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Abstract
We propose a method for analysing the dynamics of systems exhibiting slow relaxation, which is based on mesoscopic non-equilibrium thermodynamics. The method allows us to obtain kinetic equations of the Fokker–Planck type for the probability functional and their corresponding Langevin equations. Our results are compared with those obtained by other authors.

1. Introduction

The problem of the glass transition has attracted much attention in recent years, and has been the subject of intense experimental, computational, and theoretical investigation. Mode-coupling theories and replica techniques have been able to capture some trends of the phenomenology of these systems. Although interesting theoretical results have been obtained by means of these theories, the understanding of the problem is far from complete [1, 2].

Supercooled liquids and colloids near a glass transition are characterized by extremely slow relaxation of the density variable. As the glass transition is essentially a dynamic transition, it becomes important to provide a dynamical description of the evolution of the density variable. In addition, the presence of slow dynamics in such systems emphasizes the importance of activated processes, since they are the main mechanism able to make the system evolve and escape from being trapped in metastable states. A complete description of these systems should then take such processes into account.

In this paper we present a simple mesoscopic formalism that allows one to derive kinetic equations of the Fokker–Planck type for the probability functional of the density fields in supercooled liquids and dense colloidal systems. This approach is based on the hypothesis of local equilibrium in the phase space of the system, which allows us to describe the processes leading to variations in the state of the system by means of non-equilibrium thermodynamics. The extension of that theory to the mesoscopic level of description has been referred to as mesoscopic non-equilibrium thermodynamics [3–9].

The plan of the paper is as follows. In section 2, we derive the kinetic equation for the probability distribution functional of the momentum-density and mass-density fields. By

adiabatic elimination of the momentum density we obtain the kinetic equation describing the slow dynamics, giving the configurational changes in the system. In section 3, we introduce fluctuations of the distribution functionals, obtaining the corresponding Langevin equation. Finally, in section 4, we conclude by summarizing our main results.

2. Kinetic equations

We consider the system, either a pure liquid or a colloidal suspension, as a continuum divided into tiny cells of volume v_0. In each cell we define a mass density $\rho(r)$ and a momentum density $g(r) = \rho v(r)$, with r being the position vector of a cell and v the velocity field. For simplicity, we will introduce the compact notation $\{\underline{\Gamma}\} \equiv \{\rho, g\}$.

Let us consider $\hat{P}(\{\underline{\Gamma}\}, t)$ as the distribution functional in phase space, normalized according to the relation

$$\int \hat{P}(\{\underline{\Gamma}\}, t) \, \delta\underline{\Gamma} = N \tag{1}$$

where N is the number of possible states in phase space. Related to this distribution functional we introduce the phase-space entropy $S(\hat{P}(\{\underline{\Gamma}\}, t))$, which satisfies the Gibbs equation introduced by mesoscopic non-equilibrium thermodynamics [10]:

$$\Delta S = -\frac{1}{T} \int \mu(\{\underline{\Gamma}\}, t) \, \Delta \hat{P}(\{\underline{\Gamma}\}, t) \, \delta\underline{\Gamma}. \tag{2}$$

Here T is the temperature, Δ represents a virtual change of the corresponding quantity, and μ is a chemical potential defined in phase space satisfying

$$\mu = -T \frac{\delta S}{\delta \hat{P}}. \tag{3}$$

Its expression can be obtained with the help of the Gibbs entropy postulate [10]

$$S = -k \int \hat{P} \ln \frac{\hat{P}}{\hat{P}^{\text{leq}}} \, \delta\underline{\Gamma} + S^{\text{leq}} \tag{4}$$

where k is the Boltzmann constant. In this expression

$$\hat{P}^{\text{leq}} = \exp\{-\beta[\mu_0 + H_K\{\underline{\Gamma}\} + H_U\{\rho\}]\} \tag{5}$$

is the distribution functional at local equilibrium, with $\beta = 1/kT$, and μ_0 the chemical potential at local equilibrium. Moreover, we have defined the kinetic energy functional

$$H_K\{\rho, g\} = \frac{1}{2} \int \frac{g(r)^2}{\rho(r)} \, \mathrm{d}r \tag{6}$$

and the potential energy functional

$$H_U\{\rho\} = \int f\{\rho\} \, \mathrm{d}r \tag{7}$$

where $f\{\rho\}$ is the free-energy-density functional.

By considering variations in equation (4) we can obtain

$$\Delta S = -k \int \Delta \hat{P} \ln \frac{\hat{P}}{\hat{P}^{\text{leq}}} \, \delta\underline{\Gamma} + \Delta S^{\text{leq}} \tag{8}$$

where

$$\Delta S^{\text{leq}} = -\frac{1}{T} \mu_0 \, \Delta N = -\frac{1}{T} \int \mu_0 \, \Delta \hat{P} \, \delta\underline{\Gamma}. \tag{9}$$

Thus, from comparison of equations (2) and (8), we can infer the expression for the chemical potential:

$$\mu = \mu_0 + kT \ln \frac{\hat{P}}{\hat{P}^{\text{leq}}}. \tag{10}$$

We now assume that the distribution functional evolves according to the continuity equation

$$\frac{\partial \hat{P}}{\partial t} + \int \left(\frac{\delta}{\delta \rho} \dot{\rho} \hat{P} + \frac{\delta}{\delta \boldsymbol{g}} \cdot \dot{\boldsymbol{g}} \hat{P} \right) \mathrm{d}\boldsymbol{r} = - \int \frac{\delta}{\delta \boldsymbol{g}} \cdot \boldsymbol{J}_g \, \mathrm{d}\boldsymbol{r} \tag{11}$$

where the dot over the field variables indicates a time derivative and $\boldsymbol{J}_g$ is a diffusive current in momentum space.

From equations (2) and (11) we can obtain the rate of the entropy variation, which can be written as

$$\frac{\partial S}{\partial t} = \frac{\partial_e S}{\partial t} + \Sigma. \tag{12}$$

In this expression, we can identify the first term on the right-hand side as the rate at which entropy is supplied to the system by its surroundings through the external constraints, given by

$$\frac{\partial_e S}{\partial t} = \frac{1}{T} \iint \mu \left(\frac{\delta}{\delta \rho} \dot{\rho} \hat{P} + \frac{\delta}{\delta \boldsymbol{g}} \cdot \dot{\boldsymbol{g}} \hat{P} \right) \mathrm{d}\boldsymbol{r} \, \delta \underline{\Gamma}. \tag{13}$$

The second contribution corresponds to the entropy produced inside the system due to the irreversible processes, whose value is

$$\Sigma = -\frac{1}{T} \iint \boldsymbol{J}_g \cdot \frac{\delta \mu}{\delta \boldsymbol{g}} \, \delta \underline{\Gamma} \, \mathrm{d}\boldsymbol{r} \tag{14}$$

where a partial integration has been performed. This entropy production has the usual form of flux-force pairs from which we can infer the phenomenological relation

$$\boldsymbol{J}_g = -\frac{1}{T} \int \underline{L}(\boldsymbol{r}, \boldsymbol{r}') \cdot \frac{\delta \mu}{\delta \boldsymbol{g}} \, \mathrm{d}\boldsymbol{r}' \tag{15}$$

where the Onsager coefficients $\underline{L}$ satisfy the Onsager relations $\underline{L}(\boldsymbol{r}, \boldsymbol{r}') = \underline{L}(\boldsymbol{r}', \boldsymbol{r})^{\dagger}$, in which † stands for the Hermitian conjugate. By computing the functional derivative and assuming locality in the coordinates, i.e. $\underline{L}(\boldsymbol{r}, \boldsymbol{r}') = \underline{L}(\boldsymbol{r})\delta(\boldsymbol{r} - \boldsymbol{r}')$, one obtains

$$\boldsymbol{J}_g = -\underline{H}(\boldsymbol{r}) \cdot \left(\beta^{-1} \frac{\delta}{\delta \boldsymbol{g}} + \frac{\delta H_K}{\delta \boldsymbol{g}} \right) \hat{P} \tag{16}$$

where $\underline{H}(\boldsymbol{r}) \equiv \underline{L}(\boldsymbol{r})/T\hat{P}$ can be interpreted as a mobility tensor. Its expression follows from the Navier–Stokes equation [11]

$$\underline{H}(\boldsymbol{r}) = -\eta \left(\tfrac{1}{3} \boldsymbol{\nabla}\boldsymbol{\nabla} + \underline{1}\nabla^2 \right) - \xi \boldsymbol{\nabla}\boldsymbol{\nabla} \tag{17}$$

with η and ξ being the shear and bulk viscosities, respectively, and $\underline{1}$ the unit tensor.

On introducing the current that we have obtained in equation (16) into the continuity equation (11) and using the expressions for $\dot{\rho}$ and $\dot{\boldsymbol{g}}$ given by the reversible part of the Navier–Stokes equation [11], this yields

$$\frac{\partial \hat{P}}{\partial t} = \int \left\{ \frac{\delta}{\delta \rho} \boldsymbol{\nabla} \cdot \boldsymbol{g} + \frac{\delta}{\delta \boldsymbol{g}} \cdot \left[\rho \boldsymbol{\nabla} \frac{\delta H_U}{\delta \rho} + \boldsymbol{\nabla} \cdot \frac{\boldsymbol{g}\boldsymbol{g}}{\rho} \right] + \frac{\delta}{\delta \boldsymbol{g}} \cdot \underline{H}(\boldsymbol{r}) \cdot \left[\beta^{-1} \frac{\delta}{\delta \boldsymbol{g}} + \frac{\delta H_K}{\delta \boldsymbol{g}} \right] \right\} \hat{P} \, \mathrm{d}\boldsymbol{r} \tag{18}$$

which constitutes the functional Fokker–Planck equation for the probability distribution functional $\hat{P}(\{\underline{\Gamma}\}, t)$.

In the diffusive regime, when equilibration in momentum has occurred and only configurational changes are possible, this equation simplifies considerably. To derive the corresponding equation we define the reduced distribution functional

$$P(\{\rho\}, t) \equiv \int \hat{P} \, \delta \boldsymbol{g} \tag{19}$$

and the current

$$\boldsymbol{J}_\rho \equiv \int \boldsymbol{g} \hat{P} \, \delta \boldsymbol{g}. \tag{20}$$

By taking the time derivative of equation (19) and using equation (18) we obtain

$$\frac{\partial P}{\partial t} = \int \frac{\delta}{\delta \rho} \boldsymbol{\nabla} \cdot \boldsymbol{J}_\rho \, \mathrm{d}\boldsymbol{r}. \tag{21}$$

The probability current defined through equation (20) evolves according to

$$\frac{\partial \boldsymbol{J}_\rho}{\partial t} = \int \boldsymbol{g} \frac{\partial \hat{P}}{\partial t} \, \delta \boldsymbol{g} = \iint \frac{\delta \hat{P}}{\delta \rho(r')} \boldsymbol{g}(r) \boldsymbol{\nabla} \cdot \boldsymbol{g}(r') \, \delta \boldsymbol{g} \, \mathrm{d}\boldsymbol{r}$$
$$- \int \hat{P} \boldsymbol{\nabla} \cdot \frac{\boldsymbol{g}\boldsymbol{g}}{\rho} \delta \boldsymbol{g} - \rho P \boldsymbol{\nabla} \frac{\delta H_U}{\delta \rho} - \frac{1}{\rho} \underline{H} \cdot \boldsymbol{J}_\rho \tag{22}$$

where we have used equation (18), and partial integrations have been performed taking into account that $\delta \boldsymbol{g}(r)/\delta \boldsymbol{g}(r') = \delta(\boldsymbol{r} - \boldsymbol{r}')$. We now assume that $(1/\rho)\underline{H} \cdot \boldsymbol{J}_\rho \simeq \tau^{-1} \boldsymbol{J}_\rho$, where τ is the characteristic timescale of the inertial regime. In the diffusive regime when $\tau \ll t$, assuming equilibration in momentum we can write [12]

$$\hat{P} = \Phi\{\underline{\Gamma}\} P(\{\rho\}, t) \tag{23}$$

where

$$\Phi = Z\{\rho\}^{-1} \exp\left(-\beta/2 \int \frac{\Delta \boldsymbol{g}^2}{\rho} \, \mathrm{d}\boldsymbol{r} \right) \tag{24}$$

is a local Maxwellian with $\Delta \boldsymbol{g} = \boldsymbol{g} - \langle \boldsymbol{g} \rangle_\rho$. Here $\langle \boldsymbol{g} \rangle_\rho = (1/P) \int \boldsymbol{g} \hat{P} \, \delta \boldsymbol{g}$ is the conditional average, and

$$Z\{\rho\} = Z_0 \exp\left\{ \frac{3}{2v_0} \int \ln\left[\frac{\rho(r)}{\rho_0} \right] \mathrm{d}\boldsymbol{r} \right\} \tag{25}$$

with ρ_0 being the uniform mass density of the system. Thus, by substituting equation (23) in (22), performing the momentum integration, and eliminating inertial terms we arrive at [7]

$$\boldsymbol{J}_\rho = -\tau \rho(r) \boldsymbol{\nabla} \left(kT \frac{\delta}{\delta \rho} + \frac{\delta H}{\delta \rho} \right) P \tag{26}$$

with

$$H\{\rho\} = H_U - kT \ln Z = H_U - \frac{3kT}{2v_0} \int \ln\left[\frac{\rho(r)}{\rho_0} \right] \mathrm{d}\boldsymbol{r} - kT \ln Z_0 \tag{27}$$

where we have used the result $\int \boldsymbol{g}(r)\boldsymbol{g}(r')\Phi \, \delta \boldsymbol{g} = kT \, \underline{1} \, \rho(r)\delta(\boldsymbol{r} - \boldsymbol{r}')$. Finally, by substitution of the current $\boldsymbol{J}_\rho$ given in equation (26) into (21) we obtain

$$\frac{\partial P}{\partial t} = -\tau kT \int \frac{\delta}{\delta \rho(r)} \left[\boldsymbol{\nabla} \cdot \rho(r) \boldsymbol{\nabla} \right] \left\{ \frac{\delta}{\delta \rho(r)} + \beta \frac{\delta H}{\delta \rho(r)} \right\} P \, \mathrm{d}\boldsymbol{r} \tag{28}$$

which constitutes the functional Fokker–Planck equation in the diffusive regime, in which τkT plays the role of a diffusion coefficient. The stationary solution is the Boltzmann distribution functional $P_{st} \sim \exp(-\beta H)$ [13], thus satisfying detailed balance. This equation has been previously obtained in [12] by means of projection operator techniques. It should be mentioned, as already been pointed out [12], that the presence of a diffusive term in this equation incorporates the existence of hopping or activated processes.

3. Fluctuating kinetic equations

Our purpose in this section is to study the dynamics of the fluctuations in the distribution functional around a given reference distribution. To this end, we will consider that the distribution solution of equation (18) corresponds to the average over an initial distribution in phase space. Consequently, the actual value of the distribution functional will differ from the solution of equation (18) in the presence of fluctuations.

In our derivation of the Fokker–Planck equation, we will incorporate such fluctuations by applying fluctuating hydrodynamics in phase space [5]. Thus, we will split up the current J_g into systematic and random contributions:

$$J_g = J_g^S + J_g^R. \tag{29}$$

The former is given precisely by the linear law (15) whereas the latter defines a Gaussian white-noise stochastic process of zero mean, and the fluctuation-dissipation theorem is given by

$$\langle J_g^R(\{\underline{\Gamma}\}, r, t) J_g^R(\{\underline{\Gamma}'\}, r', t')\rangle_{\hat{P}_0} = 2k\underline{L}\delta(\{\underline{\Gamma}\} - \{\underline{\Gamma}'\})\delta(r - r')\delta(t - t') \tag{30}$$

where $\underline{L}$ has been defined in equation (15), and $\hat{P}_0$ is an initial probability distribution.

When employing the decomposition (29) in the continuity equation (11), we obtain

$$\frac{\partial \hat{P}^*}{\partial t} = -\int \left(\frac{\delta}{\delta\rho}\dot{\rho}\hat{P}^* + \frac{\delta}{\delta g} \cdot \dot{g}\hat{P}^* + \frac{\delta}{\delta g} \cdot J_g^S + \frac{\delta}{\delta g} \cdot J_g^R \right) dr \tag{31}$$

where $\hat{P}^*$ is the fluctuating probability distribution. This equation can also be expressed as

$$\frac{\partial \hat{P}^*}{\partial t} = \int \left\{ \frac{\delta}{\delta\rho}\nabla \cdot g + \frac{\delta}{\delta g} \cdot \left[\rho\nabla\frac{\delta H_U}{\delta\rho} + \nabla \cdot \frac{gg}{\rho} \right] \right. $$
$$\left. + \frac{\delta}{\delta g} \cdot \underline{H}(r) \cdot \left[\beta^{-1}\frac{\delta}{\delta g} + \frac{\delta H_K}{\delta g} \right] \right\} \hat{P}^* \, dr + \int \frac{\delta}{\delta g} \cdot J_g^R \, dr \tag{32}$$

which corresponds to the fluctuating functional Fokker–Planck equation.

Using the same adiabatic elimination procedure as was performed in the previous section we can obtain the fluctuating functional Fokker–Planck equation in the diffusive regime, yielding

$$\frac{\partial P^*}{\partial t} = -\tau kT \int \frac{\delta}{\delta\rho(r)} [\nabla \cdot \rho(r)\nabla] \left\{ \frac{\delta}{\delta\rho(r)} + \beta\frac{\delta H}{\delta\rho(r)} \right\} P^* \, dr + \tau \int \frac{\delta}{\delta\rho}\nabla \cdot \int J_g^R \, \delta g \, dr. \tag{33}$$

From this equation it is possible to get the Langevin equation for the first moment of the distribution functional, defined through

$$\overline{\rho}(r, t) = \int \rho(r) P^*(\{\rho\}, t) \, \delta\rho(r). \tag{34}$$

By multiplying equation (33) by $\rho(\boldsymbol{r})$ and integrating, one obtains

$$\frac{\partial \overline{\rho}(\boldsymbol{r}, t)}{\partial t} = \tau k T \int [\boldsymbol{\nabla} \cdot \rho(\boldsymbol{r})\boldsymbol{\nabla}] \left\{ \frac{\delta}{\delta\rho(\boldsymbol{r})} + \beta \frac{\delta H}{\delta\rho(\boldsymbol{r})} \right\} P^* \, \delta\rho(\boldsymbol{r}) + \eta(\boldsymbol{r}, t) \quad (35)$$

where $\eta(\boldsymbol{r}, t) = -\tau \boldsymbol{\nabla} \cdot \int \boldsymbol{J}_g^R \, \delta\rho \, \delta\boldsymbol{g}$ is the noise term whose correlation, once equation (30) has been used, is seen to be

$$\langle \eta(\boldsymbol{r}, t)\eta(\boldsymbol{r}', t') \rangle = 2kT\tau \boldsymbol{\nabla}_r \cdot \overline{\rho}(\boldsymbol{r}, t)\boldsymbol{\nabla}_{r'}\delta(\boldsymbol{r} - \boldsymbol{r}')\delta(t - t'). \quad (36)$$

The first term inside the bracket in equation (35) is the noise-induced drift [14], which arises from the non-linear character of the dynamics which is due to the density dependence of the kinetic coefficient.

Assuming $P^* = \delta(\{\rho\} - \{\overline{\rho}\})$, equation (35) yields

$$\frac{\partial \overline{\rho}(\boldsymbol{r}, t)}{\partial t} = \tau \boldsymbol{\nabla} \cdot \overline{\rho}(\boldsymbol{r}, t)\boldsymbol{\nabla} \frac{\delta H(\{\overline{\rho}(\boldsymbol{r}, t)\})}{\delta\overline{\rho}(\boldsymbol{r}, t)} + \eta(\boldsymbol{r}, t) \quad (37)$$

which coincides with the stochastic equation in terms of the number-density field $\rho(\boldsymbol{r}, t)$ of [13, 15–19]. The average over the noise of equation (37) yields the mean-field equation proposed in [20].

4. Conclusions

In this paper, we have proposed a method for obtaining Fokker–Planck equations for the probability distribution functional of the density fields for a liquid in the framework of mesoscopic non-equilibrium thermodynamics [7]. Keeping the essentials of non-equilibrium thermodynamics, and extending its range of validity to the mesoscopic domain, we have proposed a Gibbs equation where the entropy depends on the probability distribution functional in phase space. The peculiar dynamics of glassy systems enables one to assume the existence of two dynamical regimes, one related to the fast processes or inertial regime, the other related to the slow relaxation processes or diffusive regime. After adiabatic elimination of the fast degrees of freedom [7], we have obtained the Fokker–Planck equation for the probability distribution functional of the fluid mass density, which describes the slow dynamics of the system. The previous description is independent of the underlying microscopic model. The important requirement is the existence of well separated scales of time and length in the system, which sustain the validity of the local equilibrium hypothesis in phase space. Supercooled liquids and dense colloidal suspensions are known to satisfy this requirement.

At the mesoscopic level we have considered the hydrodynamic fields of the liquid as stochastic variables whose deterministic dynamics is governed by the Navier–Stokes equations. From these equations we can identify the phenomenological coefficients in the kinetic equations. We have also analysed fluctuations of the distribution functional by adding a stochastic contribution to the current in phase space which satisfies a fluctuation-dissipation theorem. From this procedure we obtain a Langevin equation for the mass density.

One of the advantages of the formalism that we have proposed in this paper is that the dynamic description in terms of a probability functional provides complete information on the slow dynamics of the system [12]. In addition, its validity is not restricted to the particular situations addressed in this paper. The same kind of description is perfectly applicable to a wide variety of different situations, among which we might mention the cases of granular materials [21] or nucleation and phase transitions in inhomogeneous media [22, 23].

Acknowledgments

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