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Optimized random-phase approximations for arbitrary reference systems: Extremum conditions and thermodynamic consistence

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The optimized random-phase approximation (ORPA) for classical liquids is reexamined in the framework of the generating functional approach to the integral equations. We show that the two main variants of the approximation correspond to the addition of the same correction to two different first order approximations of the homogeneous liquid free energy. Furthermore, we show that it is possible to consistently use the ORPA with arbitrary reference systems described by continuous potentials and that the same approximation is equivalent to a particular extremum condition for the corresponding generating functional. Finally, it is possible to enforce the thermodynamic consistence between the thermal and the virial route to the equation of state by requiring the global extremum condition on the generating functional. [S1063-651X(97)05612-2]

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I. INTRODUCTION

The optimized random-phase approximation (ORPA) [1] for classical liquids has been extensively used in the last decades to obtain information on the structure and, to a minor extent, on the thermodynamics of simple liquids and mostly liquid metals [1–6]. The approximation was originally developed in the context of the perturbative approach to the thermodynamic and structure of simple liquids [1]. More recently, this approximation has been used as an ingredient for studying liquids in porous media [7] and critical phenomena in simple liquids [8]. The standard implementation of ORPA is based on the splitting of the interparticle potential into a repulsive (reference) and an attractive (perturbation) part. The effect of the attraction on the pair correlation functions of the purely repulsive reference system is treated at the level of the random-phase approximation (RPA) at large distances and by enforcing the excluded volume effect at short distances.

Numerical studies have shown that the ORPA yields a very accurate description of the structure factor and thermodynamics of simple fluids. At present, for simple liquids, the quality of the ORPA results is comparable to that of state-of-the-art calculations based on the modified hypernetted chain (MHNC) approximation [9,10] or other modern integral equations like the HMSA [11].

Usually, the reference system is modeled by hard sphere interactions. However, in some cases, either the nature of the interactions or results from other theoretical approaches indicate that a soft reference system could provide a better reference system for the ORPA. The original derivation of the ORPA does not allow a direct extension of the formulas to the case of a reference system interacting without hard core. A nonstandard implementation for liquid alkali metals using a one component plasma as reference system [6], although providing good results, was not general enough and was subject to some criticisms [12].

More recently, motivated by the need of improving some variational calculations for liquid metals [13], we reviewed the ORPA from the computational as well from the theoretical point of view. In a previous paper [14], we showed that the solution of the ORPA equations is unique and we proposed a robust, accurate and efficient numerical algorithm to solve the equations. In the present paper we address the problem of reformulating the theory in order to deal in a consistent way with continuous reference systems without any intermediate introduction of auxiliary hard-sphere systems [1]. We give a solution to this problem in the same spirit of Gillan's extension of the mean spherical approximation for soft potentials [15] and subsequent elaborations by Rosenfeld [16].

We found it useful to recast the ORPA equations in the framework of the generating functionals for the integral equations of the theory of liquids [17]. We show that the two different first order expansions of the free energy functional corresponding to the well-known Gibbs-Bogolioubov and Weeks-Chandler and Andersen approximations for the free energy [18] can be transformed into two closely related forms of the ORPA by addition of the same functional. The resulting correlation functions differ by the choice of the reference system pair correlation function.

Moreover, we are able to show that our condition for a continuous ORPA correction to the pair correlations is equivalent to an extremum condition for the ORPA generating functional. Since only the variational determination of all the free parameters of the functional allows the identification of its value with the Helmoltz free energy, this choice enforces the thermodynamic consistence in a natural way.

The paper is organized as follows. In Sec. II, we show how two versions of the ORPA differing only in the treatment of the reference system correlations can be obtained from a variational problem for two related functionals. In Sec. III we show that it is possible to define a consistent ORPA for continuous potentials and that such an extension is equivalent to an additional requirement of extremum for the ORPA functionals. In Sec. IV the issue of the thermodynamic consistency of the two approximations is briefly discussed. Conclusions are summarized in Sec. V.

II. TWO GENERATING FUNCTIONALS FOR THE ORPA

The starting point of the ORPA is a suitable decomposition of the interatomic potential $\phi(r)$ into a reference potential $\phi_0(r)$ and a perturbation (the rest) $\phi_1(r)$:

$$\phi(r)=\phi_0(r)+\phi_1(r). \tag{1}$$

Although the original ORPA [1] was based on a specific choice of such a decomposition, in the following discussion we temporarily leave unspecified the exact characterization of $\phi_0(r)$. Equation (1) naturally leads to a similar decomposition of the total and the direct correlation functions $h(r)$ and $c(r)$:

$$h(r)=h_0(r)+\Delta h(r), \tag{2}$$

$$c(r)=c_0(r)+\Delta c(r), \tag{3}$$

where $h_0(r)$ and $c_0(r)$ are the correlation functions of a reference fluid whose particles interact via the potential $\phi_0(r)$. The thermodynamics and the correlation functions of the reference system are considered as known quantities. $\Delta h(r)$ and $\Delta c(r)$ are defined by Eqs. (2) and (3) and are the unknown functions of the theory. A relation among them, for a fluid whose number density is ρ, is provided by the Ornstein-Zernike equation

$$h(r)=c(r)+\rho\int d^3\mathbf{r}'h(r')c(|\mathbf{r}-\mathbf{r}'|), \tag{4}$$

which, taking into account the fact that $h_0(r)$ and $c_0(r)$ do satisfy the same equation, results in the following relation between the Fourier transforms of $\Delta h(r)$ and $\Delta c(r)$:

$$\Delta\hat{h}(q)=\frac{\Delta\hat{c}(q)S_0^2(q)}{1-\rho\Delta\hat{c}(q)S_0(q)}. \tag{5}$$

In formula (5), $S_0(q)=1+\rho\hat{h}_0(q)$ is the structure factor of the reference system. A caret on a function of q indicates the three-dimensional Fourier transforms of the corresponding function defined in the r space, while ρ is the number density of the system.

So far no approximation has been introduced. By complementing Eq. (5) with any approximate relation between $\Delta h(r)$, $\Delta c(r)$, and $\phi_1(r)$ we get a closed set of nonlinear integral equations that has to be solved.

In particular, the ORPA closure corresponds to the dual relations:

$$\Delta c(r)=-\beta\phi_1(r)\quad \text{for } r>\sigma, \tag{6}$$

$$\Delta h(r)=0\quad \text{for } r<\sigma. \tag{7}$$

These equations impose, up to the finite crossover distance σ, the matching of the asymptotic long range behavior of $\Delta c(r)$ [Eq. (6)] and the condition that the approximation would not modify the pair correlation function at short distances [Eq. (7)]. Due to the presence of relation (5) one could use as an independent variable either the values of $\Delta h(r)$ at distances beyond σ or, more conveniently, the values of the function $\chi(r)=\Delta c(r)$ for $r<\sigma$ ($\chi(r)=0$ for $r>0$).

It is easy to show that Eq. (7) corresponds to the extremum condition for the following functional [1,17] of $\chi(r)$:

$$F_{\text{RING}}[\chi(r)]=\frac{1}{2(2\pi)^3\rho}\int d^3\mathbf{q}\{\ln[1+S_0(q)p(q)] -p(q)S_0(q)\}, \tag{8}$$

where $p(q)=\rho[\beta\hat{\phi}_1(q)-\hat{\chi}(q)]$. In a diagrammatic treatment, F_{RING} would correspond to the sum of *ring*-like diagrams and, as is well known, $\chi(r)=0$ corresponds to the random phase approximation, which usually violates the core condition (7). The ORPA enforces such a condition.

Indeed, by taking the functional derivative with respect to $\Delta\hat{c}(q)$ we have

$$\frac{\delta F_{\text{RING}}}{\delta\Delta\hat{c}(q)}=\frac{\rho}{(2\pi)^3}\Delta\hat{h}(q) \tag{9}$$

and Fourier transforming to the r space we get for all the values of r:

$$\frac{\delta F_{\text{RING}}}{\delta\Delta c(r)}=\Delta h(r). \tag{10}$$

For $0<r<\sigma$, Eq. (10) becomes an integral equation for the unknown $\chi(r)$, different from zero only in such a region:

$$\frac{\delta F_{\text{RING}}}{\delta\chi(r)}=0\quad \text{for } r<\sigma. \tag{11}$$

Thus, Eq. (11) is equivalent to imposing an extremum condition on F_{RING} with respect to variations of $\Delta c(r)=\chi(r)$ (inside σ). If the reference potential is such that $g_0(r)$ inside σ is zero, we see that the extremum condition is equivalent to the physical requirement that the size of the exclusion hole of the reference system is preserved by the perturbation.

It is quite easy to verify that the solution of Eq. (7), provided it exists, is actually unique and corresponds to the maximum of the ORPA generating functional [14] (8).

To complete the description of the system, an explicit prescription for the reference system pair correlation function $g_0(r)$ is required. In the usual approach to ORPA, the choice of $g_0(r)$ is treated as a separate step. Here we prefer to define a ''total'' generating functional from which the full ORPA $g(r)$ is derived. Actually we can introduce two functionals having both F_{RING} as a generator of the ''ORPA'' contribution to the pair correlations and differing in the resulting g_0.

For a homogeneous liquid interacting through a pair potential ϕ, the Helmoltz free energy per particle F can be considered [18] a functional of $\phi(r)$ as well as a functional of the function $e(r)=e^{-\beta\phi(r)}$. It is easy to show that

$$\frac{\delta\beta F}{\delta\beta\phi(r)}=\frac{\rho}{2}g(r) \tag{12}$$

and that

$$\frac{\delta\beta F}{\delta e(r)}=-\frac{\rho}{2}y(r), \tag{13}$$

where $y(r)$ is the so-called cavity correlation function $[y(r)=g(r)e^{\beta\phi(r)}]$. We introduce two functionals — $\mathcal{F}_{\mathrm{GB}}[\phi]$ and $\mathcal{F}_{\mathrm{WCA}}[e]$ — as follows:

$$\mathcal{F}_{\mathrm{GB}}[\phi]=\frac{\rho}{2}\int d\mathbf{r}g_0(r)\beta\Delta\phi(r) -\frac{1}{2\rho}\left(\frac{1}{2\pi}\right)^3\int d\mathbf{q}\{p(q)S_0(q) -\ln[1+p(q)S_0(q)]\}, \tag{14}$$

$$\mathcal{F}_{\mathrm{WCA}}[e]=-\frac{\rho}{2}\int d\mathbf{r}y_0(r)\Delta e(r) -\frac{1}{2\rho}\left(\frac{1}{2\pi}\right)^3\int d\mathbf{q}\{p(q)S_0(q) -\ln[1+p(q)S_0(q)]\}, \tag{15}$$

where $\Delta\phi(r)=\phi(r)-\phi_0(r)$ and $\Delta e(r)=e(r)-e_0(r)$.

By functional differentiation of $\mathcal{F}_{\mathrm{GB}}$ and $\mathcal{F}_{\mathrm{WCA}}$ with respect to $\beta\phi(r)$ and $e(r)$, respectively, we get

$$g=g_0+\Delta h(r) \tag{16}$$

and

$$y=y_0+e^{\beta\phi}\Delta h(r). \tag{17}$$

From the last equation we get immediately the $g(r)$ resulting from $\mathcal{F}_{\mathrm{WCA}}$ as

$$g=y_0e^{-\beta\phi(r)}+\Delta h(r). \tag{18}$$

Thus, the functionals $\mathcal{F}_{\mathrm{GB}}$ and $\mathcal{F}_{\mathrm{WCA}}$ are such that the deviation from the reference system pair correlation function is always given by the ORPA approximation $\Delta h(r)$ [Eq. (5)], but the reference system pair correlation function is g_0 in one case and $y_0e^{-\beta\phi}$ in the other case. Due to the form of the reference system pair correlation functions and the corresponding generating functionals, we refer to the former approximation as the Gibbs-Bogoliubov ORPA (GB-ORPA) and to the latter as the Weeks-Chandler-Andersen ORPA (WCA-ORPA).

Notice that at this level the two functionals have been introduced just as generating functionals for the pair correlation functions and we are not allowed yet to identify the values of the two functionals at the extremum with the Helmoltz free energy.

III. ORPA FOR CONTINUOUS POTENTIALS

For a general value of the parameter σ, the solution $\chi(r)$ of Eq. (11) and the resulting $\Delta h(r)$ are discontinuous at σ no matter if the reference system potential is continuous or not. While such a discontinuity looks relatively harmless if the reference $g_0(r)$ has a hard core of diameter σ, a discontinuity in $\Delta h(r)$ would be spurious in connection with a continuous reference system.

For a similar problem, occurring in the case of the mean spherical approximation (MSA), a satisfactory solution was found [15] by determining σ in such a way that the resulting correlation functions were continuous at σ. Also in the context of the different but related soft-MSA closure [19], Narten *et al.* [20] proposed a similar criterion for the detesrmination of σ.

Here, we can similarly impose the continuity of $\Delta h(r)$ [or equivalently $\Delta c(r)$] at $r=\sigma$. Thus, we add the condition

$$\Delta h(\sigma^+)=0 \tag{19}$$

as an additional equation for σ.

Moreover, still in analogy with the MSA case, we can prove that the continuity condition at σ is equivalent to an extremum condition of the ORPA functional (8) as a function of σ.

As shown in the Appendix we have

$$\partial F_{\mathrm{ORPA}}/\partial\sigma=2\pi\rho\sigma^2\chi^2(\sigma^-). \tag{20}$$

Thus, the continuity condition on the correlation functions implies that the GB-ORPA and WCA-ORPA functionals have an extremum (inflection point) at σ. As we will discuss in the next section, this extremum condition is also the clue for a thermodynamic consistent theory.

Here we just notice that there is a manifold of solutions of Eq. (19). However, a lower limit for σ is given by the size of the excluded volume region of the reference system. That is, the region such that

$$g(r)\approx 0. \tag{21}$$

A choice of σ smaller than the reference system exclusion hole would result again in an unphysical ORPA $g(r)$. On the other hand, since $\mathcal{F}_{\mathrm{WCA}}$ and $\mathcal{F}_{\mathrm{GB}}$ are increasing functions of σ [Eq. (20)], the minimum value will be achieved for the first value of σ larger than the reference system exclusion hole. Moreover, increasing σ, the size of the ORPA correction to the reference system thermodynamics and correlations rapidly decreases.

IV. GENERATING FUNCTIONALS AND THERMODYNAMIC CONSISTENCE

Now we are in the position to discuss the thermodynamic interpretation of the functionals $\mathcal{F}_{\mathrm{GB}}$ and $\mathcal{F}_{\mathrm{WCA}}$ and the specific issue of the thermodynamic consistency.

It is well known that approximate integral equation theories for the correlation functions show quantitative violations of fundamental thermodynamic equalities. In particular, here we are concerned with the equalities generated by the identification of the generating functional with the Helmoltz free energy per particle f. The most obvious of such equalities is the equality between the pressure p obtained from the free energy per particle f,

$$\frac{\beta p}{\rho} = \rho \frac{\partial(\beta f)}{\rho} \tag{22}$$

and that found through the virial theorem,

$$\frac{\beta p}{\rho} = 1 - \frac{1}{6}\rho \int g(r) r \beta \phi'(r) d\mathbf{r}. \tag{23}$$

A necessary condition to ensure that a functional $F[\phi]$ is actually a free energy functional is the validity of Eq. (12) [or (13)] [21,22].

Such a condition would be fulfilled by the functionals defined in Eqs. (14) and (15) if the dependence of such functionals on all the parameters of the reference system, on σ (say a_i) and on $\Delta\chi$ vanishes. Then we have to satisfy the following equations:

$$\frac{\partial F}{\partial a_i} = 0, \tag{24}$$

$$\frac{\partial F}{\partial \sigma} = 0, \tag{25}$$

$$\frac{\delta F}{\delta \chi(r)} = 0. \tag{26}$$

Equation (26) corresponds to the ORPA formula [7] while Eq. (24) is a way of determining the reference system parameters. Equation (25), as we have shown in the previous section, is also related to the continuity of the resulting correlation functions. Therefore, in order to have thermodynamic consistency we have to ensure that the functional would be an extremum with respect to variations of *all* the parameters. An analogous requirement for the choice of the reference system in connection with the modified hypernetted chain approximation (MHNC) was derived by Lado *et al.* [10]. Even closer to the present problem is the analysis of the choice of the reference system within the WCA perturbation theory provided by Lado [23].

Different choices of the reference system parameters are certainly conceivable and actually this is the existing situation. It is not easy to anticipate what is the best choice for all possible systems and a final assessment should be left to explicit numerical investigations. However, here we can notice that only the choices corresponding to extrema of the generating functionals or choices completely independent of the thermodynamic state would ensure the free energy nature of the generating functionals and then, as a consequence, the consistence of the energy and virial routes to the equation of state.

V. CONCLUSIONS

In the present paper we have rephrased the ORPA in the language of the generating functionals for the pair correlation function. In this way we could easily obtain three main results:

(1) We can derive from a unified treatment the two prescriptions for the reference system $g(r)$ present in the literature [Eqs. (16) and (18)].

(2) We can show how the ORPA can be extended to deal with continuous reference system interactions, potentially increasing the range of applicability of this approximation.

(3) We show that the closure equations, the removal of the discontinuity in the resulting pair correlations and the identification of the generating functionals with the Helmoltz free energy can be reduced to the unique and unifying requirement of a variational principle on the functionals with respect to all the independent variables and parameters.

The theory presented in this paper provides a general scheme corresponding to many possible choices for the individual ingredients of the ORPA. Actually, depending on the reference system and on the flavor of the ORPA (GB or WCA), we have introduced different possibilities. For this reason we postpone detailed numerical investigations to the application of the approximation to specific problems.

Taking into account the already satisfactory level of accuracy of the standard implementations of the ORPA, and judging from preliminary calculations, we can anticipate a good quality of the numerical results. In particular thermodynamical investigations could now benefit from the clarified status of thermodynamic consistency in the ORPA. In this respect, we believe that the ORPA could play an important role as one of the best candidates for the investigation of the fluid phase diagrams.

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APPENDIX

The proof of Eq. (20) is given as follows. Let

$$p(q) = \beta\rho\hat{\phi}_1(q) - \rho\hat{\chi}(q). \tag{A1}$$

Since the only dependence of $\mathcal{F}_{\rm WCA}$ or $\mathcal{F}_{\rm WCA}$ on σ is through χ, the derivative of $F_{\rm RING}$ [Eq. (8)], we have to evaluate

$$\frac{\partial F_{\rm RING}}{\partial\sigma}=\frac{1}{2\rho}\left(\frac{1}{2\pi}\right)^{3}\int d\mathbf{q}[S_0(q)-S(q)]\frac{\partial p(q)}{\partial\sigma}$$

$$=-\frac{\rho}{2}\left(\frac{1}{2\pi}\right)^{3}\int d\mathbf{q}\Delta\hat{h}(q)\frac{\partial\hat{\chi}(q)}{\partial\sigma}. \qquad (A2)$$

Now, taking into account the finite support of $\chi(r)$,

$$\frac{\partial\hat{\chi}(q)}{\partial\sigma}=\frac{4\pi}{q}\sigma\chi(\sigma^{-})\sin(q\sigma)+\int_0^{\sigma}r\frac{\partial\chi(\sigma)}{\partial\sigma}\frac{4\pi}{q}\sin(qr)dr.$$

By using Parseval's equality, Eq. (A2) becomes

$$\frac{\partial F_{\rm RING}}{\partial\sigma}=-\frac{\rho}{2}\int d\mathbf{r}\Delta h(r)\frac{\partial\chi(r)}{\partial\sigma}-\frac{\rho}{2}\left(\frac{1}{2\pi}\right)^{3}(4\pi)^{2}$$

$$\times\int_0^{\infty}q\Delta\hat{h}(q)\sigma\chi(\sigma)\sin(q\sigma)dq. \qquad (A3)$$

The first term in Eq. (A3) is zero because when $\Delta h\neq 0$, the other term is zero and the reverse also follows. Equation (A3) eventually reduces to

$$\frac{\partial F_{\rm RING}}{\partial\sigma}=-2\pi\rho\sigma^{2}\chi(\sigma^{-})\Delta h(\sigma^{+})=-2\pi\rho\sigma^{2}\chi^{2}(\sigma^{-}), \qquad (A4)$$

giving Eq. (20) when we take into account that $F_{\rm RING}$ appears in Eqs. (14) and (15) with a negative sign.

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[1] J.D. Weeks, D. Chandler, and H.C. Andersen, J. Chem. Phys. **54**, 5237 (1971).

[2] C. Regnault, J. Phys. F **16**, 295 (1986).

[3] H.C. Andersen, D. Chandler, and J.D. Weeks, J. Chem. Phys. **56**, 3812 (1972).

[4] D. Henderson and J.A. Barker, Rev. Mod. Phys. **48**, 587 (1976).

[5] G. Kahl and J. Hafner, Phys. Rev. A **29**, 3310 (1984).

[6] G. Pastore and M.P. Tosi, Physica B **124**, 383 (1984).

[7] E. Kierlik, M.L. Rosinberg, G. Tarjus, and P.A. Monson, J. Chem. Phys. **106**, 264 (1997).

[8] A. Parola and L. Reatto, Phys. Rev. A **31**, 3309 (1985).

[9] Y. Rosenfeld and N.W. Ashcroft, Phys. Rev. A **20**, 1208 (1979).

[10] F. Lado, S.M. Foiles, and N.W. Ashcroft, Phys. Rev. A **28**, 2374 (1983).

[11] G. Zerah and J.P. Hansen, J. Chem. Phys. **84**, 2336 (1986).

[12] G. Kahl and J. Hafner, Z. Phys. B **58**, 283 (1985).

[13] Z. Badirkhan, O. Akinlade, G. Pastore, and M.P. Tosi, J. Phys.: Condens. Matter **4**, 6173 (1992).

[14] G. Pastore, F. Matthews, O. Akinlade, and Z. Badirkhan, Mol. Phys. **84**, 653 (1995).

[15] M.J. Gillan, Mol. Phys. **38**, 1781 (1979).

[16] Y. Rosenfeld, J. Stat. Phys. **37**, 215 (1984).

[17] W. Olivares and D.A. McQuarrie, J. Chem. Phys. **65**, 3604 (1976).

[18] J.P. Hansen and I.R. Mc Donald, *Theory of Simple Liquids* (Academic Press, London, 1986).

[19] L. Blum and A.H. Narten, J. Chem. Phys. **56**, 5197 (1972).

[20] A.H. Narten, L. Blum, and R.H. Fowler, J. Chem. Phys. **60**, 3378 (1974).

[21] S. Hǿye and G. Stell, J. Chem. Phys. **67**, 439 (1977).

[22] T. Morita and K. Hiroike, Prog. Theor. Phys. **23**, 1003 (1960).

[23] F. Lado, Mol. Phys. **52**, 871 (1984).