilibrium equation of state for the pressure tensor as a function of the shear rate in the dilute and concentrated regimes by determining the non-analytic dependences observed in simple and complex fluids [1]–[3], [12].

The paper is organized as follows. In section 2, we derive the Fokker–Planck equation describing the dynamics of a dilute gas of Brownian particles beyond the point particle approximation and obtain the hydrodynamic equations from the hierarchy of evolution equations for the moments of the probability distribution. In section 3, expressions of the mobility and transport coefficients depending on frequency and shear rate are derived from hydrodynamics through the Faxén theorem. In section 4, non-equilibrium equations of state valid in the dilute
limit are proposed whereas section 5 is devoted to the case of higher concentrations. Finally, in section 6, we summarize our main results.

2. Thermodynamics of a ‘gas’ of Brownian particles in external flow

We consider a ‘gas’ of Brownian particles in contact with a heat bath and subjected to conditions creating a velocity field \( \vec{v}_0 = \vec{v}_0(\vec{r}, t) \). The dynamic description of the particles is accomplished by means of the single-particle probability density \( P(\vec{r}, \vec{u}, t) \), where \( \vec{r} \) is the position of a particle and \( \vec{u} \) its instantaneous velocity. This probability is normalized to the number of particles and obeys the conservation law

\[
\frac{\partial}{\partial t} P + \nabla \cdot (\vec{u} P) = -\frac{\partial}{\partial \vec{u}} \cdot (P \vec{v}_0),
\]

where \( P \vec{v}_0 \) represents an unknown probability current in \( \vec{u} \)-space and \( \nabla = \frac{\partial}{\partial \vec{r}} \).

The explicit expression of the current \( P \vec{v}_0 \) can be found by analysing the dissipation taking place in \( \vec{u} \)-space, or equivalently, the entropy production. To this end, we will propose a mesoscopic thermodynamic description based on the assumption of local equilibrium in phase space leading us to formulate the Gibbs equation

\[
T \rho \delta s = \rho \delta e - \int \mu \delta P \, d\vec{u}. \tag{2}
\]

This expression is reminiscent of that introduced in non-equilibrium thermodynamics and differs from it in the fact that the entropy depends on the probability density and not on the mass density. The Gibbs equation formulated in this form is able to describe changes in the entropy due to irreversible processes taking place at the mesoscale in which fluctuations may play an important role. Here, \( \rho(\vec{r}, t), s(\vec{r}, t), e(\vec{r}, t) \) and \( \mu(\vec{r}, \vec{u}, t) \) are the density, entropy, internal energy and the non-equilibrium chemical potential per unit of mass, respectively, \( T \) is the temperature, assumed to be constant. The density field is defined as

\[
\rho(\vec{r}, t) = m \int P(\vec{u}, \vec{r}, t) \, d\vec{u}, \tag{3}
\]

where \( m \) is the mass of the particle. The average velocity field \( \vec{v}(\vec{r}, t) \) is given by the first moment

\[
\rho \vec{v}(\vec{r}, t) = m \int \vec{u} P(\vec{u}, \vec{r}, t) \, d\vec{u}. \tag{4}
\]

The Gibbs equation formulated in (2) must be compatible with the Gibbs entropy [17]

\[
s(t) = -k_B \int c_{\vec{u}} \ln \frac{P}{P_{\text{le}}} \, d\vec{u} + s_{\text{le}}. \tag{5}
\]

Here, \( k_B \) is the Boltzmann constant, \( c_{\vec{u}} = P/\rho \) the mass fraction of the Brownian particles, \( s_{\text{le}} \) the local equilibrium entropy and \( P_{\text{le}} \) the probability density of the local equilibrium reference.
state given by \[18\]

\[
P_{le} = \exp \left\{ \frac{m}{k_B T} \left[ \mu_{le} - \frac{1}{2} (\vec{u} - \vec{v}_0)^2 \right] \right\},
\]

where \(\mu_{le}\) is the chemical potential at local equilibrium, and \(\frac{1}{2} (\vec{u} - \vec{v}_0)^2\) the kinetic energy per unit mass corresponding to the relative motion of the particles with respect to the flow. Making variations with respect to \(P\) in equation (5) and comparing the result with (2), we infer the value of the chemical potential \[18\]

\[
\mu = \frac{k_B T}{m} \ln P + \frac{1}{2} (\vec{u} - \vec{v}_0)^2.
\]

The entropy production follows by taking the time derivative of equation (5) and by using equations (1), (2) and (6), and the corresponding equation for \(c_{\vec{u}}\) \[18\]. After integrating by parts and assuming that the probability current vanishes at the boundaries, one obtains

\[
\sigma = -\frac{m}{T} \int P \vec{v}_{\vec{u}} \cdot \frac{\partial \mu}{\partial \vec{u}} \, d\vec{u} - \frac{m}{T} \int \vec{J} \cdot \nabla \left[ \frac{1}{2} (\vec{u} - \vec{v}_0)^2 \right] - \frac{m}{T} \int \vec{J}_0 \cdot \vec{F} \, d\vec{u},
\]

where \(\vec{F} = \frac{\partial \vec{v}_0}{\partial t}\) is the force per unit of mass exerted by the flow on the particle. In deriving equation (8), we have also used the balance equation for the internal energy \(e\), assumed isothermal conditions, neglected the energy dissipation arising from viscous heating \[17\] and defined \(\frac{d}{dt} \equiv \frac{\partial}{\partial t} + \vec{v} \cdot \nabla\). The first contribution to the entropy production (8) is related to the diffusion process in \(\vec{u}\)-space. The second originates from the relative current \(\vec{J} = (\vec{u} - \vec{v}) P\), whereas the third, involving the current \(\vec{J}_0 = (\vec{u} - \vec{v}_0) P\), comes from the dependence on time of the external velocity field \(\vec{v}_0(\vec{r}, t)\) \[18\].

According to the Onsager theory \[17\], we may now establish couplings between fluxes and forces of the same tensorial order appearing in equation (8). In particular, the diffusion current in \(\vec{u}\)-space is given by

\[
P \vec{v}_{\vec{u}} = -\vec{\xi} P \cdot \frac{\partial \mu}{\partial \vec{u}} - \vec{\epsilon} P \cdot (\vec{u} - \vec{v}_0) \cdot \nabla \vec{v}_0 + \vec{\zeta} \cdot \vec{F} P,
\]

where we have introduced the coefficients \(\vec{\xi}, \vec{\epsilon}\) and \(\vec{\zeta}\) which may, in general, be functions of position and time \[22\]. Their dependence on position accounts for spatial inhomogeneities whereas the dependence on time introduces memory effects \[7, 22, 23\]. Notice that equation (9) constitutes the linear law expressing the probability current in terms of the thermodynamic mesoscopic forces. The linear approach is enough to describe the mesoscopic dynamics since Fokker–Planck equations are linear in the probabilities.

By substituting now equation (9) into (1), one arrives at the Fokker–Planck equation

\[
\frac{\partial}{\partial t} P + \nabla \cdot (\vec{u} P) = \frac{\partial}{\partial \vec{u}} \left[ \vec{\beta} \cdot (\vec{u} - \vec{v}_0) P + \frac{k_B T}{m} \frac{\partial P}{\partial \vec{u}} \right] - \frac{\partial}{\partial \vec{u}} \left[ \vec{\xi} \cdot \vec{F} P \right],
\]

where we have introduced the friction tensor \(\vec{\beta}\) related to \(\vec{\xi}\) through \(\vec{\beta} = \vec{\xi} + \vec{\epsilon} \cdot \nabla \vec{v}_0\). In this equation, which describes the dynamics of the system beyond the point particle approximation,
the inertial and surface forces that the bath exerts on the particle during its motion are associated with the terms $\vec{z} \cdot \vec{F}$ and $\vec{z} \cdot \nabla \vec{v}_0$, respectively.

It is important to stress that the Fokker–Planck equation (10) has been obtained under the assumption that the local-equilibrium hypothesis can be formulated in the phase space of the system. In the mesoscopic non-equilibrium thermodynamic theory we propose, the probability density and its conjugate chemical potential are interpreted as mesoscopic thermodynamic quantities [19]. In this way, the theory provides a more general framework than that of non-equilibrium thermodynamics [17] in which local equilibrium concerns only to equilibration in position space which occurs at longer time scales in which fluctuations have already relaxed.

From the Fokker–Planck equation (10), we can directly derive the evolution equations for the moments of the distribution which correspond to the hydrodynamical fields [18]. In particular, the mass conservation equation

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \vec{v})$$

(11)

can be obtained by taking the time derivative of equation (3), using (10) and integrating by parts. By following a similar procedure, from equation (4) we may derive the momentum conservation law

$$\rho \frac{d \vec{v}}{dt} + \nabla \cdot \vec{P} = -\rho \vec{\beta} \cdot (\vec{v} - \vec{v}_0) + \rho \vec{z} \cdot \vec{F},$$

(12)

in which we have introduced the kinetic part of the pressure tensor $\vec{P} (\vec{r}, t)$

$$\vec{P} (\vec{r}, t) = m \int (\vec{u} - \vec{v})(\vec{u} - \vec{v}) P(\vec{u}, \vec{r}, t) d\vec{u},$$

(13)

whose evolution equation is

$$\frac{d}{dt} \vec{z}^k P + 2 \left( \vec{z}^k \cdot \tau^{-1} \right) s = \frac{2k_B T}{m} \rho \vec{z},$$

(14)

Here, the exponent $s$ refers to the symmetric part and the matrix of relaxation times $\vec{\tau}$ is defined by

$$\vec{\tau} = \left[ \vec{\beta} + \nabla \vec{v} + \frac{1}{2} (\nabla \cdot \vec{v}) \vec{1} \right]^{-1}.$$  

(15)

In equation (14), we have neglected the contribution of the third centred moment and higher order moments related to the Burnett and super-Burnett approximations since their characteristic relaxation times are much smaller than those appearing in equations (11)–(14) [18]. It is important to stress that equation (14) constitutes a general expression from which one may obtain the constitutive equation for $\vec{z}^k P$ which may incorporate memory effects.

At times $t \gg \beta_{ij}^{-1}$, the particle enters the diffusion regime governed by the corresponding Smoluchowski equation for $\rho(\vec{r}, t)$ [18]. In this regime, equation (14) yields

$$\frac{\vec{z}^k P}{m} \sim \frac{k_B T}{m} \rho \vec{z} - \left[ \vec{z} \cdot \vec{v}_0 \right]^k.$$

(16)
where we have assumed that, for sufficiently long times, $\vec{v} \approx \vec{v}_0 + O(\nabla \ln \rho)$ and the Brownian ($\eta_B$) and hydrodynamic ($\eta_H$) viscosities are defined respectively by

$$\eta_B = \frac{k_B T}{m} \frac{\rho^2}{\beta} \quad \text{and} \quad \eta_H = \frac{k_B T}{m} \frac{\rho^2}{\beta^2} \cdot \vec{e}.$$  \hfill (17)

The former originates from the stresses caused by the Brownian particle in its motion, whereas the latter is a consequence of the finite size of the particle which introduces inertial effects. Equation (16) will constitute the starting point for the derivation of the non-equilibrium equations of state of the gas.

3. The generalized Faxén theorem

The explicit form of the coefficients $\vec{\beta}$, $\vec{\epsilon}$ and $\vec{\zeta}$ can be obtained by making use of the Faxén theorem [24] giving the force exerted by the fluid on a particle of finite size, which has been generalized to the case of a shear flow [26]. For simplicity, we will neglect the contribution due to Brownian motion in equations (12) and (16) and assume that $\vec{\beta} = \vec{\beta}_1$, $\vec{\epsilon} = \vec{\epsilon}_1$ and $\vec{\zeta} = \vec{\zeta}_1$. By substituting equation (16) into (12), simplifying for $\rho$ and taking the Fourier transform of the resulting equation, one obtains

$$\vec{v}(\omega) = G(\omega) \left[ \beta \vec{v}_0(\omega) + \frac{k_B T}{m} \rho \beta^{-1} (1 - \epsilon) \nabla^2 \vec{v}_0(\omega) - i\omega \vec{\zeta} \vec{v}_0(\omega) \right],$$  \hfill (18)

where we have defined the propagator of the velocity $G \equiv (-i\omega + \beta)^{-1}$ and $\vec{v}(\omega) \equiv (2\pi)^{-\frac{1}{2}} \int \vec{v} e^{-i\omega t} \, dt$. The quantities $\vec{v}_0(\omega)$ and $\nabla^2 \vec{v}_0(\omega)$ appearing in equation (18) can be expressed as a linear combination of the averages of the unperturbed velocity over the surface and the volume of the particle defined, respectively, as

$$\bar{\vec{v}}_0^S(\omega) = \frac{1}{4\pi a^2} \int \vec{v}_0(\omega) \, dS \approx \vec{v}_0(\omega) + \frac{a^2}{3!} \nabla^2 \vec{v}_0(\omega),$$  \hfill (19)

and

$$\bar{\vec{v}}_0^V(\omega) = \frac{3}{4\pi a^3} \int \vec{v}_0(\omega) \, dV \approx \vec{v}_0(\omega) + \frac{a^2}{10} \nabla^2 \vec{v}_0(\omega),$$  \hfill (20)

where $a$ is the radius of the particle and the derivatives of the velocity are evaluated at the centre of mass. Using these relations, equation (18) can be written as

$$\vec{v}(\omega) = G(\omega) \left[ \frac{k_B T}{m} \frac{\rho \beta^{-1} (1 - \epsilon)}{a^2} - \frac{3}{2} \beta + \frac{3}{2} \xi i \omega \right] \bar{\vec{v}}_0^S(\omega) \quad \quad -G(\omega) \left[ \frac{k_B T}{m} \frac{\rho \beta^{-1} (1 - \epsilon)}{a^2} - \frac{5}{2} \beta + \frac{5}{2} \xi i \omega \right] \bar{\vec{v}}_0^V(\omega),$$  \hfill (21)
which coincides with Faxén’s theorem obtained from hydrodynamics [24] if we make the following identifications:

\[ \beta = \beta_0 \left( 1 + a\alpha\omega + \frac{1}{5}a^2\alpha^2\omega^2 \right), \tag{22} \]

\[ \epsilon = \frac{1}{6} \frac{m}{k_BT} a^2 \beta_0^2 \left( 1 + 2a\alpha\omega + \frac{59}{45}a^2\alpha^2\omega^2 \right), \tag{23} \]

and \( \zeta = \frac{\rho_p}{\rho_f} \). Here, \( \beta_0 \) is the Stokes friction coefficient, \( \alpha\omega \equiv \sqrt{-i\omega\nu} \) the inverse of the penetration length [25], \( \nu \) is the kinematic viscosity of the solvent and \( \rho_p \) and \( \rho_f \) are the particle and fluid densities.

The case of a stationary flow \( \vec{v}_0 = \vec{v}_0(\vec{r}) \) and zero-frequency can also be analysed by simply considering the average over the surface of the particle since, in this case, inertial effects vanish. The mobility tensor \( \vec{\beta}^{-1} \) can also, in this case, be compared with the one calculated from hydrodynamics [26]

\[ \vec{\beta}^{-1} = \beta_0^{-1} \left( 1 - \vec{M} \alpha\gamma \right). \tag{24} \]

One also obtains

\[ \vec{\epsilon} = \frac{1}{6} \frac{m}{k_BT} a^2 \left[ \vec{\beta} \cdot \vec{\beta} - \left( \frac{3}{5}\frac{\zeta}{\epsilon} \vec{\beta} \cdot \nabla \vec{v}_0 \right) \right], \tag{25} \]

where \( \alpha\gamma \equiv \sqrt{\frac{\nu}{D_0}} \) is the inverse of the penetration length of the perturbation related to the shear flow, with \( \gamma \) being the shear rate and \( \vec{M} \) a matrix whose elements depend on the boundary conditions on the surface of the particle [27].

4. Non-equilibrium equations of state

Once the expressions of the transport coefficients have been found, we will proceed to derive the equations of state for the different elements of the pressure tensor as functions of the shear rate \( \gamma \) in the zero-frequency case.

The gas of Brownian particles constitutes a fluid with a viscosity coefficient proportional to the diffusiveness \( D_0 = \frac{k_BT}{6\pi a\eta_f} \), with \( \eta_f \) being the viscosity of the heat bath. Hence, in this case we will introduce the inverse penetration length \( \lambda_\gamma \equiv \sqrt{\frac{\nu}{D_0}} \), where we have replaced the kinematic viscosity \( \nu \) of the heat bath by the diffusivity \( D_0 \) given by the Stokes–Einstein relation.

In the case of a simple shear along the \( x \)-axis, the expressions for the elements of the pressure tensor \( \vec{P}^k \) can be obtained by substituting equations (24) and (25) into the long time limit of equation (14). For the diagonal components, we obtain

\[ P_{xx}^k = \frac{k_BT}{m} \rho \left[ 1 - \beta_{xx}^{-1}\epsilon_{yy}\gamma \right] - \beta_{xx}^{-1} \left[ \beta_{yy} + \gamma \right] P_{xy}^k, \tag{26} \]

\[ P_{yy}^k = \frac{k_BT}{m} \rho - \beta_{xx}^{-1} \beta_{xy} P_{xy}^k. \tag{27} \]
The only non-diagonal component different from zero is

\[ p_{xy}^k = \frac{k_B T}{2m} \rho G_0^{-1} \left[ 1 + \epsilon_{yy} - \beta_{xx}^{-1} \beta_{yy} \epsilon_{yy} \right] \gamma, \]  

(29)

where we have used equations (26) and (27) and defined \( G_0 \equiv \beta_{xx} - \beta_{yy}^{-1} \beta_{yx} \beta_{xy} \).

By substituting now equations (24) and (25) into equations (26)–(29), we obtain the propagator \( 1 - M_{xx} a \lambda \gamma \) for the elements of the pressure tensor and, from here, we may conclude that non-Newtonian effects appear at lower shear rates when the radius of the particle is increased.

We will now proceed to analyse equations (26)–(29) by assuming \( \gamma < D_0 / a^2 \). In this limit, equation (29) can be approximated up to the second order in \( \gamma \) to obtain

\[ p_{xy}^k \simeq -[\eta_B + \eta_H] \gamma, \]  

(30)

where

\[ \eta_B = \frac{k_B T}{m \beta_0} \rho \left[ 1 - M_{xx} a \lambda \gamma + 2 M_{xy} M_{yx} a^2 \lambda_y^2 \right], \]  

(31)

and

\[ \eta_H = \frac{1}{6} \beta_0 a^2 \rho \left[ 1 + M_{xx} a \lambda \gamma + (M_{xx}^2 - M_{xy} M_{yx}) a^2 \lambda_y^2 \right]. \]  

(32)

In figure 1, we present both viscosities normalized to their value at zero \( \gamma \), as a function of the shear rate for different values of \( a \). At low shear rates, Brownian viscosity (dash-dotted and solid lines) exhibits shear thinning, whereas shear thickening in the hydrodynamic viscosity (dotted and broken lines) arises at higher shear rates [28].

The rheological equations of state follow by substituting equation (30) with (31) and (32) into equations (26) and (27), obtaining

\[ p_{xx}^k \simeq \frac{k_B T}{m} \rho + \left[ \frac{k_B T}{m \beta_0} - \frac{1}{3} \left( \frac{M_{yx}}{M_{yy}} - \frac{1}{2} \right) \beta_0 a^2 \right] M_{xy} a v^{-1} \rho \gamma^2, \]  

(33)

and

\[ p_{yy}^k \simeq \frac{k_B T}{m} \rho + \left( \frac{k_B T}{m \beta_0} + \frac{1}{6} \beta_0 a^2 \right) M_{yy} a v^{-1} \rho \gamma^2, \]  

(34)

from which one concludes that the lowest-order contribution to the normal stress difference is proportional to \( \gamma^2 \). Our results containing corrections to the viscosity have the same shear rate dependence as those obtained in [1] for simple fluids.

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Figure 1. The Brownian (—— and · · · · · ·) and hydrodynamic (—— and · · · · · · · ·) viscosities as functions of the shear rate for different values of the radius of the Brownian particle. The figure shows the shear thinning and shear thickening effects. The values of the parameters we have used are \( \beta_0 \simeq 10^6 \text{s}^{-1} \), \( D_0 \simeq 10^{-6} \text{cm}^2 \text{s}^{-1} \) and \( \rho \simeq 0.2 \text{cm}^3 \).

5. Non-equilibrium equations of state for a non-ideal gas

Thermodynamics of a gas of interacting Brownian particles can also be formulated as in the dilute case. Within a mean-field approximation in which one assumes that the dynamics is that of a Brownian particle moving through an effective medium consisting of the fluid and the remaining particles, the Fokker–Planck equation is [21] given by

\[
\frac{\partial}{\partial t} P + \nabla \cdot (\bar{u} P) - \nabla \left( \frac{k_B T}{m} \ln f \right) \cdot \frac{\partial P}{\partial \bar{u}} = \frac{\partial}{\partial \bar{u}} \left[ \bar{\gamma} \cdot \left( \bar{u} - \bar{v}_0 \right) P + \frac{k_B T}{m} \bar{\xi} \cdot \frac{\partial P}{\partial \bar{u}} \right] - \frac{\partial}{\partial \bar{u}} \cdot \left( \bar{\xi} \cdot \bar{F} P \right).
\]

(35)

Interactions have been taken into account through the activity coefficient \( f = \exp \left[ \frac{m}{k_B T} \rho \ln \left( \frac{\rho}{\rho_{\text{int}}} \right) \right] \) measuring the deviation of the Brownian gas with respect to the ideal case, with \( \rho_{\text{int}} \) being the excess of osmotic pressure [21].

Proceeding along the lines indicated in section 3, one may use equation (35) to derive the evolution equation of the momentum

\[
\rho \frac{d \bar{v}}{dt} = -\rho (\bar{v} - \bar{v}_0) \cdot \bar{\beta} - \nabla \cdot \bar{P} + \left[ \frac{k_B T}{m} \ln f \right] \nabla \rho + \rho \bar{\xi} \cdot \bar{F},
\]

(36)

where we have defined the total pressure tensor by \( \bar{P} = \bar{P}^{k} + \rho \bar{P}^{\text{int}} \). The expression of the kinetic part of the pressure tensor is given by \( P_{yx}^{k} \simeq \frac{k_B T}{m} \rho \left( \eta_B(\omega) + \eta_H(\omega) \right) \gamma \), with dependences of the viscosities different from those in equation (16). In deriving the corresponding expression of \( \bar{P} \), we have assumed that the relaxation of the kinetic part of the pressure tensor is much faster than that of normal (structural) stresses.
5.1. Viscoelastic effects

As in the previous section, the transport coefficients can be identified by using the Faxén theorem. At higher volume fractions $\phi$ of the Brownian gas, one may assume that these coefficients can be expressed in terms of modified penetration lengths.

In the creeping flow case, the mobility coefficient can be expanded up to the first order in terms of the modified inverse penetration length

$$\alpha_\omega \equiv \frac{1}{\Delta_\omega^\alpha (\tau_\omega)^{\delta_\omega}}, \quad (37)$$

where the scaling factor $\Delta_\omega$ and the exponent $\delta_\omega$ can, in general, be functions of the volume fraction $\phi$ [21]. In equation (37), we have introduced the characteristic diffusion time $\tau \equiv \frac{a^2}{6D_0}$. By using equation (37), the corresponding relation for $\beta_\omega$ and $\epsilon_\omega$ can be expressed by [21]

$$\beta_\omega = \beta_0 (1 + a \alpha_\omega) \quad \text{and} \quad \epsilon_\omega = \frac{1}{6} \frac{m}{k_B T} a^2 \beta_0^2 (1 + 2 a \alpha_\omega). \quad (38)$$

Consequently, the frequency-dependent Brownian viscosity coefficient is now given by

$$\eta_B(\omega) = \frac{k_B T}{m \rho} \rho \left[ 1 - \Delta_\omega^{-1} (\tau_\omega)^{\delta_\omega} + \Delta_\omega^{-2} (\tau_\omega)^{2\delta_\omega} \right], \quad (39)$$

and the hydrodynamic viscosity coefficient by

$$\eta_H(\omega) = \frac{1}{12} \beta_0 a^2 \rho \left[ 1 + \Delta_\omega^{-1} (\tau_\omega)^{\delta_\omega} - \Delta_\omega^{-2} (\tau_\omega)^{2\delta_\omega} \right]. \quad (40)$$

The first normal stress difference is accordingly

$$P_{xx} - P_{yy} \simeq \beta^{-1} [\eta_B(\omega) + \eta_H(\omega)] \gamma^2, \quad (41)$$

which then becomes a function of frequency and volume fraction. At sufficiently low shear rates, the quadratic dependence on the shear rate in the first normal stress difference has been reported in the literature [10]. Notice that in the ideal case, similar dependence can be obtained in this regime.

5.2. Non-Newtonian effects

In the stationary flow case, we will assume that the mobility can be expanded in terms of the modified inverse penetration length $\Lambda_\gamma$

$$\Lambda_\gamma \equiv \frac{1}{\Delta_\gamma^\gamma (\tau_\gamma)^{\delta_\gamma}}, \quad (42)$$

where $\Delta_\gamma$ and $\delta_\gamma$ are functions of the volume fraction $\phi$. The mobility can be expressed as

$$\beta_\gamma^{-1} = \beta_0^{-1} \left( 1 - \frac{\gamma}{Ma \Lambda_\gamma} \right), \quad (43)$$
and the explicit expression of $\epsilon_\gamma$ can be found by using equation (25). In this case, the contributions to the viscosity are given by

$$\eta_B(\gamma) = \frac{k_B T}{m \beta_0} \rho \left[ 1 - M_{xx} \Delta^{-1}_\gamma (\tau \gamma)^{\delta_\gamma} + M_{xy} M_{yx} \Delta^{-2}_\gamma (\tau \gamma)^{2\delta_\gamma} \right],$$

(44)

and

$$\eta_H(\gamma) = \frac{1}{\delta} \beta_0 a^2 \rho \left[ 1 + M_{xx} \Delta^{-1}_\gamma (\tau \gamma)^{\delta_\gamma} + (M_{xx}^2 - M_{xy} M_{yx}) \Delta^{-2}_\gamma (\tau \gamma)^{2\delta_\gamma} \right].$$

(45)

The shear-rate dependent first normal stress difference is now

$$P_{xx} - P_{yy} \simeq -\frac{M_{xy}}{3} \beta_0 a^2 \rho \Gamma^{-1} (\tau \gamma)^{\delta_\gamma} \gamma^{1+\delta_\gamma}.$$  

(46)

These results show that the form of the equations of state is affected by the interactions by modifying the magnitude of the Brownian viscosity and the dependence of the exponents on the volume fraction, which is responsible for the loss of universality in the power law behaviour of the viscosity in concentrated systems [30].

Figure 2 illustrates the differences in shear thinning behaviour in both the ideal and non-ideal cases. Since in the general case the inverse penetration length depends on the sum of the frequency and the shear rate [21], we have calculated the value of the exponent $\delta_\gamma$ by using the results of [21] for a density of particles $\rho \simeq 0.46$. From this figure and equations (44) and (45), one concludes that shear thinning effects are more pronounced in the non-ideal case at lower values of $\gamma$. 

Figure 2. Comparison of the normalized Brownian viscosity in the ideal (---) and non-ideal cases (--- and ----) as a function of the shear rate $\gamma$ for two values of $a$. In the non-ideal case, we have chosen $\Delta_\gamma = 0.5$ and $\delta_\gamma = \frac{1}{2}$ which correspond to a density of particles of 0.46 [21].
6. Discussion

By means of a reformulation of the local equilibrium hypothesis in the domain of the mesoscale, we have shown that a non-equilibrium thermodynamic treatment including the presence of fluctuations and of external forces driving the system to non-equilibrium steady states is possible. Using this scheme, we have obtained the Fokker–Planck equation which, in the case of an inhomogeneous bath, is coupled to the evolution equations of the fields characterizing the state of the bath. The evolution equations of the hydrodynamic fields are derived from the Fokker–Planck equation; their stationary solutions lead to non-equilibrium equations of state.

We have studied, in particular, the case of a gas of Brownian particles in contact with a heat bath when the whole system is in motion. The ideal and non-ideal cases have been analysed. In both cases, we have obtained non-equilibrium equations of state showing a dependence of the pressure tensor of the gas on the frequency and on the shear rate, thus revealing the presence of viscoelastic and non-Newtonian effects.

In the ideal case, the non-analytical dependence on the shear rate of the corrections to the first normal stress difference and the viscosities coincide with those reported in [1] for a simple fluid. In the non-ideal case, non-equilibrium equations of state have been derived by assuming that the inverse penetration length is similar to that of the ideal case with an exponent and a scaling factor depending on the volume fraction of the ‘gas’ of Brownian particles. Our results show that, at sufficiently low shear flows, the first normal stress difference is a quadratic function of the shear rate thus coinciding with the simulations reported in [10]. At higher shear flows, non-Newtonian effects are manifested through a power law dependence on the shear rate of the first normal stress difference and on the viscosities [12].

Our general framework can be used in the study of the dynamics of small systems subjected to driving forces or gradients for which the presence of fluctuations may play a significant role.

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