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Rapid Communication

The method of collective variables: a link with the density functional theory

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Recently, based on the method of collective variables the statistical field theory for multicomponent inhomogeneous systems was formulated [O. Patsahan, I. Mryglod, J.-M. Caillol, Journal of Physical Studies, 2007, **11**, 133]. In this letter we establish a link between this approach and the classical density functional theory for inhomogeneous fluids.

Key words: *functional methods of statistical physics, method of collective variables, density functional theory, multicomponent inhomogeneous system*

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The powerful tools for the study of equilibrium and non-equilibrium properties of many-particle interacting systems are those based on the functional methods. In many cases the partition function of such systems can be re-expressed as a functional integral after performing the Hubbard-Stratonovich (HS) transformation [1, 2], a simple device proposed in the 50ies. Nearly at the same time another method, the method of collective variables (CVs), that allows one in an explicit way to derive a functional representation for many-particle interacting systems, was developed [3, 4]. The method, proposed initially in the 1950s [3–5] for the description of the classical charged many particle systems and developed later for the needs of the phase transition theory [6–10], was in fact one of the first successful attempts to attack the problems of statistical physics using the functional integral representation. The CV method is based on: (i) the concept of collective coordinates being appropriate for the physics of the system considered (see, for instance, [11]) and (ii) the functional integral identity

$$\exp\left(F[\hat{\rho}]\right) = \int \mathscr{D}\rho \, \delta_{\mathscr{F}}\left[\rho - \hat{\rho}\right] \exp\left(F[\rho]\right) \tag{1}$$

valid for classical systems and permitting to derive an exact functional representation for the configurational Boltzmann factor. Being applied to the fluids, the CV method uses the idea of the reference system (RS), one of the basic ideas in the liquid state theory [12].

Recently, the rigorous scalar field KSSHE (Kac-Siegert-Stratonovich-Hubbard-Edwards) theory [13, 14], which uses the HS transformation, was developed to describe the phase equilibria in simple and ionic fluids. As was shown [15, 16], both theories (KSSHE and CVs) are in close relation.

Another valuable theoretical approach, which has been extensively employed to study the structural and thermodynamic properties of inhomogeneous systems is the classical density-functional theory (DFT) (for an overview we refer to [17, 18]). The central quantity of DFT is the Helmholtz excess free energy expressed as a functional of the single-particle density. There are few systems for which this functional is known exactly. Thus, successful application of DFT critically depends on judicious choice of an appropriate Helmholtz energy functional suitable for the system under investigation [12]. The main goal of this letter is to constitute a link between the CVs based theory and the classical DFT.

Let us consider the general case of a classical m-component system consisting of N particles among which there exist N_1 particles of species 1, N_2 particles of species 2, ... and N_m particles of species m.The potential energy of the system is assumed to be of the form

$$\mathcal{U}_{N_1\ldots N_m} = \frac{1}{2}\sum_{\alpha,\beta}^{m}\sum_{i\neq j}^{N_\alpha,N_\beta} U_{\alpha\beta}(\mathbf{r}_i,\mathbf{r}_j) + \sum_{\alpha=1}^{m}\sum_{i=1}^{N_\alpha}\psi_\alpha(\mathbf{r}_i), \tag{2}$$

where $U_{\alpha\beta}(\mathbf{r}_i,\mathbf{r}_j)$ denotes the interaction potential of two particles and the second term is the potential energy due to external forces.

The pair interaction potential $U_{\alpha\beta}(\mathbf{r}_i,\mathbf{r}_j)$ can be considered as the sum

$$U_{\alpha\beta}(\mathbf{r}_i,\mathbf{r}_j) = v^0_{\alpha\beta}(\mathbf{r}_i,\mathbf{r}_j) + w_{\alpha\beta}(\mathbf{r}_i,\mathbf{r}_j), \tag{3}$$

where $v^0_{\alpha\beta}(\mathbf{r}_i,\mathbf{r}_j)$ is a potential of a short-range repulsion which in general describes the mutual impenetrability of the particles, while $w_{\alpha\beta}(\mathbf{r}_i,\mathbf{r}_j)$, on the contrary, mainly describes the behaviour at moderate and large distances. The system with the interaction potential $v^0_{\alpha\beta}(\mathbf{r}_i,\mathbf{r}_j)$ can be regarded as the reference system (RS). The fluid of hard spheres is most frequently used as the RS in the liquid state theory since its thermodynamic and structural properties are well known.

Introducing the microscopic density of the αth species in a given configuration

$$\widehat{\rho}_\alpha(\mathbf{r}) = \sum_{i=1}^{N_\alpha}\delta(\mathbf{r}-\mathbf{r}_i)$$

we can present the grand canonical partition function of the system as follows [19]:

$$\Xi[\{\nu_\alpha\}] = \sum_{N_1\geqslant 0}\frac{1}{N_1!}\sum_{N_2\geqslant 0}\frac{1}{N_2!}\cdots\sum_{N_m\geqslant 0}\frac{1}{N_m!}\int(\mathrm{d}\Gamma)\exp\left[-\beta\mathcal{V}^{RS}_{N_1\ldots N_m} - \frac{\beta}{2}\langle\widehat{\rho}_\alpha|w_{\alpha\beta}|\widehat{\rho}_\beta\rangle + \langle\bar{\nu}_\alpha|\widehat{\rho}_\alpha\rangle\right] \tag{4}$$

with $(\mathrm{d}\Gamma) = \prod_\alpha \mathrm{d}\Gamma_{N_\alpha}$, $\mathrm{d}\Gamma_{N_\alpha} = \mathrm{d}\mathbf{r}_1^\alpha\mathrm{d}\mathbf{r}_2^\alpha\ldots\mathrm{d}\mathbf{r}^\alpha_{N_\alpha}$, being the element of the configurational space of N particles. In the right hand side of equation (4) Dirac's brackets notations

$$\sum_{\alpha\beta}\int\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\ \widehat{\rho}_\alpha(\mathbf{r})w_{\alpha\beta}(\mathbf{r},\mathbf{r}')\widehat{\rho}_\beta(\mathbf{r}') = \langle\widehat{\rho}_\alpha|w_{\alpha\beta}|\widehat{\rho}_\beta\rangle,$$

$$\sum_{\alpha}\int\mathrm{d}\mathbf{r}\,\psi_\alpha(\mathbf{r})\widehat{\rho}_\alpha(\mathbf{r}) = \langle\psi_\alpha|\widehat{\rho}_\alpha\rangle$$

are introduced and summation over repeated indices is meant. In (4), $\mathcal{V}^{RS}_{N_1\ldots N_m}$ denotes the contribution from a m-component RS,

$$\overline{\nu}_\alpha(\mathbf{r}) = \nu_\alpha + \nu_\alpha^{\mathrm{S}} - \beta\psi_\alpha(\mathbf{r}) \tag{5}$$

is the local chemical potential of the αth species, $\nu_\alpha = \beta\mu_\alpha - 3\ln\Lambda_\alpha$, Λ_α is the de Broglie thermal wavelength and ν_α^{S} is the self-energy of the αth species $\nu_\alpha^{\mathrm{S}} = \beta w_{\alpha\alpha}(\mathbf{r},\mathbf{r})/2$. For a given volume V, $\Xi[\{\nu_\alpha\}]$ is a function of the temperature T and a log-convex functional of the local chemical potentials $\nu_\alpha(\mathbf{r})$.

Using (1) we can present the Boltzmann factor which does not include the RS interaction in the form

$$\exp\left(\frac{1}{2}\langle\widehat{\rho}_\alpha|w_{\alpha\beta}|\widehat{\rho}_\beta\rangle\right) = \int\mathscr{D}\rho\mathscr{D}\omega\ \exp\left(\frac{1}{2}\langle\rho_\alpha|w_{\alpha\beta}|\rho_\beta\rangle + \mathrm{i}\langle\omega_\alpha|\{\rho_\alpha - \widehat{\rho}_\alpha\}\rangle\right). \tag{6}$$

Here $\rho_\alpha(\mathbf{r})$ is the collective variable which describes the field of the number particle density of the αth species.The functional integrals which enter the above equation can be given a precise meaning in the case where the domain of volume V occupied by particles is a cube of side L with periodic boundary conditions which will be implicitly assumed henceforth [15, 19]. This means that we restrict ourselves to the fields $\rho_\alpha(\mathbf{r})$ and $\omega_\alpha(\mathbf{r})$ which can be written as Fourier series.

Inserting equation (6) in the definition (4) of the grand canonical partition function one obtains an exact functional representation

$$\Xi[\{\nu_\alpha\}] = \int\mathscr{D}\rho\mathscr{D}\omega\ \exp\left(-\mathscr{H}[\{\nu_\alpha\},\{\rho_\alpha,\omega_\alpha\}]\right), \tag{7}$$

where the action $\mathscr{H}[\{\nu_\alpha\},\{\rho_\alpha,\omega_\alpha\}]$ of the CV field theory reads as

$$\mathscr{H}\left[\{\nu_\alpha\},\{\rho_\alpha,\omega_\alpha\}\right]=\frac{\beta}{2}\left\langle\rho_\alpha|w_{\alpha\beta}|\rho_\beta\right\rangle-\mathrm{i}\left\langle\omega_\alpha|\rho_\alpha\right\rangle-\ln\Xi_{\mathrm{RS}}\left[\{\overline{\nu}_\alpha-\mathrm{i}\omega_\alpha\}\right]. \tag{8}$$

In (8) $\Xi_{\mathrm{RS}}[\{\overline{\nu}_\alpha-\mathrm{i}\omega_\alpha\}]$ is the grand canonical partition function of a m-component RS defined as follows:

$$\Xi_{\mathrm{RS}}[\{\nu^*_\alpha\}] = \sum_{N_1\geqslant 0}\frac{1}{N_1!}\sum_{N_2\geqslant 0}\frac{1}{N_2!}\dots\sum_{N_m\geqslant 0}\frac{1}{N_m!}\int(\mathrm{d}\Gamma)\exp\Big(-\beta\mathscr{V}^{\mathrm{RS}}_{N_1\dots N_m}+\langle\nu^*_\alpha|\widehat{\rho}_\alpha\rangle\Big) \tag{9}$$

with

$$\nu^*_\alpha(\mathbf{r})=\overline{\nu}_\alpha(r)-\mathrm{i}\omega_\alpha(\mathbf{r}). \tag{10}$$

Some comments are in order. It should be emphasized that the description (7)–(10) is based on the two sets of variables $\{\rho_\alpha\}$ and $\{\omega_\alpha\}$ and valid for repulsive, attractive as well as arbitrary pair interactions. One can distinguish the following alternative approaches to the application of equations (7)–(10):

- Let $\mathbf{W}$ denote the matrix of elements $w_{\alpha\beta}(\mathbf{r},\mathbf{r}')$. If $\mathbf{W}$ is the positive-definite matrix, the integration over $\{\rho_\alpha\}$ can be easily performed. As a result, one arrives at the same functional representation as that obtained by means of the HS transformation. Thus, we stress that the HS transformation has a narrower region of applicability compared to the CV method.

- Let matrix $\mathbf{W}$ be arbitrary. In this case, one can start with integration over $\{\omega_\alpha\}$. In general, $\Xi_{\mathrm{RS}}[\{\nu^*_\alpha\}]$ cannot be calculated exactly. In order to develop a perturbation theory we present the logarithm of the grand partition function of the RS in the form of a cumulant expansion

$$\ln\Xi_{\mathrm{RS}}[\{\nu^*_\alpha\}] = \sum_{n\geqslant 0}\frac{(-\mathrm{i})^n}{n!}\sum_{\alpha_1,\dots,\alpha_n}\int\mathrm{d}1\dots\int\mathrm{d}n\,\mathfrak{M}_{\alpha_1\dots\alpha_n}(1,\dots,n)\omega_{\alpha_1}(1)\dots\omega_{\alpha_n}(n), \tag{11}$$

  where $i\equiv\mathbf{r}_i$ and $\mathrm{d}i\equiv\mathrm{d}\mathbf{r}_i$. In (11) the nth cumulant $\mathfrak{M}_{\alpha_1\dots\alpha_n}(1,\dots,n)$ is equal to the n-particle partial truncated (connected) correlation function of RS at $\nu^*_\alpha(\mathbf{r})=\overline{\nu}_\alpha(\mathbf{r})$. Substituting (11) in (7) we obtain

$$\begin{aligned}\Xi[\{\nu_\alpha\}] &= \Xi_{\mathrm{RS}}\left[\{\overline{\nu}_\alpha\}\right]\int\mathscr{D}\rho\mathscr{D}\omega\,\exp\Big\{-\frac{\beta}{2}\left\langle\rho_\alpha|w_{\alpha\beta}|\rho_\beta\right\rangle\\ &\quad+\mathrm{i}\left\langle\omega_\alpha|\rho_\alpha\right\rangle+\sum_{n\geqslant 1}\frac{(-\mathrm{i})^n}{n!}\sum_{\alpha_1,\dots,\alpha_n}\int\mathrm{d}1\dots\int\mathrm{d}n\,\mathfrak{M}_{\alpha_1\dots\alpha_n}(1,\dots,n)\omega_{\alpha_1}(1)\dots\omega_{\alpha_n}(n)\Big\}.\end{aligned} \tag{12}$$

  The calculation of correlation functions of RS, $\mathfrak{M}_{\alpha_1\dots\alpha_n}(1,\dots,n)$, is a separate task. If RS is a hard sphere mixture, one can use the fundamental-measure theory [20] and the Percus-Yevick or Carnahan-Starling approximations [21, 22] in the non-uniform and uniform cases, respectively.

  Equation (12) can be evaluated in a systematic way using the Gaussian distribution as a basic one. In particular, using the Gaussian averages one can develop a loop expansion of the grand partition function as it was done recently for a one-component fluid [15].

- Another way of integrating over $\{\omega_\alpha\}$ is to use the steepest descent method. If RS is a mixture of ideal gases, the integration in (9) can be performed exactly. We consider this special case in detail.

Let RS be a m-component mixture of point particles that corresponds, in turn, to the condition $\mathscr{V}^{RS}_{N_1\dots N_m}=0$ in equation (9). In this case the right hand side of (9) can be easily calculated

$$\begin{aligned}\Xi_{\mathrm{id}}[\{\nu^*_\alpha\}] &= \sum_{N_1\geqslant 0}\frac{1}{N_1!}\sum_{N_2\geqslant 0}\frac{1}{N_2!}\dots\sum_{N_m\geqslant 0}\frac{1}{N_m!}\prod_{\alpha=1}^{m}\int\mathrm{d}\mathbf{r}^\alpha_1\dots\mathrm{d}\mathbf{r}^\alpha_{N_\alpha}\exp\left(\sum_{i=1}^{N_\alpha}\nu^*_\alpha(\mathbf{r}^\alpha_i)\right)\\ &= \prod_{\alpha=1}^{m}\left[\sum_{N_\alpha\geqslant 0}\frac{1}{N_\alpha!}\left(\int\mathrm{d}\mathbf{r}\exp(\nu^*_\alpha(\mathbf{r})\right)^{N_\alpha}\right]=\exp\left[\sum_\alpha\int\mathrm{d}\mathbf{r}\exp\left(\nu^*_\alpha(\mathbf{r})\right)\right].\end{aligned} \tag{13}$$

Using (13) we can rewrite the action (8) as follows:

$$\mathscr{H}\left[\{\nu_\alpha\},\{\rho_\alpha,\omega_\alpha\}\right]=\frac{\beta}{2}\left\langle\rho_\alpha|w_{\alpha\beta}|\rho_\beta\right\rangle-\mathrm{i}\left\langle\omega_\alpha|\rho_\alpha\right\rangle-\sum_\alpha\int\mathrm{d}\mathbf{r}\exp\left(\overline{\nu}_\alpha(\mathbf{r})-\mathrm{i}\omega_\alpha(\mathbf{r})\right). \tag{14}$$

In (14) we take into account the equation (10). It is worth noting that in a uniform case, the action (14) coincides with the corresponding expression obtained in [23].

In order to integrate in (7) over the CV fields $\omega_\alpha(\mathbf{r})$ we use the steepest descent method. In this case the equation

$$\left.\frac{\delta\mathscr{H}\left[\{\nu_\alpha\},\{\rho_\alpha,\omega_\alpha\}\right]}{\delta\omega_\alpha}\right|_{\omega_\alpha=\overline{\omega}_\alpha}=0$$

leads to the relation

$$\rho_\alpha(\mathbf{r})=\exp\left(\overline{\nu}_\alpha(\mathbf{r})-\mathrm{i}\overline{\omega}_\alpha(\mathbf{r})\right). \tag{15}$$

Introducing the notation $\rho^0_\alpha=\exp(-\ln\Lambda^3_\alpha+\nu^s_\alpha)$ we can rewrite (15) as

$$-\mathrm{i}\overline{\omega}_\alpha(\mathbf{r})=\ln\frac{\rho_\alpha(\mathbf{r})}{\rho^0_\alpha}-\beta\mu_\alpha+\beta\psi_\alpha(\mathbf{r}). \tag{16}$$

Substituting (16) in equation (14) we finally get for $\Xi\left[\{\nu_\alpha\}\right]$

$$\Xi\left[\{\nu_\alpha\}\right]=\int\mathscr{D}\rho\,\exp\left(-\mathscr{H}[\{\nu_\alpha\},\{\rho_\alpha\}]\right), \tag{17}$$

where the action $\mathscr{H}[\{\rho_\alpha\}]$ has the form:

$$\mathscr{H}[\{\nu_\alpha\},\{\rho_\alpha\}]=\sum_\alpha\int\mathrm{d}\mathbf{r}\,\rho_\alpha(\mathbf{r})\left[\ln\frac{\rho_\alpha(\mathbf{r})}{\rho^0_\alpha}-1\right]+\frac{\beta}{2}\left\langle\rho_\alpha|w_{\alpha\beta}|\rho_\beta\right\rangle-\left\langle\rho_\alpha|\beta\mu_\alpha\right\rangle+\left\langle\rho_\alpha|\beta\psi_\alpha\right\rangle. \tag{18}$$

It is remarkable that the contribution from quadratic fluctuations of $\Delta\omega_\alpha=\omega_\alpha-\overline{\omega}_\alpha$ vanishes in the thermodynamic limit [24]. Therefore, the functional representation of the grand partition functional given by (17)–(18) is exact for the model with the interaction potential (2)–(3) under condition $v^0_{\alpha\beta}(r)=0$. This contradicts the assumption made in [25] about a purely phenomenological character of functional Hamiltonians which are employed in the field-theoretical formalism.

For a one-component case, equations (17)–(18) coincide with the functional integral representation obtained in [24, 26, 27].

Based on (18) one can formulate the MF theory. To this end, from the stationary-point condition

$$\left.\frac{\partial\mathscr{H}[\{\nu_\alpha\},\{\rho_\alpha\}]}{\partial\rho_\alpha}\right|_{\rho_\alpha=\bar{\rho}_\alpha}=0$$

we obtain the following set of equations for the MF density

$$\ln\bar{\rho}_\alpha(r)=\overline{\nu}_\alpha(r)-\beta\sum_\beta\int\mathrm{d}\mathbf{r}'\,w_{\alpha\beta}(\mathbf{r},\mathbf{r}')\bar{\rho}_\beta(\mathbf{r}'). \tag{19}$$

Then, from (17)–(18), the MF grand potential reads

$$\ln\Xi_{\mathrm{MF}}\left[\{\nu_\alpha\}\right]=\sum_\alpha\int\mathrm{d}\mathbf{r}\bar{\rho}_\alpha(\mathbf{r})+\frac{\beta}{2}\left\langle\bar{\rho}_\alpha|w_{\alpha\beta}|\bar{\rho}_\beta\right\rangle.$$

The Helmholtz free energy of the system defined as the Legendre transform

$$F\left[\{\rho_\alpha\}\right]=\left\langle\rho_\alpha|\mu_\alpha\right\rangle-\beta^{-1}\ln\Xi\left[\{\nu_\alpha\}\right],$$

has the following form in the MF approximation

$$F_{\mathrm{MF}}\left[\{\rho_\alpha\}\right]=\beta^{-1}\sum_\alpha\int\mathrm{d}\mathbf{r}\rho_\alpha(\mathbf{r})\left[\ln\left(\frac{\rho_\alpha(\mathbf{r})}{\rho^0_\alpha}\right)-1\right]+\frac{1}{2}\left\langle\rho_\alpha|w_{\alpha\beta}|\rho_\beta\right\rangle+\left\langle\rho_\alpha|\psi_\alpha\right\rangle.$$

Introducing an intrinsic free energy $\mathscr{F}$ [12] by the relation $\mathscr{F}=F-\left\langle\rho_\alpha|\psi_\alpha\right\rangle$ one can present the MF intrinsic free energy of the system as follows:

$$\mathscr{F}_{\mathrm{MF}}\left[\{\rho_\alpha\}\right]=\beta^{-1}\sum_\alpha\int\mathrm{d}\mathbf{r}\rho_\alpha(\mathbf{r})\left[\ln\left(\frac{\rho_\alpha(\mathbf{r})}{\rho^0_\alpha}\right)-1\right]+\frac{1}{2}\left\langle\rho_\alpha|w_{\alpha\beta}|\rho_\beta\right\rangle. \tag{20}$$

Note that $\mathscr{F}_{\text{MF}}\left[\{\rho_\alpha\}\right]$ is the functional of the local density $\rho_\alpha(\mathbf{r})$ and has no explicit dependence on the external potential $\psi_\alpha(\mathbf{r})$. Functional (20) has the form of the approximate free energy functional used in the DFT when the excess free energy functional arising from the interactions is treated at the MF level. In this case the variational principle

$$\frac{\delta}{\delta\rho_\alpha(\mathbf{r})}\Big[\mathscr{F}\left[\{\rho_\alpha\}\right]-\left\langle\rho_\alpha|(\mu_\alpha-\psi_\alpha)\right\rangle\Big]=0$$

leads to the equation (19) and, in turn, to a coincidence of the MF density $\bar{\rho}_\alpha(\mathbf{r})$ with the equilibrium local density.

Summarizing, we have derived the exact field theoretical representation (equations (17)–(18)) for the m-component inhomogeneous system that does not include the hard sphere interaction. Within the framework of the MF formulation of the theory we have found the functional of the free energy which is analogous to that used in the MF DFT.

It is worth noting that the long-range interactions within the framework of the DFT are usually treated within the MF approximation. By contrast, the CVs based theory enables one to develop the perturbation scheme in order to take into account the correlation effects. Moreover, the latter theory can be applied to the systems with more complicated interactions than those considered in this work.

We have also demonstrated that the density functional integral formulation derived in [24, 26–28] can be obtained from the exact CVs functional representation in some special case.

We note that in general the integration over $\{\omega_\alpha\}$ can be performed exactly in thermodynamic limit if the RS describes noninteracting particles. When short-range interactions are included into the RS the method of steepest descent will produce additional contributions describing the correlations between particles in the RS. In particular, this is the case of a hard sphere RS that will be considered elsewhere. However, even for RSs of noninteracting particles there are several models where the method developed above can be very useful. One of such examples is connected with the statistical field theory of anisotropic fluids where the RS may be considered as the system of noninteracting rigid rotators (see, for instance, [29]).

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Метод колективних змінних: зв’язок з теорією функціоналу густини

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Недавно, використовуючи метод колективних змінних, було сформульовано статистико-польову теорію для багатокомпонентних неоднорідних систем [O. Patsahan, I. Mryglod, J.-M. Caillol, Journal of Physical Studies, 2007, **11**, 133]. В цьому повідомленні ми встановлюємо зв’язок між цим підходом і класичною теорію функціоналу густини для неоднорідних плинів.

Ключові слова: *функціональні методи статистичної фізики, метод колективних змінних, теорія функціонілу густини, багатокомпонентна неоднорідна система*