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Microscopic Analyses of the Dynamical Density Functional Equation of Dense Fluids[1]

Kyozi Kawasaki[2]

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We briefly review the recent microscopic derivation of the generalized dynamical density functional equation with some modification as well as the time evolution equation of the configuration distribution function. We then describe our attempt to analyze the microscopic memory kernel operator that enters these equations. In particular we give a matrix continued-fraction recursion formula of the memory kernel operator.

KEY WORDS: Mode coupling theory; dynamical density functional theory; memory kernel operator; matrix continued fraction.

1. INTRODUCTION

The mode coupling theory to be abbreviated as MCT hereafter, which is now a standard technique to incorporate cooperative motion of many particles in dynamical aspects of condesnsed systems, was originally conceived in the 1960's in attempting to understand critical divergences of transport coefficients.(1–3) MCT for critical dynamics was then superceded by the dynamical renormalization group theory(4) which combined the MCT idea and Wilson's renormalization group idea, and the critical dynamics has now become an exact science where forefront of research is ever higher precision and minute details. Subsequently MCT played a useful role in describing the so-called long time tail phenomena (for a recent review, see ref. 5).

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[1] This article is dedicated to Leo P. Kadanoff, whose early paper with J. Swift is instrumental to the popularity of the mode coupling theory today.

[2] Department of Natural Science and Mathematics, Chubu University, Kasugai, Aichi 487-8501, Japan.

MCT was imbued with a new life in the 1970's when it was realized that the MCT idea can be used to develop theories of liquid dynamics, which had been one of the toughest problems in statistical physics. This development was culminated in the papers by Sjögren(6) in 1980, where he was able to reproduce theoretically the dynamical scattering structure factor of liquid rubidium with no adjustable parameters. The success of this new application of MCT apparently provided a motivation to go a step forward to apply it to supercooled liquid and glass transition. This new development is influencing recent glass transition studies as can be seen in the review articles compiled recently by Sidney Yip.(7)

At this stage, the author cannot emphasize too strongly the fundamental difference of the nature of the two problems to which the same MCT formalism was applied, namely, the critical dynamics and the liquid and glass dynamics. Once understood, the former is essentially a clearcut and simpler problem in the sense that we can focus on asymptotic behavior near a genuine singularity characterized by fluctuations of indefinitely increasing length and time scales. Thus, microscopic details are only secondary. The central issue was to discover universal features, for which the renormalization group provided an ideal tool. The situation with respect to the latter is totally different. The author has an impression that the fact that MCT successfully dealt with critical singularity influenced its application to glass transition where attention was focused on singular behavior near the putative glass transition.(8) It turned out that in contrast to critical dynamics there is no genuine singularity which is an artifact of the mean field like approximation used. The only possible exception is the case of colloidal glass where thermal noise effects are very small(9) which, however, is enough to establish the value of the recent applications of MCT.(8) In other cases the singularity is smeared out and should be regarded more as a cross-over from one behavior to another. This may well be related to the fact that here one is dealing with rather short length scales of a few nanometers although time scales can be enormous. Thus in applying MCT and related continuum-type formalisms to supercooled liquid and glass transition a new rationale is required. Here we argue that there is a close parallel to the static density functional theory (DFT) of inhomogeneous fluids.(10). In this type of theories a homogeneous fluid in an equilibrium (or metastable) state is taken as a reference system whose properties such as the direct correlation function are assumed to be known. One then constructs a free energy density functional for fluid with an arbitrary inhomogeneous density profile which can be generated by a (real or ficticious) external field. This free energy functonal is minimized with respect to the density profile under whatever the constraints required such as the conservation law or boundary conditions. In this way one can discuss transition of fluid to crystals or amorphous solids, or fluids near a wall or an interface. This theory is couched in the continuum language and is still addressed to *short scale* heterogeneities. A rationale for this approach is provided by the variational principle. Thus, if this theory can be extended to dynamics, we have also a rationale for treating short scale dynamics in a continuum language. Indeed such attempts were made sometime ago. Munakata(11) and Bagchi(12) formally extended the static density functional theory to dynamics obtaining a closed equation governing time evolution of density profile. We have considered a similar theory(13) with a motivation to reformulate the standard self-consistent MCT applied to glass transition.(8) All these theories may be termed dynamical density functional theories (DDFT). The major problem facing such a dynamical extension is the lack of clear-cut criterion for choosing a proper set of the gross variables that give adequate description of *short scale* long time dynamics, and also the need to delineate the conditions under which the existing DDFT holds. These problems have never been made explicit until recently.(14) Thus there is clearly a necessity to look at microscpic bases of the extising DDFT.

The purpose of this contribution is first to briefly review the DDFT (Section 2) and the recent microscopic derivations with some modification of formally exact generalized configuration space equation and dynamical density functional equation (DDFE), which still contain a complicated memory kernel operator that involves the untractable projector (Section 3). We then describe our attempts to analyze this memory kernel operator (Section 4). Although all the results obtained are formal at this stage, we think that this is still useful prior to introduction of approximation schemes or computer analyses which are eventually necessary. In this sense this part of the paper is a progress report of our efforts to attack this challenging problem.

2. DYNAMICAL DENSITY FUNCTIONAL THEORY

As was mentioned in the preceding section, we have proposed the dynamical density functional equation (DDFE) as an alternative formulation to the current MCT for supercooled liquids and glass transition.(13) The equation takes the following form of the stochastic equation for the probability density functional $D_t\{\rho\}$:(13)

$$\frac{\partial}{\partial t} D_t(\{\rho\}) = -L \int d\mathbf{r} \, \frac{\delta}{\delta\rho(\mathbf{r})} \nabla \cdot \rho(\mathbf{r}) \nabla \left[T \frac{\delta}{\delta\rho(\mathbf{r})} + \frac{\delta H\{\rho\}}{\delta\rho(\mathbf{r})} \right] D_t(\{\rho\}) \quad (2.1)$$

where L is a kinetic coefficient and $H\{\rho\}$ is the free energy density functional.[3] The simple version of H is the Ramakrishnan–Yussouf type,(15)

$$H\{\rho\} = T\int d\mathbf{r}\,\rho(\mathbf{r})\left[\ln\frac{\rho(\mathbf{r})}{\rho_0} - 1\right] - \frac{1}{2}T\iint d\mathbf{r}\,d\mathbf{r}'\,c(|\mathbf{r}-\mathbf{r}'|)(\rho(\mathbf{r})-\rho_0)(\rho(\mathbf{r}')-\rho_0) \tag{2.2}$$

Here $c(r)$ is the direct correlation function of the *reference liquid* which is simply related to the static structure funtion(16) and ρ_0 is the density of the reference fluid.

The above DDFE was derived by adiabatically eliminating the velocity field from the coupled equation of motion of the desnity and the velocity field.(11–13) A closely related equation was obtained much earlier by eliminating the velocity field to describe the slow time evolution of the concentration field for critical binary fluid mixtures.(17) The adiabatic elimination of the velocity field is well justified in the case of critical fluid since the concentration changes very slowly due to critical slowing-down compared to the velocity field without critical slowing-down.(4) In comparison, no such good justification exists for the case of normal fluid, and only a hand-waving argument was put forward to insist that in sufficiently dense fluids the density should be the only slow variable(18) with a supporting calculation using the revised Enskog theory of hard sphere system.(19) The argument is expected to be valid near freezing where translational motions of molcules slow down enormously by the so-called cage effect. Otherwise, however, it is hard to justify a calculation based on DDFT such as ref. 20.

We have used Eqs. (2.1) and (2.2) and the additional factorization approximation to derive the *long time* form of the self-consistent idealized MCT equation(8) for the density auto-correlator of supercooled liquids.(13) On the other hand, (2.1) contains a thermal noise term and hence should be able to describe thermally activated processes which should dominate slow dynamics in deeply super-cooled or frozen states. We have in fact shown that this is the case by first mapping DDFE onto a special kinetic Ising model,(21) and then performing Monte-Carlo simulations of this model.(22)

[3] Iteration of the functional derivative at the same spatial point $\mathbf{r}$ here is defined as the limit $\mathbf{r}' \to \mathbf{r}$ of the functional derivatives at the two different points $\mathbf{r}$ and $\mathbf{r}'$. This coincidence of the two spatial points arose from the usual choice of the molecular expression for the density which is the sum of the delta functions exactly specifying the locations of individual particles. If we smear out the delta functions, such coincidence can be avoided. However, we have not encountered any difficulty with this definition so far.

3. MICROSCOPIC DERIVATIONS

We consider a classical system consisting of N particles of mass m with coordinates $\mathbf{r}^N \equiv \mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N$ and momenta $\mathbf{p}^N \equiv \mathbf{p}_1, \mathbf{p}_2, ..., \mathbf{p}_N$ where we have adopted the convention of expressing N vectors associated with N particles by a single vector in $3N$-dimensional space by attaching a superfix N. A point in the phase space $(\mathbf{r}^N, \mathbf{p}^N)$ is simply denoted by $\hat{x}$. The Liouville equation for the phase space distribution function $\hat{D}_t(\hat{x})$ is written as

$$\frac{\partial}{\partial t} \hat{D}_t(\hat{x}) = \hat{L}(\hat{x})\, \hat{D}(\hat{x}, t) \tag{3.1}$$

Here and after we shall denote all the microscopic quantities by attaching ^ to the symbol except for $\mathbf{r}_i$, $\mathbf{p}_i$ which carry particle labels. We shall often suppress arguments $\hat{x}$ and simply write $\hat{L}$, etc instead of $\hat{L}(\hat{x})$, etc, and also abbreviate $\hat{L}'$, etc. for $\hat{L}(\hat{x}')$, etc. A standard form for the Hamiltonian $\hat{H}$ is,

$$\hat{H} = \sum_{i=1}^{N} \frac{1}{2m} \mathbf{p}_i^2 + \hat{U} \tag{3.2}$$

where $\hat{U}$ is the total potential energy, and in the case of two-body forces, is written as

$$\hat{U} = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \phi(\mathbf{r}_i - \mathbf{r}_j) \tag{3.3}$$

ϕ being the two-body potential. The Liouville operator $\hat{L}(\hat{x})$ then takes the following form:

$$\hat{L}(\hat{x}) = -\frac{\mathbf{p}^N}{m} \cdot \nabla^N + (\nabla^N \hat{U}) \cdot \frac{\partial}{\partial \mathbf{p}^N} \tag{3.4}$$

where ∇^N denotes partial differentiation with respect to N-vector $\mathbf{r}^N$.

Earlier(23) we formally eliminated all the variables other than the density by projector(24) in a single step. To actually carry this out is a formidable task because this involves averaging over equilibrium distribution function over configuration space of all the interacting particles. It is easier first to eliminate the momentum variables whose equilibrium distribution is Gaussian (the normalized Maxwell distribution $\Phi(\mathbf{p}^N)$). This will be done in the following. The first thing to do is to introduce a projector P_0 with its complement $Q_0 \equiv 1 - P_0$ by ref. 24

$$P_0 \hat{X}(\hat{x}) = \Phi(\mathbf{p}^N) \int d\mathbf{p}^N \hat{X}(\mathbf{p}^N, \mathbf{r}^N) \tag{3.5}$$

A few useful formulae are:

$$\int d\mathbf{p}^N P_0 \hat{X}(\hat{x}) = \int d\mathbf{p}^N \hat{X}(\hat{x}) \tag{3.6a}$$

$$P_0 \Phi(\mathbf{p}^N)\, X(\mathbf{r}^N) = \Phi(\mathbf{p}^N)\, X(\mathbf{r}^N) \tag{3.6b}$$

$$P_0 \hat{L} P_0 \cdots = 0 \tag{3.6c}$$

The last member of the above is due to oddness of $\hat{L}$ under time reversal.

We introduce the reduced distribution function for the configuration space $\mathbf{r}^N$ by

$$\mathscr{D}_t(\mathbf{r}^N) = \int d\mathbf{p}^N \hat{D}_t(\hat{x}) \tag{3.7}$$

We then assume that the initial phase space distribution function $D_0(\hat{x})$ is a "smooth" one such that it is equal to the projected part:

$$\hat{D}_0(\hat{x}) = P_0 \hat{D}_0(\hat{x}) = \frac{\hat{D}_e(\hat{x})}{\mathscr{D}_e(\mathbf{r}^N)} \mathscr{D}_0(\mathbf{r}^N) \tag{3.8}$$

where the distribution functions with the subscripts e always refer to the equilibrium state. It is often more convenient to work with Laplace transform $X^L(z)$ of an arbitrary function of time $X(t)$ defined by

$$X^L(\hat{x}, z) \equiv \int_0^\infty dt\, e^{-zt} X(t) \tag{3.9}$$

Thus a formal solution of the Liouville equation is:

$$\hat{D}^L_z(\hat{x}) = (z - \hat{L})^{-1} \hat{D}_{t=0}(\hat{x}) \tag{3.10}$$

Here we note the following useful operator identity:

$$P_0(z - \hat{L})^{-1} P_0 = \{z - P_0 \hat{L} P_0 - P_0 \hat{L}(z - Q_0 \hat{L})^{-1} Q_0 \hat{L} P_0\}^{-1} P_0 \tag{3.11}$$

With these preparations we find a closed equation obeyed by $\mathscr{D}_t$, (3.7), or its Laplace transform $\mathscr{D}_z^L$ of the following form:

$$\mathscr{D}_z^L = (z - \Gamma_z^N)^{-1}\, \mathscr{D}_0 \tag{3.12}$$

$$\Gamma_z^N \equiv \int d\mathbf{p}^N\, \hat{L}(z - Q_0\hat{L})^{-1}\, Q_0\hat{L}\Phi \tag{3.13}$$

Here and after we often suppress arguments $\mathbf{r}^N$ and/or $\mathbf{p}^N$ unless confusion arises. Then it is possible to transform $\Gamma_z^N(\mathbf{r}^N)$ into the following form:[25]

$$\Gamma_z^N(\mathbf{r}^N) = \nabla^N \cdot \Lambda_z(\mathbf{r}^N) \cdot [\nabla^N + (\nabla^N \beta\hat{U})] \tag{3.14}$$

$$\Lambda_z(\mathbf{r}^N) \equiv \int d\mathbf{p}^N\, \frac{\mathbf{p}^N}{m}(z - Q_0\hat{L}Q_0)^{-1}\, \frac{\mathbf{p}^N}{m}\,\Phi \tag{3.15}$$

Before reducing $\Lambda_z(\mathbf{r}^N)$ into a more tractable form which will be taken up in the next section, we note that (3.14) has the form of a generalized Smoluchowski equation where $\Lambda_z(\mathbf{r}^N)$ is a $dN \times dN$ matrix operator acting on $\mathbf{r}^N$ instead of a constant number, d being the dimensionality of space. We can then derive a dynamical density functional equation from (3.12) by slightly extending the procedure described in ref. 23 applied to the Smoluchowski equation (see Appendix B of that reference). Thus we first introduce the probability density functional by

$$D_t\{\rho\} \equiv \int d\mathbf{r}^N\, \delta\{\rho - \hat{\rho}\}\, \mathscr{D}_t(\mathbf{r}^N) \tag{3.16}$$

Here $\rho(\mathbf{r})$ is the density and its molecular expression in terms of $\mathbf{r}^N$ is denoted as $\hat{\rho}(\mathbf{r})$ and a functional dependence is expressed as $\{\cdots\}$. Typically $\hat{\rho}(\mathbf{r})$ is expressed as the sum of $\delta(\mathbf{r} - \mathbf{r}_j)$ over all the particles, but here we leave it more general. For instance we can choose the one in which the delta function is replaced by a narrow Gaussian function. The delta functional $\delta\{\rho - \rho'\}$ was defined as before in ref. 23. In order to obtain a formally closed equation for the Laplace transform of $D_t\{\rho\}$ denoted as $D_z^L\{\rho\}$ from (3.12) we assume a smooth initial condition for $\mathscr{D}$ as

$$\mathscr{D}_0(\mathbf{r}^N) = \frac{\mathscr{D}_e(\mathbf{r}^N)}{D_e\{\hat{\rho}\}}\, D_0\{\hat{\rho}\} \tag{3.17}$$

We also need another projector P_ρ defined by its action on any function $X(\mathbf{r}^N)$ as

$$P_\rho X(\mathbf{r}^N) = \frac{\mathscr{D}_e(\mathbf{r}^N)}{D_e\{\hat{\rho}\}} \int d\underline{\mathbf{r}}^N\, \delta\{\hat{\rho} - \underline{\hat{\rho}}\}\, X(\mathbf{r}^N) \tag{3.18}$$

where $\hat{\rho}$ means that it is evaluated at the configuration $\underline{\mathbf{r}}^N$. Then $P_\rho \mathscr{D}_0(\mathbf{r}^N) = \mathscr{D}_0(\mathbf{r}^N)$. Thus Eqs. (3.12), (3.16)–(3.18) imply

$$D_z^L\{\rho\} = \int d\mathbf{r}^N \, \delta\{\rho - \hat{\rho}\} \, P_\rho(z - \Gamma_z^N)^{-1} \, P_\rho \, \frac{\mathscr{D}_e(\mathbf{r}^N)}{D_e\{\hat{\rho}\}} \, D_0\{\hat{\rho}\} \tag{3.19}$$

We can again use for $P_\rho(z - \Gamma_z^N)^{-1} \, P_\rho$ the operator identity (3.11) with the replacements $P_0 \to P_\rho$, $\hat{L} \to \Gamma_z^N$. As in the case of the Smoluchowski equation,(23) we neglect in the first approximation the contribution involving a complementary projector $Q_\rho \equiv 1 - P_\rho$. This approximation becomes exact in the case of $\hat{\rho}(\mathbf{r})$ equal to the sum of delta functions since P_ρ reduces to the identity in this case as is explicitly demonstrated in Appendix. The result is

$$D_z^L\{\rho\} = \int d\mathbf{r}^N \, \delta\{\rho - \hat{\rho}\} (z - P_\rho \Gamma_z^N P_\rho)^{-1} \, \frac{\mathscr{D}_e(\mathbf{r}^N)}{D_e\{\hat{\rho}\}} \, D_0\{\hat{\rho}\} \tag{3.20}$$

Following the procedure similar to that employed in ref. 23 we arrive for an arbitrary $X\{\rho\}$ at

$$P_\rho \Gamma_z^N P_\rho \, \frac{\mathscr{D}_e(\mathbf{r}^N)}{D_e\{\hat{\rho}\}} \, X\{\hat{\rho}\} = -\frac{\mathscr{D}_e(\mathbf{r}^N)}{D_e\{\hat{\rho}\}} \int \{\rho'\} \, \mathscr{T}\{\hat{\rho}, \rho'\} \, D_e^{-1}\{\rho'\} \, X\{\rho'\} \tag{3.21}$$

$$\mathscr{T}\{\rho, \rho'\} \equiv \langle [\boldsymbol{\nabla}^N \delta\{\rho - \hat{\rho}\}] \cdot \Lambda_z(\mathbf{r}^N) \cdot [\boldsymbol{\nabla}^N \delta\{\rho' - \hat{\rho}\}] \rangle \tag{3.22}$$

The only difference from the previous case is that $\Lambda_z(\mathbf{r}^N)$ is still a complicated z-dependent matrix operator acting on $\mathbf{r}^N$, but the analyses can be carried out almost in a manner parallel to ref. 23. Thus further reduction of (3.22) is possible and we find

$$P_\rho \Gamma_z^N P_\rho \, \frac{\mathscr{D}_e(\mathbf{r}^N)}{D_e\{\hat{\rho}\}} \, X\{\hat{\rho}\} = \frac{\mathscr{D}_e(\mathbf{r}^N)}{D_e\{\hat{\rho}\}} \, \Gamma_z\{\rho\} \, X\{\rho\} \Big|_{\rho = \hat{\rho}} \tag{3.23}$$

where $\Gamma_z\{\rho\}$ is an operator acting on any functional $X\{\rho\}$ defined through

$$\begin{aligned} \Gamma_z\{\rho\} \, X\{\rho\} = \int d\{\rho'\} \iint d\mathbf{r} \, d\mathbf{r}' \, \frac{\delta}{\delta\rho(\mathbf{r})} \, W_z(\mathbf{r}\mathbf{r}'; \{\rho\}\{\rho'\}) \\ \times \left[\frac{\delta}{\delta\rho'(\mathbf{r}')} + \frac{\delta\beta H\{\rho'\}}{\delta\rho'(\mathbf{r}')} \right] X\{\rho'\} \end{aligned} \tag{3.24}$$

$$\begin{aligned} W_z(\mathbf{r}\mathbf{r}'; \{\rho\}\{\rho'\}) \equiv \langle \delta\{\rho - \hat{\rho}\} [\boldsymbol{\nabla}^N \hat{\rho}(\mathbf{r}; \mathbf{r}^N)] \cdot \Lambda_z(\mathbf{r}^N) \\ \cdot [\boldsymbol{\nabla}^N \hat{\rho}(\mathbf{r}'; \mathbf{r}^N)] \, \delta\{\rho' - \hat{\rho}\} \rangle / D_e\{\rho'\} \end{aligned} \tag{3.25}$$

where we indicated the dependences of $\hat{\rho}$ on the configuration $\mathbf{r}^N$ and $\Lambda_z(\mathbf{r}^N)$ is given by (3.15). If the rapid momentum relaxation that enters $\Lambda_z(\mathbf{r}^N)$ involves only small numbers of particles which are close together, $W_z(\mathbf{r}\mathbf{r}'; \{\rho\}\{\rho'\})$ is expected to be short-ranged in $|\mathbf{r}-\mathbf{r}'|$.

With these results the equation for $D_z^L\{\rho\}$ is written as

$$[z-\Gamma_z\{\rho\}]\, D_z^L\{\rho\} = D(\{\rho\}, t=0) \tag{3.26}$$

If $\mathbf{r}^N$ is the only slow variable in dense fluids,$^{(18)}$ we can take the limit $z \to 0+$ in (3.12), (3.14), and (3.15) and/or (3.26), (3.24) and (3.25) and obtain Markoffian stochastic equations for time evolution of $\mathbf{r}^N$ and/or $\rho(\mathbf{r})$ which can be taken as new starting points for computer analyses.

Note that if we simplify (3.24) and (3.25) by replacing $\Lambda_z(\mathbf{r}^N)$ by a constant and $\hat{\rho}(\mathbf{r})$ is chozen to be $\sum_i \delta(\mathbf{r}-\mathbf{r}_i)$, we recover (2.1). This simplification depends on this particular choice of $\hat{\rho}(\mathbf{r})$, and otherwise the form of DDF equation is more complicated than (2.1).

4. ANALYSES OF $\Lambda_z(\mathbf{r}^N)$

The operator $\Lambda_z(\mathbf{r}^N)$, (3.15), operating in the configuration space $\mathbf{r}^N$ plays a key role appearing in (3.14) and (3.25). Thus this section is devoted to its analyses. This is not an easy task because it contains a projector Q_0 whose handling creates problems. In Subsection 4.1 we relate $\Lambda_z(\mathbf{r}^N)$ to $\tilde{\Lambda}_z(\mathbf{r}^N)$, (4.1) below, governed by the usual dynamics $\hat{L}$ and obtain a few general relationships. In Subsection 4.2 we directly analyze $\Lambda_z(\mathbf{r}^N)$ itself by obtaining a kind of matrix continued fraction recursion relation.

4.1. General Relationships

We take up two similar configuration space operators, one is $\Lambda_z(\mathbf{r}^N)$, (3.15), and another is denoted by $\tilde{\Lambda}_z(\mathbf{r}^N)$ and is defined as follows,

$$\tilde{\Lambda}_z(\mathbf{r}^N) \equiv \int d\mathbf{p}^N \frac{\mathbf{p}^N}{m} (z-\hat{L})^{-1} \frac{\mathbf{p}^N}{m} \Phi \tag{4.1}$$

We first discuss a few general properties of these operators and and then establish the relation between them. For this purpose let us first define the modified Liouville operators as

$$\hat{L}^{**} \equiv Q_0 \hat{L} Q_0 \tag{4.2a}$$

$$\hat{L}^{*} \equiv P_0 \hat{L} P_0 + P_0 \hat{L} Q_0 + Q_0 \hat{L} P_0 \tag{4.2b}$$

so that we have

$$\hat{L} = \hat{L}^{**} + \hat{L}^{*} \tag{4.3}$$

and

$$A_z(\mathbf{r}^N) \equiv \int d\mathbf{p}^N \frac{\mathbf{p}^N}{m} (z - \hat{L}^{**})^{-1} \frac{\mathbf{p}^N}{m} \Phi \tag{4.4}$$

We then define adjoints $\hat{O}^{\dagger}$ and $O(\mathbf{r}^N)^{\dagger}$ of a phase space operator $\hat{O}$ and a configuration space operator $O(\mathbf{r}^N)$, respectively, through the following relations where $\hat{X}$, $\hat{Y}$ and $X(\mathbf{r}^N)$, $Y(\mathbf{r}^N)$ are, respectively, arbitrary phase space and configurationspacefunctions:

$$\int d\hat{x}\, \hat{X} \hat{O}^{\dagger} \hat{Y} \hat{D}_e = \int d\hat{x}\, \hat{Y} \hat{O} \hat{X} \hat{D}_e \tag{4.5}$$

$$\int d\mathbf{r}^N X(\mathbf{r}^N)\, O^{\dagger}(\mathbf{r}^N)\, Y(\mathbf{r}^N)\, \mathscr{D}_e(\mathbf{r}^N) = \int d\mathbf{r}^N\, Y(\mathbf{r}^N)\, O(\mathbf{r}^N)\, X(\mathbf{r}^N)\, \mathscr{D}_e(\mathbf{r}^N) \tag{4.6}$$

Sometimes operators $\hat{O}$ and/or $O(\mathbf{r}^N)$ can form $3N$-dimensional matrices $\hat{\mathbf{O}}$ and/or $\mathbf{O}(\mathbf{r}^N)$ like A. In those cases, adjoint of an operator means taking transpose of the matrix as well. We then immediately find taking into account the commutativity of $\hat{L}$ and $\hat{D}_e$,

$$\hat{L}^{\dagger} = -\hat{L}, \qquad P_0^{\dagger} = P_0, \qquad \hat{L}^{**\dagger} = -\hat{L}^{**} \tag{4.7}$$

the last one above following from the first two. One can then readily verify the following properties:

$$A_z^{\dagger} = -A_{-z}, \qquad \tilde{A}_z^{\dagger} = -\tilde{A}_{-z} \tag{4.8}$$

We now use the identity,

$$(z - \hat{L}^{**})^{-1} - (z - \hat{L})^{-1} = -(z - \hat{L}^{**})^{-1} \hat{L}^{*} (z - \hat{L})^{-1} \tag{4.9}$$

to find

$$A_z - \tilde{A}_z = -\int d\mathbf{p}^N \frac{\mathbf{p}^N}{m} (z - \hat{L}^{**})^{-1} \hat{L}^{*} (z - \hat{L})^{-1} \frac{\mathbf{p}^N}{m} \Phi \tag{4.10}$$

This result can be transformed using

$$\int d\mathbf{p}^N \frac{\mathbf{p}^N}{m}(z-\hat{L}^{**})^{-1} P_0 \cdots = 0$$

$$\begin{aligned} P_0(z-\hat{L})^{-1} \frac{\mathbf{p}^N}{m}\Phi &= z^{-1}\Phi \int d\underline{\mathbf{p}}^N \underline{\hat{L}}(z-\underline{\hat{L}})^{-1} \frac{\underline{\mathbf{p}}^N}{m}\underline{\Phi} \\ &= -z^{-1}\Phi\nabla^N \cdot \tilde{\Lambda}_z \end{aligned} \tag{4.11}$$

$$\hat{L}\Phi \cdots = -\Phi \frac{\mathbf{p}^N}{m} \cdot [\nabla^N + \beta(\nabla^N \hat{U})] \cdots$$

and the explicit form (3.4) of $\hat{L}$ where $\mathbf{p}^N$ is replaced by $\underline{\mathbf{p}}^N$ in the underlined quantities. We then find

$$\Lambda_z - \tilde{\Lambda}_z = -\frac{1}{z}\int d\mathbf{p}^N \frac{\mathbf{p}^N}{m}(z-\hat{L}^{**})^{-1} \hat{L}P_0\hat{L}(z-\hat{L})^{-1} \frac{\mathbf{p}^N}{m}\Phi \tag{4.12}$$

and

$$\cdots \hat{L}P_0\hat{L} \cdots = \cdots \frac{\mathbf{p}^N}{m}\Phi \cdot [\nabla^N + (\nabla^N \beta\hat{U})]\,\nabla^N \cdot \int d\underline{\mathbf{p}}^N \frac{\underline{\mathbf{p}}^N}{m}(\underline{\cdots}) \tag{4.13}$$

Thus the final result is

$$\Lambda_z - \tilde{\Lambda}_z = -z^{-1}\Lambda_z \cdot [\nabla^N + (\nabla^N \beta\hat{U})]\,\nabla^N \cdot \tilde{\Lambda}_z \tag{4.14}$$

This relationsip enables us to express the operator containing the unwieldly projected dynamics in terms of that with the normal dynamics. Also we obtain the following in a similar manner:

$$\tilde{\Lambda}_z - \Lambda_z = z^{-1}\tilde{\Lambda}_z \cdot [\nabla^N + (\nabla^N \beta\hat{U})]\,\nabla^N \cdot \Lambda_z \tag{4.15}$$

(4.15) follows directly from (4.14) as well by taking the adjoint of the latter, changing the sign of z, and using (4.8) as well as the self-adjoint property of the operator

$$\mathbf{R} \equiv [\nabla^N + (\nabla^N \beta\hat{U})]\,\nabla^N$$

The last-mentioned property readily follows by the alternative form of $\mathbf{R}$ as

$$\mathbf{R} = \mathscr{D}_e \nabla^N \mathscr{D}_e^{-1} \nabla^N$$

The seeming danger of the $z \to 0+$ limit of the rhs of Eqs. (4.14), (4.15) is only apparent since $\nabla^N \cdot \tilde{\Lambda}_z$ is seen to vanish in this limit (See the middle equation of (4.11)), and (4.15) follows by taking the adjoint of (4.14). The results (4.14) and (4.15), although formal, may serve as starting points for introducing approximation methods such as the systematic expansion of(26) leading to the revised Enskog equation for dense hard sphere systems. We note that the equilibrium average $\langle \tilde{\Lambda}_z \rangle$ of $\tilde{\Lambda}_z$ is closely related to the frequency(z)-dependent self-diffusion constant.[4] Vanishing of $\nabla^N \cdot \tilde{\Lambda}_z$ in the $z \to 0+$ limit implies a care needed in approximating the rhs of (4.14). For instance, factorization like

$$\langle \Lambda_z \cdot [\nabla^N + (\nabla^N \beta \hat{U})]\, \nabla^N \cdot \tilde{\Lambda}_z \rangle \to \langle \Lambda_z \rangle \cdot \langle [\nabla^N + (\nabla^N \beta \hat{U})]\, \nabla^N \rangle \cdot \langle \tilde{\Lambda}_z \rangle$$

makes no sense. $\tilde{\Lambda}_z$ itself describes the diffusion process in the $3N$-dimensional configuration space.

4.2. Reduction Formulae of $\Lambda_z(\mathbf{r}^N)$

We will now transform $\Lambda_z(\mathbf{r}^N)$. For this purpose we introduce a set of orthonormal polynomials $\psi_\mu(\mathbf{p}^N)$ which can be chosen to be real. The orthonormality condition reads

$$\int \psi_\mu(\mathbf{p}^N)\, \psi_\nu(\mathbf{p}^N)\, \Phi(\mathbf{p}^N)\, d\mathbf{p}^N = \delta_{\mu\nu} \tag{4.16}$$

We also assume the completeness condition as follows:

$$\sum_\mu \psi_\mu(\mathbf{p}^N)\, \psi_\mu(\underline{\mathbf{p}}^N)\, \Phi(\mathbf{p}^N)\, d\mathbf{p}^N = \delta(\mathbf{p}^N - \underline{\mathbf{p}}^N) \tag{4.17}$$

Then an arbitrary function $X(\mathbf{p}^N)$ can be expanded as

$$X(\mathbf{p}^N) = \Phi(\mathbf{p}^N) \sum_\mu \gamma_\mu^X \psi_\mu(\mathbf{p}^N) \tag{4.18}$$

$$\gamma_\mu^X \equiv \int \psi_\mu(\mathbf{p}^N)\, X(\mathbf{p}^N)\, d\mathbf{p}^N \tag{4.19}$$

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[4] The diagonal element $[\langle \tilde{\Lambda}_z \rangle]_{1x1x}$ of the matrix $\langle \tilde{\Lambda}_z \rangle$ is the z-dependent self-diffusion constant. The off-diagonal elements like $[\langle \tilde{\Lambda}_z \rangle]_{1x2x}$ vanish in the thermodynamic limit in the rest frame of the entire system. All other elements like $[\langle \tilde{\Lambda}_z \rangle]_{ixjy}$ vanish if the spatial isotropy is assumed.

The first two groups of members of the orthonormal set for the 3-dimension are:

$$\psi_0(\mathbf{p}^N) = 1 \tag{4.20a}$$

$$\psi_{1a}(\mathbf{p}^N) = \frac{p_a}{\sqrt{mk_B T}} \tag{4.20b}$$

with

$$a = 1x,\ 1y,\ 1z,\ 2x,\ 2y,\ 2z, \ldots,\ Nx,\ Ny,\ Nz \tag{4.20c}$$

The expansion in terms of this orthonormal set can be conveniently utilized to handle projectors.[5] Thus for example, we find

$$P_0 \hat{X}(\hat{x}) = \Phi(\mathbf{p}^N)\, \gamma_0^X(\mathbf{r}^N) \tag{4.21}$$

$$Q_0 \hat{X}(\hat{x}) = \Phi(\mathbf{p}^N) \sum_{\mu \neq 0} \gamma_\mu^X(\mathbf{r}^N)\, \psi_\mu(\mathbf{p}^N) \tag{4.22}$$

This permits us to write $Q_0 \hat{L} Q_0$ of (3.15) as

$$Q_0 \hat{L} Q_0 = \hat{\mathscr{L}}(\hat{x}) \tag{4.23}$$

$$\hat{\mathscr{L}}(\hat{x})\, \hat{X}(\hat{x}) \equiv \sum_\mu{}' \sum_\nu{}' L_{\mu\nu}(\mathbf{r}^N)\, \Phi(\mathbf{p}^N)\, \psi_\mu(\mathbf{p}^N) \int d\underline{\mathbf{p}}^N\, \psi_\nu(\underline{\mathbf{p}}^N)\, \hat{X}(\mathbf{r}^N \underline{\mathbf{p}}^N) \tag{4.24}$$

$$L_{\mu\nu}(\mathbf{r}^N) \equiv \int d\mathbf{p}^N\, \psi_\mu(\mathbf{r}^N)\, \hat{L}(\mathbf{r}^N \mathbf{p}^N)\, \psi_\nu(\mathbf{p}^N)\, \Phi(\mathbf{p}^N) \tag{4.25}$$

where $\sum'_\mu$ is the sum over $\mu \neq 0$ and $\hat{X}(\hat{x})$ is an arbitrary phase function. The second member of the above equation is also written as

$$\int d\mathbf{p}^N\, \psi_\mu(\mathbf{p}^N)\, \hat{\mathscr{L}}(\mathbf{r}^N \mathbf{p}^N)\, \psi_\nu(\mathbf{p}^N) = L_{\mu\nu}(\mathbf{r}^N) \qquad \mu, \nu \neq 0 \tag{4.26}$$

Note that $L_{\mu\nu}(\mathbf{r}^N)$ is still an operator acting on $\mathbf{r}^N$.

With these as matrix elements, we introduce the matrix operator $\mathbf{L}(\mathbf{r}^N)$ defined in the space of $\mu, \nu \neq 0$ and denote the unit matrix in the same space by $\mathbf{1}$. We can then write $\Lambda_z(\mathbf{r}^N)$ given by (3.15) in matrix form as

$$\Lambda_z(\mathbf{r}^N) = \frac{k_B T}{m} [(z\mathbf{1} - \mathbf{L}(\mathbf{r}^N))^{-1}]_{11} \tag{4.27}$$

---

[5] A special case is the set of polynomials that appear in the Grad 13 moments. But we do not want to make a specific choice at this time.

where $[\cdots]_{11}$ is the $dN \times dN$ submatrix of $[\cdots]$ composed of matrix elements $[\cdots]_{1a1b}$.

Here we show that the expression for $\Lambda_z(\mathbf{r}^N)$, (4.27), can be transformed into a form that permits reduction. For this purpose we first regroup the orthonormal set $\psi_\mu(\mathbf{p}^N)$ into mutually orthogonal subsets $\psi_{ja}(\mathbf{p}^N)$ where $j = 0, 1, 2,\ldots$ designates subset and a a member in a subset. Thus the orthonormality (4.16) now reads

$$\int \psi_{ja}(\mathbf{p}^N)\, \psi_{lb}(\mathbf{p}^N)\, \Phi(\mathbf{p}^N)\, d\mathbf{p}^N = \delta_{jl}\delta_{ab} \tag{4.28}$$

The particular cases $j = 0, 1$ correspond to $\psi_0(\mathbf{p}^N)$, $\psi_{1a}(\mathbf{p}^N)$, (4.20). A natural choice of $\psi_{ja}(\mathbf{p}^N)$ which is made here is the Hermite polynomial-type products of the j $\mathbf{p}^N$'s. However, we note that this is not necessary if the condition (4.46) below is met. We can then define a series of projectors P_j as

$$P_j \hat{X}(\hat{x}) = \Phi(\mathbf{p}^N) \sum_a \gamma^X_{ja}(\mathbf{r}^N) \tag{4.29}$$

with $Q_j \equiv 1 - P_j$. The coefficients $\gamma^X_{ja}(\mathbf{r}^N)$ which are still functions of $\mathbf{r}^N$ are defined by (4.20) where μ is replaced by ja. We have

$$P_j P_l = \delta_{jl} P_j \tag{4.30}$$

We also introduce the following projectors for $j \geqslant 1$

$$P_j^> \equiv \sum_{l \geqslant j} P_l = 1 - Q_j^> \tag{4.31a}$$

$$Q_j^> \equiv \sum_{l < j} P_l \tag{4.31b}$$

We then rewrite

$$\Lambda_z(\mathbf{r}^N) = \int d\mathbf{p}^N\, \frac{\mathbf{p}^N}{m} P_1 (z - P_1^> \hat{L} P_1^>)^{-1} P_1 \frac{\mathbf{p}^N}{m} \Phi \tag{4.32}$$

We now apply the operator identity (3.11) where $P_0, \hat{L}$ are replaced, respectively, by $P_1, P_1^> \hat{L} P_1^>$. That is, using $Q_1 P_1^> = P_1^> Q_1 = P_2^>$ and $P_1 \hat{L} P_1 = 0$ we find

$$P_1 (z - P_1^> \hat{L} P_1^>)^{-1} P_1 = \{z - P_1 \hat{L} P_2^> (z - P_2^> \hat{L} P_2^>)^{-1} P_2^> \hat{L} P_1\}^{-1} P_1 \tag{4.33}$$

We note

$$P_2^> \hat{L} P_2^> \hat{X}(\mathbf{r}^N, \mathbf{p}^N) = \Phi \sum_{\mu}^{\geqslant 2} \sum_{\nu}^{\geqslant 2} \psi_\mu(\mathbf{p}^N)\, L_{\mu\nu}(\mathbf{r}^N) \int d\underline{\mathbf{p}}^N\, \psi_\nu(\underline{\mathbf{p}}^N)\, \hat{X}(\mathbf{r}^N, \underline{\mathbf{p}}^N)$$

$$= L_2^>(\hat{x})\, \hat{L}(\hat{x}) \tag{4.34}$$

where the sums are over $\mu, \nu = j, a$ with $j \geqslant 2$ and we have also defined the operator $L_2^>(x)$ which acts only in the subspace spanned by the projector $P_2^>$. Next we can write

$$P_2^> \hat{L} P_1 \hat{X} = \Phi \boldsymbol{\psi}_2^> \cdot \mathbf{L}_{21}^> \cdot \tilde{\mathbf{P}}_1 \hat{X} \tag{4.35a}$$

$$P_1 L P_2^> \hat{X} = \Phi \boldsymbol{\psi}_1 \cdot \mathbf{L}_{12}^> \cdot \tilde{\mathbf{P}}_2^> \tag{4.35b}$$

where $\boldsymbol{\psi}_1$ is the vector formed by the components ψ_{1a} in the subspace and $\tilde{\mathbf{P}}_1$ is the operator (not a projector) defined by

$$\tilde{\mathbf{P}}_1 \hat{X} = \int d\underline{\mathbf{p}}^N\, \boldsymbol{\psi}_1(\underline{\mathbf{p}}^N)\, \hat{X}(\mathbf{r}^N, \underline{\mathbf{p}}^N) \tag{4.36}$$

Also $\boldsymbol{\psi}_2^>$ is the vector formed by the components ψ_{ja} with $j \geqslant 2$ and $\tilde{\mathbf{P}}_2^>$ is the operator (not a projector) defined by

$$\tilde{\mathbf{P}}_2^> \hat{X} = \int d\underline{\mathbf{p}}^N\, \boldsymbol{\psi}_2^>(\underline{\mathbf{p}}^N)\, \hat{X}(\mathbf{r}^N, \underline{\mathbf{p}}^N) \tag{4.37}$$

$\mathbf{L}_{12}^>$ is the submatrix of the matrix formed by $L_{\mu\nu}$, (4.25), with $\mu = 1a$, $\nu = jb$ with $j \geqslant 2$. Likewise, $\mathbf{L}_{21}^>$ is the submatrix of the matrix formed by $L_{\mu\nu}$, (4.25), with $\mu = ja$, $\nu = 1b$ with $j \geqslant 2$. Both of these are still operators acting on $\mathbf{r}^N$. After some algebra we obtain the following for the operator in (4.33):

$$P_1 \hat{L} P_2^> (z - P_2^> \hat{L} P_2^>)^{-1} P_2^> \hat{L} P_1 \hat{X} = \Phi \boldsymbol{\psi}_1 \cdot \mathbf{Z} \cdot \tilde{\mathbf{P}}_1 X \tag{4.38}$$

where

$$\mathbf{Z}_1 \equiv \mathbf{L}_{12}^> \cdot (z \mathbf{1}_2^> - \mathbf{L}_2^>)^{-1} \cdot \mathbf{L}_{21}^> \tag{4.39}$$

where $\mathbf{1}_2^>$, $\mathbf{L}_2^>$ are, respectively, the identity submatrix and the submatrix composed of $L_{\mu\nu}$ which have elements only in the subspace spanned by the projector $P_2^>$. We notice that $\mathbf{Z}_1$ is a submatrix in the space spanned by

$\psi_{1a}(\mathbf{p}^N)$. If we denote the identity submatrix in this subspace by $\mathbf{1}_1$, (4.32) can be rewritten as

$$\Lambda_z(\mathbf{r}^N) = \frac{k_B T}{m} [z\mathbf{1}_1 - \mathbf{Z}_1(\mathbf{r}^N)]^{-1} \tag{4.40}$$

What we have shown amounts in view of (4.27) to

$$[(z\mathbf{1}_1^> - \mathbf{L}_1^>(\mathbf{r}^N))^{-1}]_{11} = [z\mathbf{1}_1 - \mathbf{Z}_1(\mathbf{r}^N)]^{-1} \tag{4.41}$$

where on the lhs we have noted that $\mathbf{1}$ and $\mathbf{L}$ in (4.27) are the matrices in the space spanned by $P_1^>$. If we can choose the orthonormal set in such a way that $L_{\mu\nu}$ vanishes unless the subset numbers of μ, ν differ by 1, which is the case for Hermite polynomial type functions, we can make the following replacements:

$$\mathbf{L}_{21}^> \to \mathbf{L}_{21}, \qquad \mathbf{L}_{12}^> \to \mathbf{L}_{12} \tag{4.42}$$

where $\mathbf{L}_{jl}$ is the submatrix of $\mathbf{L}$ consisting of elements $L_{ja,lb}$. Then (4.39) can be replaced by

$$\mathbf{Z}_1 \equiv \mathbf{L}_{12} \cdot [(z\mathbf{1}_2^> - \mathbf{L}_2^>)^{-1}]_{22} \cdot \mathbf{L}_{21} \tag{4.43}$$

where $[\cdots]_{22}$ is the $dN \times dN$ submatrix of $[\cdots]$ composed of matrix elements $[\cdots]_{2a2b}$ This procedure can be formally continued in a straightforward manner redefining various notations in an obvious way as

$$[(z\mathbf{1}_j^> - \mathbf{L}_j^>(\mathbf{r}^N))^{-1}]_{jj} = [z\mathbf{1}_j - \mathbf{Z}_j(\mathbf{r}^N)]^{-1} \tag{4.44}$$

$$\mathbf{Z}_j \equiv \mathbf{L}_{j,j+1} \cdot [(z\mathbf{1}_{j+1}^> - \mathbf{L}_{j+1}^>)^{-1}]_{jj} \cdot \mathbf{L}_{j+1,j} \tag{4.45}$$

The required condition is

$$P_j \hat{L} P_j = 0 \tag{4.46}$$

This condition would be lifted at the expense of some complexities. We can also find the following recursion formula:

$$\mathbf{Z}_j = \mathbf{L}_{j,j+1} \cdot (z\mathbf{1}_{j+1} - \mathbf{Z}_{j+1})^{-1} \cdot \mathbf{L}_{j+1,j} \tag{4.47}$$

Thus we have obtained what might be called matrix continued fraction expansion, which is reminiscent of the Mori continued fraction expansion.(27) The latter is, in essence, a rearragement of short time moment expansion whereas here no such frequency moments enter.

Recently the DDFT equation of the type (2.1) was successfully applied to understand the results of molecular dynamics simulation of solvation dynaqmics,(28) where the coefficient L in (2.1), which is denoted as D_b in ref. 28, was found to be considerably smaller than the self-diffusion constant. Microscopic analysis presented in this section might shed some light on this problem in future.

Another area where the DDFT or its generalization might be useful is the transport in confined space where one has to deal with short scale dynamics.(29) A deeper understanding of this problem will give us insights into glassy dynamics where short scale spatial heterogeneities appear to play an important role.(30)

5. DISCUSSION

In the preceding sections we have described our recent works on dynamical density functional theory focusing on its miroscopic bases. However, we have only touched on its formal aspects where we did not even specify the actual microscopic form of $\hat{\rho}(\mathbf{r})$. In order for the approach to be useful, spatial coarse-graining is inevitable at some stage. Without coarse-graining the density profile has the same information as the N particle configuration since labelling of particles are irrelevant. One suggestion for coarse-graining comes from the normal mode analyses of liquids recently put forward by T. Keyes and others.(31) It seems natural that the variables describing stable directions associated with real frequencies can be projected out. On the other hand coarse-graining can bring in variables other than the density. For instance the local stress tensor, which undergoes enormous slowing-down near freezing, cannot be expressed in terms of a coarse-grained density alone although expressible in terms of $\hat{\rho}(\mathbf{r})$ as a sum of delta functions.[6] Such slow variables are expected to play some role near freezing and a way must be found to incorporate them.

One of the motivation for developing the DDFT is to go beyond the exisitng perturbative or self-conststent MCT. Recently a novel approach is put forward in ref. 33 where instead of truncating mode coupling at a certain fixed order, say bilinear or trilinear, a new criterion is used to limit mode coupling terms by the total decay rates of the products of modes. This gives rise to a new possibility of using the MCT idea in attacking slow dynamics in a much more efficient manner. However, so far it is limited to to the cases of purely dissipative dynamics. A main problem in applying the idea to our case is that our generalized DDFT equation or the configuration space equation is not purely dissipative. But this method may open a new way of looking at handling our generalized DDFT.

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[6] Such a variable is known under the name of composite operator and plays a role in quantum field theory and critical phenomena.(32)

Finally we mention the vigorous activity in the application of the time-dependent density functional theory for many electron problems.(34) However it is beyond the scope of this work to relate the present theory to this activity.

APPENDIX. CONFIGURATION SPACE AND DENSITY PROFILE

Here we explicitly demonstrate the intuitively obvious fact that if the microscopic expression of the density $\hat{\rho}(\mathbf{r})$ is chosen to be the sum of delta functions given by

$$\hat{\rho}(\mathbf{r}) \equiv \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i) \tag{A.1}$$

then, the information contained in the density profile is equivalent to the information contained in giving a point in the N particle configuration space $\mathbf{r}^N \equiv \mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$ apart from irrelevant particle labelling. We demonstrate this for the case of lattice gas, and regard the continuous case by taking a contnuum limit afterward. In this way we can avoid singularities associated with delta functions. Thus we let $\hat{\rho}(\mathbf{r})$ be defined instead of (A.1) by

$$\hat{\rho}(\mathbf{r}) \equiv \sum_{j=1}^{N} \Delta(\mathbf{r}, \mathbf{r}_i) \tag{A.2}$$

where Δ is the Kronecker delta and the size of a cell was chosen in such a way that a cell can accommodate at most a single particle due to strong repulsive interaction. Here $\mathbf{r}, \mathbf{r}_i$ and the density function $\hat{\rho}(\mathbf{r})$ are discrete variables. Thus the delta functional $\delta\{\rho - \rho'\}$ is replaced by the product of Kronecker's delta:

$$\delta\{\rho - \rho'\} \to \Delta[\rho, \rho'] \equiv \prod_{\mathbf{r}} \Delta(\rho(\mathbf{r}), \rho(\mathbf{r})') \tag{A.3}$$

The probability density functional now becomes

$$D_t[\rho] = \sum_{\mathbf{r}^N} \Delta[\rho, \hat{\rho}(\mathbf{r}^N)]\, \mathscr{D}_t(\mathbf{r}^N) \tag{A.4}$$

where the configurational space dependency of $\hat{\rho}$ is indicated, which may be suppressed for brevity. Let us now fix $[\hat{\rho}(\mathbf{r})]$ at all the lattice points $\mathbf{r}$, which is equivalent to fixing a point $\mathbf{r}^N$ in the configuration space apart from labelling of particles. Thus $D_t[\hat{\rho}]$ is proportional to $\mathscr{D}_t(\mathbf{r}^N)$ where the latter is chosen to be invariant under relabelling of particles. In fact we then find

$$D_t[\hat{\rho}] = N!\,\mathscr{D}_t(\mathbf{r}^N) \tag{A.5}$$

This can be seen by considering normalization of the both sides of (A.5). Namely, since there are $N!$ ways of labelling N particles, we find

$$\sum_{\hat{\rho}} \cdots = \frac{1}{N!} \sum_{\mathbf{r}^N} \cdots \tag{A.6}$$

Thus, from the definition (A.4) with $[\rho]$, $[\hat{\rho}]$, and $\mathbf{r}^N$ replaced, respectively, by $[\hat{\rho}]$, $\underline{[\hat{\rho}]}$, and $\underline{\mathbf{r}}^N$ we obtain

$$\begin{aligned} D_t[\hat{\rho}] &= \sum_{\underline{\mathbf{r}}^N} \varDelta[\hat{\rho}, \underline{\hat{\rho}}(\underline{\mathbf{r}}^N)]\, \mathscr{D}_t(\underline{\mathbf{r}}^N) \\ &= N! \sum_{\underline{\hat{\rho}}} \varDelta[\hat{\rho}, \underline{\hat{\rho}}(\underline{\mathbf{r}}^N)]\, \mathscr{D}_t(\underline{\mathbf{r}}^N) = N!\,\mathscr{D}_t(\mathbf{r}^N) \end{aligned} \tag{A.7}$$

Next we consider the projector P_ρ introduced by (3.18) acting on $\mathscr{D}_t(\mathbf{r}^N)$

$$P_\rho \mathscr{D}_t(\mathbf{r}^N) = \frac{\mathscr{D}_e(\mathbf{r}^N)}{D_e[\hat{\rho}]} D_t[\hat{\rho}] = \frac{1}{N!} D_t[\hat{\rho}] = \mathscr{D}_t(\mathbf{r}^N) \tag{A.8}$$

In general, for a symmetric configuration space function the use of (A.6) yields,

$$\begin{aligned} P_\rho X(\mathbf{r}^N) &= \frac{\mathscr{D}_e(\mathbf{r}^N)}{D_e\{\hat{\rho}\}} \sum_{\underline{\mathbf{r}}^N} \varDelta[\hat{\rho} - \underline{\hat{\rho}}]\, X(\underline{\mathbf{r}}^N) \\ &= \frac{1}{N!} \sum_{\underline{\mathbf{r}}^N} \varDelta[\hat{\rho} - \underline{\hat{\rho}}]\, X(\underline{\mathbf{r}}^N) \\ &= \sum_{\underline{\hat{\rho}}} \varDelta[\hat{\rho} - \underline{\hat{\rho}}]\, X(\underline{\mathbf{r}}^N) = X(\mathbf{r}^N) \end{aligned} \tag{A.9}$$

Hence we have shown that P_ρ amounts to mere identity.

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