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2000 J. Phys.: Condens. Matter 12 6343

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## Theoretical methods dealing with slow dynamics

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Received 28 February 2000

**Abstract.** The traditional strategy for dealing with slow dynamics is summarized. Direct application of this strategy to supercooled liquids and glasses gives rise to problems. Two types of reduced description, namely, microcanonical and canonical versions of dynamical density functional theories, are explained. The non-equilibrium projector technique is used to develop this canonical reduced description. Some speculative proposals as regards how to deal with the barrier crossing regime are outlined.

### 1. Introduction

In condensed matter physics one encounters fast dynamics with the timescale of  $10^{-13}$  to  $10^{-14}$  s or less involving a small number of degrees of freedom (or molecules) which can be easily dealt with by computers, and also slow dynamics ranging from  $10^{-9}$  s to thousands of years which is typically cooperative involving a large number of molecules and is challenging even with the help of computers. Of course, in future the time may come when many of today's challenging problems can be handled by computers. In that case, however, scientists could still be at a loss confronted by a deluge of computer output. Therefore there will always be a need and room for theoretical study of the latter more challenging problems. It should be mentioned also that many important processes are slow. A typical such example is protein folding.

The traditional strategy for the theory of slow dynamics goes like this:

- (1) Identify slow variables.
- (2) Derive a closed kinetic equation for the slow variables.
- (3) Solve the kinetic equation to obtain results of physical interest.

Historically the most successful and well-known example is provided by the dynamics of dilute gas [1]. Here the slow variable is the single-particle phase-space distribution function. The kinetic equation for this slow variable is just the Boltzmann equation. By solving this equation we obtain the hydrodynamic equation containing the transport coefficients expressed in terms of properties of molecules constituting the gas. The second successful example is critical dynamics [2]. Here, thanks to the universality of the problem and the advent of the renormalization group technique which handles the universal behaviour best, many detailed theoretical predictions can be made which have been successfully tested by experiments. Yet another example is the late-stage scaling regime of phase-ordering dynamics [3] although analytic theories are less successful.

In the three examples mentioned above, the reason for the success is easy to recognize: the existence of well-defined mesoscopic regimes with distinct characteristic scales of length and time. These characteristic scales are: the mean free path and mean free time for dilute gas; the correlation length and lifetime of critical fluctuations for critical dynamics; and the characteristic length scale of domain wall patterns and typical growth time for late-stage phase-ordering dynamics.

However, in most other cases, the existence of such a mesoscale is never clear cut. For example, we take up the case of supercooled liquids and glasses which is the theme of the workshop to which this Special Issue is devoted. Certainly here we are dealing with processes involving a very wide range of timescales. However, there is apparently no corresponding wide range of length scales by which one can identify the type of relevant dynamical processes. It is possible that there exist such length scales which are too subtle to have been identified so far.

Under such circumstances, it came as a surprise that a simple theory like the mode-coupling theory (MCT) was used to attack the difficult problem of supercooled liquids and glasses and succeeded in making testable predictions [4]. Despite its impressive successes achieved so far, the recent experimental evidence showing the absence of the predicted ‘knee’ [5] for laboratory glasses except for colloidal glasses indicates a need for a more basic theoretical framework, by means of which one can smoothly link the two domains above and below the mode-coupling critical temperature  $T_c$  by taking into account the obscure ‘hopping processes’ in a theoretically more satisfactory manner.

The dynamical density functional theory (DDFT) proposed by us [6, 7, 15] was designed to meet such a need. The equation that we have proposed for fluids at high density takes the following form for the density probability functional  $P(\{\rho\}, t)$ :

$$\frac{\partial}{\partial t} P(\{\rho\}, t) = -L \int d\mathbf{r} \frac{\delta}{\delta \rho(\mathbf{r})} \nabla \cdot \rho(\mathbf{r}) \nabla \left[ T \frac{\delta}{\delta \rho(\mathbf{r})} + \frac{\delta H\{\rho\}}{\delta \rho(\mathbf{r})} \right] P(\{\rho\}, t) \quad (1)$$

where  $L$  is the kinetic coefficient that incorporates rapid temporal variation of the momentum density, and  $\rho(\mathbf{r})$  is the local number density with  $\rho_0$  its average value. For the free-energy functional, we use the following Ramakrishnan–Yussouff-type one [8]:

$$H\{\rho\} = T \int d\mathbf{r} \rho(\mathbf{r}) \left[ \ln \frac{\rho(\mathbf{r})}{\rho_0} - 1 \right] - \frac{1}{2} T \int \int d\mathbf{r} d\mathbf{r}' c(\mathbf{r} - \mathbf{r}') [\rho(\mathbf{r}) - \rho_0] [\rho(\mathbf{r}') - \rho_0] \quad (2)$$

where  $c(\mathbf{r})$  is the direct correlation function.

Some numerical results are presented in [6]. There we have shown indications of barrier crossing processes which are beyond the scope of current MCT and computer simulations. But, strangely enough, we failed to reproduce numerically the shorter-time  $\alpha - \beta$  relaxations predicted by the idealized MCT. Since the self-consistent equation of the idealized MCT follows from our DDFT by further introducing the factorization approximation [7] or one-loop-order renormalized perturbation theory [13], this leads to the strange conclusion that the inadequacy of our DDFT is cancelled by the error incurred by the factorization approximation since the prediction of the idealized MCT is verified quantitatively by the recent computer simulations [14]. This point needs clarification, perhaps with the help of a computer.

There are still other loose ends in the theory. The theory is based on the intuitive argument that in dense fluid where particles are jammed together the local mass or particle number density is the only slow variable and thus other variables like the momentum density are adiabatically eliminated. This, however, is far from obvious. For instance, fast vibrational motions which are still allowed in a jammed condition involve also momentum displacements of particles,

and hence density change<sup>†</sup>. In section 3 we will discuss the relevance of the reaction rate theory to this problem. It appears that DDFT obtained by eliminating the momentum variable corresponds to the high-friction limit of the Kramers rate theory [11]. This means that the region of validity of DDFT should be limited to a certain high-temperature region.

In the derivation of (1) the density variable was supposed to consist of the sum of the delta functions specifying the exact locations of each particle. However, in the continuum theory of this type a spatially coarse-grained density variable would be more appropriate. There is no unambiguous way of constructing such a variable but we shall comment on this question later in section 3.

Yet another problem was pointed out in a recent work by Marconi and Tarazona [9]. They derived a dynamical equation obeyed by the non-equilibrium *averaged* density field where the free-energy density functional of the inhomogeneous fluid naturally appears. In particular, they argue that the free-energy density functional that enters other existing dynamical density functional theories is the microcanonical one, which is tied to the local equilibrium in which the density profile itself (*not* the averaged one) is precisely specified. Thus they did not discuss fluctuation effects. We will show that one can still talk about fluctuation effects in such situations as well. However, by its construction the usual canonical free-energy density functional is defined only for locally stable states that can be induced by an external field. Hence the equation derived by Marconi and Tarazona [9] cannot deal with problems like spinodal decomposition and barrier crossing since there we have to deal with the density profile for which the free-energy functional is locally unstable. Average effects of such processes must be implicitly included in the equation itself.

On the other hand, one may question the ultimate justification for using the MCT or existing dynamical density functional theories for such problems as supercooled liquids, the glass transition, and solvation dynamics, where the spatial scales involved appear microscopic although the timescale is enormous, because MCT and related ideas were most successful for critical phenomena, and was able to deal most effectively with long-spatial-scale cooperative processes<sup>‡</sup>.

## 2. Canonical reduced description

### 2.1. The two types of reduced description

Once we identify the gross variables, a convenient tool for implementing the idea of reduced description is the projector technique which was pioneered by Nakajima, Zwanzig, and Mori [12]. Broadly speaking, one can think of the two types of reduced description which may be called microcanonical and canonical. The microcanonical one introduced by Zwanzig chooses to specify the precise values for the gross variables and projects onto states where all other degrees of freedom are relaxed to the local equilibrium state with these fixed values for the gross variables. On the other hand, the canonical one projects onto states where only the average values of the gross variables are fixed. If all the gross variables are the extensive ones, these two types of description are essentially equivalent in the thermodynamic limit in the sense that the fluctuations of gross variables are not important. However, the gross variables often represent certain density variables like the local mass density and the local momentum density,

<sup>†</sup> Various cases of elimination of fast variables are discussed in [10]. Adiabatic elimination of the velocity field mentioned above belongs to the first category discussed in this reference, whereas approaches belonging to other categories should also be explored.

<sup>‡</sup> We must make a distinction from static quantum or classical mechanical density functional theories, which have rigorous variational principle foundations. See [33].

and then fluctuation effects are no longer negligible. The two types of reduced description necessarily involve two types of free-energy functionals of gross variables.

One way to circumvent this problem is to make an assumption that the equilibrium distribution function of the gross variables is Gaussian. Then the free-energy functional that enters this distribution is the same as the one that results from using the Ramakrishnan–Yussouff-type density functional in the quadratic approximation of fluctuations, as we have done elsewhere [7]. Here we address this question without making this phenomenological assumption.

Since the microcanonical reduced description was described elsewhere [15], we here focus on the canonical reduced description. At this point, we mention that if we were content with looking at near-equilibrium situations where only the effects linear in deviations from equilibrium are retained, such a reduced description is already provided by Mori's well-known work [16] and we have nothing to add. But here we will be interested in situations arbitrarily far from equilibrium, such as those encountered in the cases of supercooled liquids and glasses. Such a description can also be found in the literature (see [17] and earlier references quoted therein; also see [18]). However, this is not yet fully worked out and there is a room for further developments. Thus we begin the next subsection by reviewing our old work [17] together with some new results.

The material in this section is highly formal and may give the impression of merely being an academic exercise. However, it should be mentioned that this sort of formal framework played an important role in making early predictions about non-analytic shear thinning in fluids before computers [17] and is still a subject of active discussion today [19]. The canonical reduced description is useful for studying the average behaviour when the processes caused by whatever instabilities are present, like barrier crossings, are averaged out—for instance, glassy rheology. Recently, the same projector as is described below was applied to the problem of aging [21].

## 2.2. The non-equilibrium projection operator

We consider a classical system whose microscopic state can be specified by a point in the phase space denoted by  $\hat{x}$ . We choose to denote microscopic quantities by attaching a hat  $\hat{\cdot}$ . The normalized microscopic distribution function at a time  $t$  is then denoted by  $\hat{D}_t(\hat{x})$ . A set of gross variables are represented by the phase-space functions  $A_j(\hat{x})$ ,  $j = 1, 2, \dots$ . It will turn out to be convenient to employ vector notation where the set of gross variables are arranged in a vector denoted by  $\mathbf{A}(\hat{x})$ . The time evolution is then given by the following Liouville equation:

$$\partial_t \hat{D}_t(\hat{x}) = -\hat{L}(\hat{x}) \hat{D}_t(\hat{x}) \quad (3)$$

where  $-\hat{L}(\hat{x})$  is the Liouville operator and the partial time derivative is denoted by  $\partial_t$ . In the following we often omit the phase-space variable  $\hat{x}$  where no confusion arises.

A canonical local equilibrium state is generally written as

$$\hat{D}_t^c(\hat{x}) = e^{\hat{\sigma}_t^c(\hat{x})} \quad (4)$$

$$\hat{\sigma}_t^c(\hat{x}) \equiv -\Phi(\mathbf{b}_t) + \mathbf{b}_t \cdot \mathbf{A}. \quad (5)$$

Here  $\mathbf{b}_t$  is the vector conjugate to  $\mathbf{A}$  and is so chosen as to reproduce the same average values  $\alpha_t$  of  $\mathbf{A}$  in  $\hat{D}_t(\hat{x})$ .  $\Phi(\mathbf{b}_t)$  then guarantees the normalization of  $\hat{D}_t^c(\hat{x})$ :

$$\text{Tr} \hat{D}_t^c(\hat{x}) = 1 \quad (6)$$

where Tr denotes the phase-space integration. Hence we have  $\Phi(\mathbf{b}_t) = \ln \text{Tr} e^{\mathbf{b}_t \cdot \mathbf{A}}$  which is like a free energy. The averages over  $\hat{D}_t(\hat{x})$  and  $\hat{D}_t^c(\hat{x})$  are, respectively, denoted by  $\langle \cdot \cdot \cdot \rangle_t$

and  $\langle \dots \rangle_t^c$ . Thus we must have

$$\mathbf{a}_t = \langle \mathbf{A} \rangle_t = \langle \mathbf{A} \rangle_t^c. \quad (7)$$

We also use the notation  $\delta_t \hat{X} \equiv \hat{X} - \langle \hat{X} \rangle_t^c$  for an arbitrary phase function  $\hat{X}$ . We can then define a time-dependent generalized susceptibility matrix  $\chi_t$  and its inverse by

$$\chi_t \equiv \frac{\partial}{\partial \mathbf{b}_t} \mathbf{a}_t = \langle \delta_t \mathbf{A} \delta_t \mathbf{A} \rangle_t^c \quad (8a)$$

$$\chi_t^{-1} = \frac{\partial}{\partial \mathbf{a}_t} \mathbf{b}_t. \quad (8b)$$

We then find

$$\frac{\partial \Phi}{\partial \mathbf{b}_t} = \mathbf{a}_t \quad \frac{\partial \hat{\sigma}_t^c(\hat{x})}{\partial \mathbf{b}_t} = \delta_t \mathbf{A} \quad \frac{\partial \hat{\sigma}_t^c(\hat{x})}{\partial \mathbf{a}_t} = \chi_t^{-1} \cdot \delta_t \mathbf{A}. \quad (9)$$

In general we have

$$\frac{\partial}{\partial \mathbf{b}_t} \langle \hat{X} \rangle_t^c = \langle \delta_t \mathbf{A} \hat{X} \rangle_t^c \quad (10a)$$

$$\frac{\partial}{\partial \mathbf{a}_t} \langle \hat{X} \rangle_t^c = \chi_t^{-1} \cdot \langle \delta_t \mathbf{A} \hat{X} \rangle_t^c. \quad (10b)$$

We are now ready to introduce a time-dependent projector onto  $\hat{D}_t^c$ , namely  $P_t^c$ , which is defined by

$$P_t^c \hat{X} \equiv \hat{D}_t^c \text{Tr} \hat{X} + \frac{\partial \hat{D}_t^c}{\partial \mathbf{a}_t} \cdot \text{Tr} \hat{X} \delta_t \mathbf{A}. \quad (11)$$

Then we can show the following:

$$P_t^c \hat{D}_t = \hat{D}_t^c \quad \partial_t \hat{D}_t^c = P_t^c \partial_t \hat{D}_t \quad P_s^c P_t^c = P_s^c \quad Q_s^c Q_t^c = Q_t^c \quad (12)$$

where the complement projector is defined by  $Q_s^c \equiv 1 - P_s^c$ . It is then possible to derive a formal closed equation for  $\hat{D}_t^c$  [17].

Hereafter we skip details of the algebraic manipulations due to space limitations.

In order to study the time evolution of a dynamical variable such as  $\mathbf{A}(t)$  it is useful to consider the adjoint of an operator, say  $O$ , denoted as  $O^\dagger$  and defined as follows:

$$\text{Tr} \hat{X} O \hat{Y} = \text{Tr} \hat{Y} O^\dagger \hat{X}. \quad (13)$$

The Liouville operator here is assumed to have the property  $\hat{L}^\dagger = -\hat{L}$ . We then obtain that an adjoint of  $P_t^c$  can be denoted simply by  $P_t \equiv (P_t^c)^\dagger = (\hat{D}_t^c)^{-1} P_t^c \hat{D}_t^c$ :

$$P_t \hat{X} \equiv \langle \hat{X} \rangle_t^c + \delta_t \mathbf{A} \cdot \chi_t^{-1} \cdot \langle (\delta_t \mathbf{A}) \hat{X} \rangle_t^c. \quad (14)$$

### 2.3. The equations for the average and deviation

We now give the time evolution of  $\mathbf{a}_t$  and its deviation  $(\delta_t \mathbf{A})_t \equiv e^{t\hat{L}} \mathbf{A} - \mathbf{a}_t$ :

$$\frac{d}{dt} \mathbf{a}_t = \langle \hat{L} \mathbf{A} \rangle_t^c - \int_0^t ds \mathbf{b}_s \cdot \mathcal{K}_0^c(ts) \quad (15)$$

$$\begin{aligned} \frac{d}{dt} (\delta_t \mathbf{A})_t &= (\delta_t \mathbf{A})_t \cdot \chi_t^{-1} \cdot \langle (\delta_t \mathbf{A}) \hat{L} \mathbf{A} \rangle_t^c - \int_0^t ds (\delta_s \mathbf{A})_s \cdot \chi_s^{-1} \cdot \mathcal{K}^c(ts) + \hat{\mathbf{f}}(t) \\ &+ \int_0^t ds e^{s\hat{L}} (\partial_s P_s) \hat{\mathbf{f}}(ts). \end{aligned} \quad (16)$$

Here we have introduced the memory kernels:

$$\mathcal{K}^c(ts) \equiv \text{Tr}(Q_s^c \hat{L} \delta_s \mathbf{A} \hat{D}_s^c) \hat{\mathbf{f}}(ts) = \langle [Q_s(\mathbf{1} + \delta_s \mathbf{A} \mathbf{b}_s) \cdot (\hat{L} \mathbf{A})] \hat{\mathbf{f}}(ts) \rangle_s^c \quad (17)$$

$$\mathcal{K}_0^c(ts) \equiv \langle \hat{\mathbf{f}}(s) \hat{\mathbf{f}}(ts) \rangle_s^c \quad (18)$$

where

$$\hat{\mathbf{f}}(ts) \equiv Q_s U_c(ts)^\dagger Q_t \hat{L} \mathbf{A} = Q_s U_c(ts)^\dagger \hat{L} \mathbf{A} \quad (19)$$

and, in particular,

$$\hat{\mathbf{f}}(t) \equiv \hat{\mathbf{f}}(tt) = Q_t \hat{L} \mathbf{A}. \quad (20)$$

Here we have introduced the projected time evolution operator as

$$U_c(ts)^\dagger \equiv \exp_- \left( \int_s^t ds' \hat{L} Q_{s'} \right) \quad (21)$$

where  $e_-$  is the inverse time-ordered exponential. We also find

$$(\partial_s P_s) \hat{\mathbf{f}}(ts) = \delta_s \mathbf{A} \cdot \chi_s^{-1} \cdot \langle \delta_s \mathbf{A} \hat{\mathbf{f}}(ts) \delta_s \mathbf{A} \rangle_s^c \cdot \chi_s^{-1} \cdot (\partial_s \mathbf{a}_s). \quad (22)$$

Thus the last term of (16) represents coupling of the drift  $\mathbf{a}_s$  and deviation  $\delta_s \mathbf{A}$  through the random force  $\hat{\mathbf{f}}(ts)$ , which is reminiscent of the mode-coupling mechanism [20] where random forces couple to the terms bilinear, trilinear, ... in gross variables.

If we neglect the memory effects and introduce the friction matrix  $\zeta$ , the average equation is simplified to

$$\frac{d}{dt} \mathbf{a}_t = (\hat{L} \mathbf{A})_t^c - \mathbf{b}_t \cdot \zeta. \quad (23)$$

The dense-fluid equation of Marconi and Tarazona [9] follows as a special case of (23) where  $\mathbf{A}$  consists of the local mass and momentum densities.

### 3. The barrier crossing regime

Recent progress in our understanding of the behaviour of dense fluids near freezing or below in terms of MCT and other ideas such as inherent structures [28] and instantaneous normal modes [24] tempts us to speculate about a strategy for finding a more comprehensive reduced description. One of our objectives is to explore a method by which the current MCT can be extended to the region below the mode-coupling critical temperature  $T_c$  in a natural manner. Another is to understand the relationship between Newtonian dynamics (ND) and stochastic dynamics (SD). Recent computer simulations revealed that fluids obeying ND and SD show very similar long-time behaviour in the high-density regions [14]. There is a well-established method for deriving a Smoluchowski equation for interacting Brownian particles immersed in a fluid consisting of atoms which are much smaller than the Brownian particles, where the smallness parameter is the square root of the mass ratio of a fluid atom and a Brownian particle [23]. Here, however, no such obvious smallness parameter exists, and the aforementioned results of computer simulation seem to suggest the need for a new type of reduced description. We argued in [15] that Newtonian fluids and Brownian fluids (that is, those described by the Smoluchowski equation) lead to the same dynamical density functional equation, from which one can derive the Götze self-consistent MCT equation after using the factorization approximation. However, the argument is far from convincing, involving drastic simplification of a complicated expression for a memory kernel, containing projectors.

At low temperatures the system is settled into one of the so-called inherent-structure states in which each particle is performing small-amplitude thermal oscillations around

its reference position. This is interrupted by occasional barrier crossing processes. The instantaneous normal-mode approach [24] attempts to capture this picture with real and imaginary eigenfrequencies corresponding to locally stable and unstable points in the  $N$ -particle configuration space, suggesting the existence of two widely separated timescales<sup>†</sup>.

If one performs a transformation of phase-space variables into normal-mode variables, one can further transform each normal-mode variable into action and angle variables. The action variables are constants of the motion as long as the oscillations are harmonic. This, of course, is not always the case, as the temperature increases and anharmonicity sets in. However, these action variables are still slow variables compared to the rapidly varying angle variables. Hence one can hope to obtain a reduced description in terms of the action variables where the angle variables are averaged out. The action variables, being adiabatic invariants for integrable systems, are known to play prominent roles in non-linear dynamics [25] and there are other examples of reduced descriptions in terms of action variables [11, 26, 27]. A possible difficulty in this scenario is that the nature of the action variables generally changes after each thermally activated process, which is like having products after each chemical reaction which will then become new reactants for the next chemical reaction. In our case we will have to describe, by a single kinetic equation representing the desired reduced description, the whole series of successive thermally activated processes requiring a new set of action variables each time, which remains a challenge. Such kinetic equations, once established, should be of enormous help in elucidating the slow dynamics as in the case of other more traditional examples outlined in section 1.

The original inherent-structure idea seeks minimum-energy states reached at zero temperature [28]. However, for our purpose it is more reasonable to choose the self-consistently renormalized states that include effects of thermal fluctuations [29]. Furthermore, for stiff interaction potentials like those for hard spheres, appropriate modifications will be needed [30, 31].

The use of action variables permits an unambiguous though formal definition of the coarse-grained density which replaces the sum of delta functions. Here sharply defined locations of particles are replaced by ones smeared out by thermal oscillations about the original reference point. At low temperatures this coarse-grained density will look as follows:

$$\rho(\mathbf{r}; \{\mathbf{r}^0\}, \{J\}) = \sum_j \frac{1}{(2\pi)^{3/2} \sqrt{\det \mathbf{Q}_j}} \exp \left\{ -\frac{1}{2} (\mathbf{r} - \mathbf{r}_j^0) \cdot [\mathbf{Q}_j]^{-1} \cdot (\mathbf{r} - \mathbf{r}_j^0) \right\} \quad (24)$$

where  $\{\mathbf{r}^0\}$  is the set of reference positions of the particles  $\mathbf{r}_j^0$  and the sum is over the particle labels  $j = 1, 2, \dots, N$ .  $\mathbf{Q}_j$  is the dyadic defined by

$$\mathbf{Q}_j \equiv \sum_{\lambda} \frac{J_{\lambda}}{m\omega_{\lambda}} \mathbf{R}_{j\lambda} \mathbf{R}_{j\lambda}. \quad (25)$$

Here  $J_{\lambda}$  is the action variable of the normal mode labelled as  $\lambda$  and  $\mathbf{R}_{j\lambda}$  the transformation vector that connects the normal coordinate labelled  $\lambda$  to  $\mathbf{r}_j - \mathbf{r}_j^0$ , the deviation of the position of the particle  $j$  from its reference point, and  $m\omega_{\lambda}$  is the particle mass times the frequency of the normal mode  $\lambda$ . If  $\mathbf{Q}_j$  is an infinitesimal small number times the unit dyadic, equation (24) reduces to the usual sum of delta functions. This coarse-grained density or its appropriate average over the action variables might be used more appropriately to construct a dynamical density functional equation at low temperatures, because the fast time variation contained in the angle variables is averaged out.

<sup>†</sup> It is unlikely that all the imaginary eigenfrequencies contribute to relevant barrier crossings. Those associated with barriers with heights less than  $k_B T$  are clearly irrelevant. It is pointed out that some imaginary frequencies come from shoulder-type portions of landscape, and also that there is a low-frequency cut-off associated with long-time-tail collective behaviour [24].



#### 4. Concluding remarks

The microcanonical version of the dynamical density functional theory (MDDFT) is a suitable stochastic model that incorporates the MC mechanism and is still capable of describing barrier crossings [6]. A distinctive feature of our MDDFT as compared to direct MD or MC simulations is that the short-distance correlation essential in dense fluids is incorporated as input through the direct correlation function. Another distinctive feature is that it is a minimal model for both Newtonian and Brownian dynamical systems as far as the long-time behaviour is concerned. Indeed, the similarity of the two systems at long times was verified by simulation as well [14]. We think that the MDDFT is a useful model, bridging between the MCT and barrier crossing regimes, but one should always keep in mind the region of its validity when applying the results of MDDFT in analysing real systems, as one often finds in the literature blind applications of the MDDFT to calculate transport coefficients of liquid and to study solvation dynamics.

We have yet to find an effective strategy of wider applicability for supercooled liquids and glasses, since this is an area where none of the traditional strategies seems adequate. On the other hand, a great deal of effort has been made on the simpler related problem of reaction rate processes [32], which might suggest a new approach. Although it would be too ambitious at this time to aim at a single scheme to cover the entire glassy dynamics, one still hopes that at least an efficient low-temperature treatment of dense fluid below the freezing point can be found where we definitely have processes with widely separated timescales. The correct extrapolation of MCT to the regime below the mode-coupling critical temperature  $T_c$  will be preceded by better understanding of the low-temperature regime dominated by barrier crossing dynamics.

#### Acknowledgments

The author has greatly benefited from conversations on the topics discussed in this work with the following individuals: A Crisanti, C Dasgupta, B Dünweg, M Fuchs, B Kim, A Latz, U Marconi, P Tartaglia, F Sciortino and R Schilling. This work was supported by the Scientific Research Fund of the Ministry of Education, Science and Culture of Japan and also by the Research Institute for Science and Technology of Chubu University.

#### References

- [1] Dorfman J R and van Beijeren H 1977 *Statistical Mechanics* vol B, ed B Berne (New York: Plenum)
- [2] Hohenberg P C and Halperin B I 1977 *Rev. Mod. Phys.* **49** 435
- [3] Bray A 1994 *Adv. Phys.* **43** 357
- [4] Yip S (guest ed) 1995 *Relaxation Kinetics in Supercooled Liquids—Mode Coupling Theory and its Experimental Tests; Transport Theory Stat. Phys.* **24** (6–8) (Theme Issues)
- [5] Barshila H C, Li G, Shen G Q and Cummins H Z 1999 *Phys. Rev. E* **59** 5625
- [6] Kawasaki K and Fuchizaki K 1998 *J. Non-Cryst. Solids* **235–237** 57  
Kawasaki K and Fuchizaki K 1999 *Physica A* **266** 400
- [7] Kawasaki K 1994 *Physica A* **208** 35
- [8] Ramakrishnan T V and Yussouff M 1979 *Phys. Rev. B* **19** 2775
- [9] Marconi U M B and Tarazona P 1999 *J. Chem. Phys.* **110** 8032
- [10] van Kampen N G 1985 *Phys. Rep.* **124** 69
- [11] Kramers H A 1940 *Physica* **7** 284
- [12] Nakajima S 1958 *Prog. Theor. Phys.* **20** 948  
Zwanzig R W 1960 *J. Chem. Phys.* **33** 1338  
Mori H 1965 *Prog. Theor. Phys.* **33** 424
- [13] Kawasaki K and Miyazima S 1997 *Z. Phys. B* **103** 423
- [14] Gleim T, Kob W and Binder K 1998 *Phys. Rev. Lett.* **81** 4404 and earlier references cited therein

- [15] Kawasaki K 1998 *Progress in Statistical Physics* ed W Sung et al (Singapore: World Scientific)  
Kawasaki K 1998 *J. Stat. Phys.* **93** 527
- [16] Mori H 1965 *Prog. Theor. Phys.* **33** 423
- [17] Kawasaki K and Gunton J D 1973 *Phys. Rev. A* **8** 2048
- [18] Nettleton R E 1998 *Open Syst. Inform. Dyn.* **4** 201
- [19] Evans D J and Morriss G P 1990 *Statistical Mechanics of Nonequilibrium Liquids* (New York: Academic)  
Sarman S S, Evans D J and Cummings P T 1998 *Phys. Rep.* **305** 1
- [20] Kawasaki K and Gunton J D 1978 *Progress of Liquid Physics* ed C A Croxton (New York: Wiley)
- [21] Latz A 2000 *J. Phys.: Condens. Matter* **12** 6353
- [22] Bouchaud J-P, Cugliandolo L F, Kurchan J and Mézard M 1996 *Physica A* **226** 243
- [23] Deutch J M and Oppenheim I 1987 *Faraday Discuss. Chem. Soc.* **83** 1
- [24] Keyes T 1997 *J. Phys. Chem. A* **101** 2921
- [25] Lichtenberg A J and Lieberman M A 1992 *Regular and Chaotic Dynamics* (Heidelberg: Springer)
- [26] Brout R and Prigogine I 1956 *Physica* **12** 621  
Prigogine I and Balescu R 1957 *Physica* **23** 555
- [27] Zwanzig R W, 1959 *Phys. Fluids* **2** 12
- [28] Stillinger F H and Weber T A 1982 *Phys. Rev. A* **25** 978
- [29] Cao J and Voth G A 1995 *J. Chem. Phys.* **103** 4211
- [30] Fixman M 1969 *J. Chem. Phys.* **51** 3270
- [31] Stoessel J P and Wolynes P G 1984 *J. Chem. Phys.* **80** 4502
- [32] Hänggi P, Talkner P and Borkovec M 1990 *Rev. Mod. Phys.* **62** 251
- [33] Laird B B, Ross R B and Ziegler T (ed) 1996 *Chemical Applications of Density-Functional Theory* (Washington, DC: American Chemical Society)