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LETTER TO THE EDITOR

On the controversy over the stochastic density functional equations

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Abstract. This letter aims to justify the stochastic equations in terms of the number density variable, which are still controversial, via complementing Dean's approach (Dean D S 1996 *J. Phys. A: Math. Gen.* **29** L613). Our approach is twofold: first, we demonstrate that standard manipulations straightforwardly transform the stochastic equation of the density *operator*, derived by Dean, to the Fokker–Planck equation for the (c-number) density distribution functional $P(\{\rho\}, t)$. Moreover, we verify the associated static solution of $P(\{\rho\}, t)$ with the help of the conditional grand canonical partition function.

1. Introduction

In supercooled liquids, due to the dense packing and strong correlation of the constituent particles, the nonvibrational diffusive motion takes much more time than collisions. In other words, the momentum and the energy flow much more quickly via collisions through the system than the slowly decaying number density. Recently, there has been a considerable effort to describe such slow dynamics in liquids (see, for instance, [1]; a reference from the viewpoint of mode-coupling theory). We shall discuss one of the approaches, in particular; the following stochastic equations in terms of the number density field $\rho(x, t)$ [2–5]:

$$\frac{\partial \rho(x,t)}{\partial t} = \nabla \cdot L[\rho(x,t)]\nabla \frac{\delta H(\{\rho\})}{\delta \rho}\bigg|_{\rho(x,t)} + \xi(x,t) \tag{1}$$

or its equivalent, i.e. the Fokker–Planck equation for the probability distribution functional $P(\{\rho\}, t)$:

$$\frac{\partial P(\{\rho\},t)}{\partial t} = -\int \mathrm{d}x\, \frac{\delta}{\delta\rho(x)} \nabla \cdot L[\rho(x)]\nabla \left[T\frac{\delta}{\delta\rho(x)} + \frac{\delta H(\{\rho\})}{\delta\rho(x)}\right] P(\{\rho\},t). \tag{2}$$

In equations (1) and (2), the Hamiltonian H is of the free energy functional form as

$$H(\{\rho\}) = \tfrac{1}{2}\int \mathrm{d}x\,\mathrm{d}y\, \rho(x)V(x-y)\rho(y) + T\int \mathrm{d}x\, \rho(x)\log\rho(x). \tag{3}$$

$L[\rho(x)]$ is the kinetic coefficient written as $L[\rho(x)] = \rho(x,t)\Gamma$, with Γ being the mobility of particles, and ξ is the divergence of a random force and its correlation function is given by

$$\langle \xi(x,t)\,\xi(y,t')\rangle = 2T\nabla_x \cdot L[\rho(x)]\nabla_y \delta(x-y)\delta(t-t'). \tag{4}$$

For the explicit representation of this averaging, see equation (7) below.

These equations have attractive features for studying the slow dynamics: one is the physically clear incorporation of the thermally activated hopping processes via the last random term ξ on the right-hand side of equation (1). Also of interest is the density dependence of the kinetic coefficient, $L \propto \rho$, that produces the nonlinear term of dynamic origin [6] and implies the relevance of these equations to describing dynamical heterogeneity [7].

Nevertheless, the stochasticity for the number density variable is still controversial. To see this, let us first mention one of several attempts [2–4], presented by Dean [2], to justify the above stochastic equations (1) and (2). Consider here a canonical system of N particles interacting via a pairwise potential $V(x)$ and surrounded by a thermal white noise heat bath. The ith particle then obeys the Langevin equation,

$$\frac{\mathrm{d}X_i(t)}{\mathrm{d}t} = -\Gamma \sum_{j=1}^{N} \nabla_i V[X_i(t) - X_j(t)] + \eta_i(t) \tag{5}$$

where the components of the noise η_i^α are taken to be uncorrelated as $\langle \eta_i^\alpha(t)\, \eta_i^\beta(t) \rangle = 2T\Gamma\delta_{ij}\delta^{\alpha\beta}\delta(t-t')$. Dean shows, using the Ito prescription for the change of variables and summing over the i, that equation (5) is transformed to the equation of the density operator, $\hat\rho(x,t) = \sum_i \hat\rho_i(x,t) = \sum_i \delta[x - X_i(t)]$:

$$\begin{aligned} \frac{\partial \hat\rho(x,t)}{\partial t} &= \nabla \cdot \hat\rho(x,t) \int \mathrm{d}y\, \hat\rho(y,t) \nabla V(x-y) + T\nabla^2 \hat\rho(x,t) + \hat\xi(x,t) \\ \hat\xi(x,t) &= -\sum_i \nabla \cdot [\hat\rho_i(x,t)\, \eta_i(t)]. \end{aligned} \tag{6}$$

Since one finds

$$\langle \hat\xi(x,t)\, \hat\xi(y,t) \rangle \equiv \int \mathrm{d}\eta_i\, \hat\xi(x,t)\, \hat\xi(y,t) \exp\left(-\int \mathrm{d}t\, \frac{\eta_i^2}{4T\Gamma} \right) \tag{7}$$

$$= 2T\nabla_x \cdot L[\hat\rho(x)] \nabla_x \delta(t-t') \tag{8}$$

equation (1) is verified so long as the operator $\hat\rho$ reads ρ of the c-number.

As expected, though, Marconi and Tarazona (MT) [8] subsequently objected to the last supposition: they claim that ρ is to be defined by averaging $\hat\rho$ over the noise as $\rho_{av} = \langle \hat\rho \rangle$, where the subscript av is appended to emphasize the procedure. Consequently, the dynamical density functional equation becomes deterministic:

$$\frac{\partial \rho_{av}(x,t)}{\partial t} = \nabla \cdot \int \mathrm{d}y\, \langle \hat\rho(x,t)\, \hat\rho(y,t) \rangle \nabla V(x-y) + T\nabla^2 \rho_{av}(x,t) \tag{9}$$

whereby the Boltzmann distribution of number density is assured as the time-independent solution [8, 9].

To settle such controversy over the stochastic density functional equations (1) and (2), this letter aims to complement Dean's argument from (5)–(8) so that the above criticism by MT may become invalid. Our strategy is twofold: first, in the next section, we demonstrate that standard manipulations [10] transform equation (6) of the density operator to the Fokker–Planck equation (2). Moreover, we verify in section 3, with the help of the conditional grand canonical partition function, the static solution $P_0(\{\rho\})$ of (2):

$$P_0(\{\rho\}) \propto \exp(-\beta H) \tag{10}$$

where $\beta = T^{-1}$. In the final section, to clarify the connection between the stochastic and the deterministic equation, we confirm using the WKB-like approximation [11] to the Fokker–Planck equation (2) that the noise-averaged deterministic equation (9) corresponds to that for the saddle-point path of $P(\{\rho\}, t)$; this reveals that MT's argument produces only the mean-field equation and not the first member of the BBGKY hierarchy [12] including the two-point equal-time correlation function.

2. From equation (6) to the Fokker–Planck equation (2)

Turning our attention to the functional space, we immediately find that the density operator $\hat{\rho}$ may be directly mapped to the distribution functional $P(\{\rho\}, t)$ as

$$P(\{\rho\}, t) = \left\langle \prod_x \delta[\hat{\rho}(x, t) - \rho(x)] \right\rangle \tag{11}$$

not via the averaging $\rho_{av} = \langle\hat{\rho}\rangle$; essentially only this definition has dissolved the MT's critique.

Let us then exhibit below that $P(\{\rho\}, t)$ with equation (6) satisfies the Fokker–Planck equation (2). We first differentiate (11) with respect to time, and obtain

$$\begin{aligned} \frac{\partial P(\{\rho\}, t)}{\partial t} &= \int \mathrm{d}x \left\langle \frac{\partial \hat{\rho}(x, t)}{\partial t} \frac{\delta}{\delta \hat{\rho}(x, t)} \delta[\hat{\rho}(x, t) - \rho(x)] \prod_{y \neq x} \delta[\hat{\rho}(y, t) - \rho(y)] \right\rangle \\ &= \int \mathrm{d}x \left\langle \left[\nabla \cdot \hat{\rho}(x, t) \int \mathrm{d}y \, \hat{\rho}(y, t) \nabla V(x - y) + T \nabla^2 \hat{\rho}(x, t) + \hat{\xi}(x, t) \right] \right. \\ &\quad \left. \times \frac{\delta}{\delta \hat{\rho}(x, t)} \delta[\hat{\rho}(x, t) - \rho(x)] \prod_{y \neq x} \delta[\hat{\rho}(y, t) - \rho(y)] \right\rangle. \end{aligned} \tag{12}$$

We may replace $\hat{\rho}$ by ρ using the δ-function, and hence equation (12) reads

$$\begin{aligned} \frac{\partial P(\{\rho\}, t)}{\partial t} &= -\int \mathrm{d}x \, \frac{\delta}{\delta \rho(x)} \left[\nabla \cdot \rho(x) \int \mathrm{d}y \, \rho(y) \nabla V(x - y) + T \nabla^2 \rho(x) \right] P(\{\rho\}, t) \\ &\quad - \int \mathrm{d}x \, \frac{\delta}{\delta \rho(x)} \left\langle \hat{\xi}(x, t) \prod_x \delta[\hat{\rho}(x, t) - \rho(x)] \right\rangle. \end{aligned} \tag{13}$$

Using the identity for an arbitrary function $F(\{\eta_i^\alpha\})$, $\langle F(\{\eta_i^\alpha\}) \, \eta_i^\alpha(t) \rangle = 2T\Gamma \left\langle \delta F(\{\eta_i^\alpha\}) / \delta \eta_i^\alpha(t) \right\rangle$, the last bracketed term on the right-hand side of (13) is further transformed to

$$\begin{aligned} \left\langle \hat{\xi}(x, t) \prod_x \delta[\hat{\rho}(x, t) - \rho(x)] \right\rangle &= -2T\Gamma \left\langle \sum_{i,\alpha} \frac{\partial \hat{\rho}_i(x, t)}{\partial x^\alpha} \frac{\delta \hat{\rho}(y, t)}{\delta \eta_i^\alpha} \frac{\delta}{\delta \hat{\rho}(y, t)} \prod_y \delta[\hat{\rho} - \rho] \right\rangle \\ &= T\Gamma \left\langle \sum_i \nabla_x \cdot \nabla_y [\hat{\rho}_i(x, t) \, \hat{\rho}_i(y, t)] \frac{\delta}{\delta \hat{\rho}(y, t)} \prod_y \delta[\hat{\rho} - \rho] \right\rangle \end{aligned} \tag{14}$$

where the superscript α denotes the component of x and η_i, and use has been made of

$$\frac{\delta \hat{\rho}_i(y, t)}{\delta \eta_i^\alpha} \longrightarrow -\frac{1}{2} \frac{\partial \hat{\rho}_i(y, t)}{\partial y_i^\alpha} \tag{15}$$

that is obtained from standard mathematical manipulation of the discretized Langevin equation [10]. Also, noting that relation $\hat{\rho}_i(x, t) \, \hat{\rho}_i(y, t) = \delta(x - y) \rho_i(x, t)$ gives

$$\nabla_x \cdot \nabla_y [\hat{\rho}_i(x, t) \, \hat{\rho}_i(y, t)] = -\nabla_x \cdot \hat{\rho}_i(x, t) \nabla_x \delta(x - y) \tag{16}$$

and replacing $\hat{\rho}$ by ρ as before, the bracketed term finally reads

$$\left\langle \hat{\xi}(x, t) \prod_x \delta[\hat{\rho}(x, t) - \rho(x)] \right\rangle = T\Gamma \nabla \cdot \rho(x, t) \nabla \frac{\delta P(\{\rho\}, t)}{\delta \rho(x, t)}. \tag{17}$$

Equation (13) with this is none other than the Fokker–Planck equation (2).

Thus it has been demonstrated that the stochastic equation of the density operator (6) leads to the Fokker–Planck equation (2) for the (c-number) density distribution functional (or equation (1)).

3. Verification of the equilibrium distribution functional (10)

We arrive at a time-independent solution of the Fokker–Planck equation in the large-time limit: $P_0(\{\rho\}) = \lim_{t\to\infty} P(\{\rho\}, t)$. Therefore, it is plausible to suppose that the noise averaging in calculating P_0 becomes equivalent to the configurational one in equilibrium:

$$P_0(\{\rho\}) \propto \frac{1}{N!}\prod_{i=1}^{N}\int \mathrm{d}X_i \prod_x \delta[\hat{\rho}(x,t) - \rho(x)] \exp\left[-\beta\sum_{i,j} V(X_i - X_j)\right]. \qquad (18)$$

The problem is then how to derive expression (10) from the above conditional partition function.

Let us move to the grand canonical system where we are to consider

$$P_0^{\Xi} = \sum_{N=0}^{\infty} P_0 \lambda^N \qquad (19)$$

with $\beta\mu = \ln\lambda$ being the chemical potential. Introducing the auxiliary field ψ as $\delta[\hat{\rho}(x) - \rho] = \int \mathrm{d}\psi\, \exp[\mathrm{i}\psi(\hat{\rho} - \rho)]$, the configurational representation of P_0^{Ξ} given by (18) and (19) reads

$$P_0^{\Xi} \propto \int D\psi\, \exp\left[-\beta\int \mathrm{d}x\,\mathrm{d}y\, \tfrac{1}{2}\rho(x)V(x-y)\rho(y) + \mathrm{i}\rho(x)\psi(x) - \mathrm{e}^{\mathrm{i}\psi(x)+\mu}\right] \qquad (20)$$

where $D\psi$ is formally defined as $\prod_x \mathrm{d}\psi(x)$. Since there is no contribution to P_0^{Ξ} of the principal quadratic fluctuation of the auxiliary field ψ around the saddle point path ψ_{sp} as shown elsewhere [13], the Gaussian approximation for ψ reduces the functional integral form (20) to

$$P_0^{\Xi} \propto \exp\left[-\beta H + \beta\int \mathrm{d}x\, \rho(x) + \mu\rho(x)\right] \qquad (21)$$

as found from substituting $\rho = \mathrm{e}^{\mathrm{i}\psi_{sp}+\mu}$ into (20).

To return to the canonical system, we have only to perform the following contour integral:

$$P_0 = \frac{1}{2\pi\mathrm{i}}\oint \mathrm{d}\lambda\, \frac{P_0^{\Xi}}{\lambda^{N+1}} \qquad (22)$$

where λ is now a complex variable. This relation, using the Cauchy's integral theorem, gives back the canonical form:

$$\begin{aligned} P_0 &\propto \exp\left[-\beta H + \beta\int \mathrm{d}x\, \rho(x)\right] \frac{1}{2\pi\mathrm{i}}\oint \mathrm{d}\lambda\, \frac{1}{\lambda^{1+[N-\int \mathrm{d}x\,\rho(x)]}} \\ &= \begin{cases} \mathrm{e}^{-\beta(H-N)} & \text{if } \int \mathrm{d}x\,\rho(x) = N \\ 0 & \text{otherwise.} \end{cases} \end{aligned} \qquad (23)$$

The static solution (10) has been thus verified, and the supplement to Dean's discussion has been completed.

4. Discussion: connection with the deterministic equation (9)

Here we would like to first confirm the saddle-point path of the Fokker–Planck (2) by exploiting the WKB-like approach used in [11]. Setting, similarly to the WKB approximation, that

$$P(\{\rho\}, t) \propto \exp[-\beta\Phi(\{\rho\}, t)] \qquad (24)$$

we obtain the Hamilton–Jacobi-like equation:

$$\frac{\partial\Phi(\{\rho\},t)}{\partial t} = \int \mathrm{d}x\, \frac{\delta\Phi(\{\rho\},t)}{\delta\rho(x)}\nabla\cdot L[\rho(x)]\nabla\left[\frac{\delta\Phi(\{\rho\},t)}{\delta\rho(x)} - \frac{\delta H(\{\rho\})}{\delta\rho(x)}\right]. \tag{25}$$

A short-cut way of deriving from this the most probable (or saddle-point) path $\{\bar{\rho}\}$ is to expand Φ and H around $\{\bar{\rho}\}$ as

$$\begin{aligned}\Phi(\{\rho\},t) &= \Phi(\{\bar{\rho}\},t) + \tfrac{1}{2}\int \mathrm{d}x\,\mathrm{d}y\,[\rho(x)-\bar{\rho}(x)]\Phi''(x-y)[\rho(y)-\bar{\rho}(y)] + \cdots \\ J(\{\rho\}) &= J(\{\bar{\rho}\}) + \left.\frac{\delta J(\{\rho\})}{\delta\rho}\right|_{\{\rho\}=\{\bar{\rho}\}}[\rho(x)-\bar{\rho}(x)] + \cdots\end{aligned} \tag{26}$$

with $J(\{\rho\}) \equiv L[\rho(x)]\nabla\delta H(\{\rho\})/\delta\rho(x)$. Substitution of these into equation (25) yields in $\mathcal{O}[\rho(x)-\bar{\rho}(x)]$

$$\frac{\partial\bar{\rho}(x,t)}{\partial t} = \nabla\cdot L[\bar{\rho}(x,t)]\nabla\left.\frac{\delta H(\{\rho\})}{\delta\rho}\right|_{\{\rho\}=\{\bar{\rho}\}}. \tag{27}$$

Since $\{\bar{\rho}\}$ is to be in accord with the noise-averaged density $\{\rho_{av}\}$, equation (27) implies that $\langle\hat{\rho}(x,t)\,\hat{\rho}(y,t)\rangle = \rho_{av}(x,t)\rho_{av}(y,t)$ for the first term on the right-hand side of (9), i.e. no spatial correlation of noise averaging. In other words, the above derivation reveals that the noise-averaged equation (9) is not the first member of the dynamical BBGKY hierarchy unlike the proposal by MT, but is only the mean-field equation for the saddle-point path of $P(\{\rho\},t)$.

We have thus validated the stochastic density functional equations, which must be a powerful tool for the understanding of supercooled fluids and glasses, via proving the irrelevance of MT's objection to Dean's argument in three ways:

(a) demonstrating that standard manipulations enable one to replace with the c-number density field ρ the corresponding operator variable $\hat{\rho}$, in the stochastic equation (6) derived by Dean;
(b) verifying the static solution (10) of the Fokker–Planck equation for the density distribution functional with the help of the conditional grand canonical partition function; and
(c) pointing out that the noise-averaged path satisfying the deterministic equation (9) merely corresponds to the saddle-point one.

The next problem is how to solve these dynamical density functional equations (stochastic or deterministic). In previous works [8, 9, 14], the static density functional theory has been exploited as input, and some justifications have also been described by Kawasaki and MT [3, 8]. However, the present discussion does not support these; from our point of view, what to assume to incorporate the static theory remains an open problem.

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