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Free energies from integral equation theories: Enforcing path independence

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A variational formalism is constructed for deriving the chemical potential and the Helmholtz free energy in various statistical-mechanical integral equation theories of fluids. Nonzero bridge functions extending the scope of the theories beyond the hypernetted chain approximation can be classified as to whether or not they imply path dependence of the free energy. Classes of bridge functions free of the path dependence problem are derived, based on which a route is devised toward direct computation of free energies from the simulation of a single state.

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Integral equation theories of fluids, particularly of the liquid state of matter, have received increased interest in recent years through their application not only to simple liquids but also to, e.g., complex species in solution, interfacial phenomena, etc. A commonly used integral equation for the determination of liquid structure is the one-dimensional (1D) "reference interaction site model" (RISM) or site-site Ornstein-Zernike (OZ) equation of molecular fluids [1]

$$\mathbf{h}=\boldsymbol{\omega}\circ\mathbf{c}\circ\boldsymbol{\omega}+\boldsymbol{\omega}\circ\mathbf{c}\circ(\rho\mathbf{h}). \tag{1}$$

It relates the total correlation function $\mathbf{h}=(h_{\alpha\gamma}(\mathbf{r}))$ (the radial distribution function is $g=h+1$) to the direct correlation function $\mathbf{c}=(c_{\alpha\gamma}(\mathbf{r}))$, $\boldsymbol{\omega}=(\omega_{\alpha\gamma}(\mathbf{r}))$ are the intramolecular correlations, ρ is the density, α,γ represent molecular sites, and $\circ$ denotes convolution. For a solvated molecule (solute sites α, solvent sites γ) in infinite dilution one has in the 1D case

$$\rho h_{\alpha\gamma}=\sum_{\alpha',\gamma'}\omega_{\alpha\alpha'}\circ c_{\alpha'\gamma'}\circ\chi_{\gamma'\gamma} \tag{2}$$

and for the 3D RISM equations, where a multisite solute is treated as a single anisotropic body [2,3],

$$\rho h_{\gamma}=\sum_{\gamma'}c_{\gamma'}\circ\chi_{\gamma'\gamma} \tag{3}$$

with the solvent susceptibility $\boldsymbol{\chi}=\rho\boldsymbol{\omega}+\rho^2\mathbf{h}$. The atomic OZ equation follows from Eq. (1) as $h=c+c\circ(\rho h)$ in the extended atom limit; the molecular OZ relation has basically an analogous form but is defined over a different domain including molecular orientations [4]. These equations must be supplied with a closure relation (β is the inverse temperature and u the pair potential)

$$h_{\alpha\gamma}=\exp(-\beta u_{\alpha\gamma}+h_{\alpha\gamma}-c_{\alpha\gamma}+B_{\alpha\gamma})-1, \tag{4}$$

which introduces the bridge function B. Despite the well-known conceptual difficulties of the RISM equations within the hypernetted chain (HNC) approximation for which $B=0$, we can use such an expression at least formally as a corrective device toward exact correlation functions. Almost all nonzero bridge functions known in the literature are typically functions of the indirect correlation function (ICF) $t=h-c$, i.e., $B=B(t)$, or of a "renormalized" ICF $B(t^*=t-\beta u_2)$ where u_2 is a "suitably chosen" long-range part of the total potential (see, e.g., [5–7]).

One of the most important properties of integral equation theories within the HNC approximation is the fact that the excess chemical potential μ and the excess Helmholtz free energy A are given in closed form [8,9] since the corresponding coupling parameter integral, given here prototypically for a molecule interacting via site-site pair potentials with a single component, homogeneous environment,

$$\mu=\rho\sum_{\alpha,\gamma}\int d\mathbf{r}\int_0^1 d\lambda\,[h_{\alpha\gamma}(\mathbf{r},\lambda)+1]\,\frac{\partial u_{\alpha\gamma}(\mathbf{r},\lambda)}{\partial\lambda}, \tag{5}$$

can be written as an exact differential that simultaneously implies independence of the path prescribed by the coupling parameter λ. A is given for a one-component system by the right-hand side of Eq. (5) multiplied by $N/2$, N being the number of particles. For nonzero bridge functions this is generally not the case, a fact that has been noticed only marginally in the literature. Apparently Kjellander and Sarman [10] were the first who discovered the path dependence for common bridge functions applied to simple liquids; later Lee [11] argued on topological grounds that the linear scaling path, i.e., $B(t(\lambda))=B(\lambda t_1)$, is the "correct" one due to the formal equivalence of the exact expression and the linear scaling result for simple bridge functions. In the case of a renormalized ICF, Lee and co-workers [6,7] assumed the renormalizing long-range potential to be constant upon λ integration. Although motivated topologically, an inconsistency is introduced in this way since at $\lambda=0$ the bridge function would not vanish as it should in the absence of any interactions. Choudhury and Ghosh [12] let both the ICF and the renormalizing potential scale linearly, without further motivation. The path dependence is conserved in any case.

For a reliable and unambiguous theory, enforcing path *independence* is, of course, of foremost importance. To this end a general formalism is needed that is capable of discriminating between path-independent and path-dependent integral equation theories of various kinds. The present article is aimed at filling this gap. We start by rephrasing the sufficient condition for path independence, namely, the existence of an

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exact differential, in terms of a variational stationarity principle. The path-independent excess chemical potential (and analogously the free energy)

$$\mu=\int_0^1 d\lambda\,\frac{\partial\mu}{\partial\lambda}=\int_0^1 d\lambda\int d\mathbf{r}\,L(\mathbf{r},\lambda)=\int_0^1 d\lambda\int d\mathbf{r}\,\frac{\partial F(\mathbf{r},\lambda)}{\partial\lambda}\tag{6}$$

is given as a functional of a function F of the coupling parameter and some spatial coordinates. If the integral equations (1)–(3) or the atomic and molecular OZ equations define the integrand, F can be found in closed form within the HNC approximation [8,9]. In other cases we can at least demand for the existence of Eq. (6) that the variation vanishes,

$$\delta\mu=0,\tag{7}$$

as can be seen from the corresponding Euler-Lagrange equation [13]

$$\frac{\delta\mu}{\delta F(\mathbf{r},\lambda)}=\frac{\partial L}{\partial F(\mathbf{r},\lambda)}-\frac{\partial}{\partial\lambda}\,\frac{\partial L}{\partial F_\lambda(\mathbf{r},\lambda)}=0$$

with F_λ indicating the partial derivative with respect to λ. For the general integrand in Eq. (5), where an explicit F is not immediately recognizable, we have to treat the definitions governing the interrelation of h and u in the form of constraints that are added to a general Lagrangian. In this manner, Eq. (7) can be satisfied by equating the functional derivatives taken independently with respect to h,c,t,u with zero. The constrained chemical potential functional reads, prototypically for the 1D case,

$$\mu=\int_0^1 d\lambda\int d\mathbf{r}\sum_{\alpha,\gamma}\left\{\rho[h_{\alpha\gamma}(\mathbf{r},\lambda)+1]\frac{\partial u_{\alpha\gamma}(\mathbf{r},\lambda)}{\partial\lambda}+p_{\alpha\gamma}(\mathbf{r},\lambda)P_{\alpha\gamma}+v_{\alpha\gamma}(\mathbf{r},\lambda)V_{\alpha\gamma}\right\}+\frac{q}{(2\pi)^3}\int_0^1 d\lambda\int d\mathbf{k}\,Q(\mathbf{k},\lambda),$$

where from Eq. (4) and the definition of t

$$P_{\alpha\gamma}=\exp(-\beta u_{\alpha\gamma}+t_{\alpha\gamma}+B_{\alpha\gamma})-h_{\alpha\gamma}-1,$$

$$V_{\alpha\gamma}=h_{\alpha\gamma}-c_{\alpha\gamma}-t_{\alpha\gamma},$$

and the integral equations are covered by an ‘‘isoperimetric’’ [13] or integral constraint: from Eq. (2) (see also [9])

$$Q^{\mathrm{1D}}=\sum_{\alpha,\alpha',\gamma,\gamma'}\hat{c}_{\alpha\gamma}\frac{\partial\hat{c}_{\alpha'\gamma'}}{\partial\lambda}\hat{\omega}_{\alpha\alpha'}\hat{\chi}_{\gamma\gamma'}-\sum_{\alpha,\gamma}\frac{\partial\hat{c}_{\alpha\gamma}}{\partial\lambda}\rho\hat{h}_{\alpha\gamma},$$

where the carets denote Fourier transforms. With a similar functional for the 3D case and from Eq. (3) we obtain

$$Q^{\mathrm{3D}}=\sum_{\gamma,\gamma'}\hat{c}_{\gamma}\frac{\partial\hat{c}_{\gamma'}}{\partial\lambda}\hat{\chi}_{\gamma\gamma'}-\sum_{\gamma}\frac{\partial\hat{c}_{\gamma}}{\partial\lambda}\rho\hat{h}_{\gamma}.$$

For the Helmholtz free energy we would write

$$Q^{\mathrm{OZ}}=\rho\hat{c}\frac{\partial\hat{c}}{\partial\lambda}\left(1+\frac{\rho\hat{c}}{1-\rho\hat{c}}\right)-\frac{\partial\hat{c}}{\partial\lambda}\rho\hat{h}$$

(cf. [8]), given here only for the OZ equation that is needed later; the first term of the Lagrangian is to be multiplied by 1/2.

As a proof of concept showing that the isoperimetric constraint is indeed sufficient we can now rederive the known 1D RISM/HNC result for μ [9]. The Euler-Lagrange equations in this case are (for functional derivatives of a k space integral with respect to r space functions see [9,14])

$$\frac{\delta\mu}{\delta h_{\alpha\gamma}}=\rho\frac{\partial u_{\alpha\gamma}}{\partial\lambda}-p_{\alpha\gamma}-q\rho\frac{\partial c_{\alpha\gamma}}{\partial\lambda}+v_{\alpha\gamma}=0,\tag{8}$$

$$\frac{\delta\mu}{\delta c_{\alpha\gamma}}=q\rho\frac{\partial h_{\alpha\gamma}}{\partial\lambda}-v_{\alpha\gamma}=0,$$

$$\frac{\delta\mu}{\delta t_{\alpha\gamma}}=p_{\alpha\gamma}(h_{\alpha\gamma}+1)-v_{\alpha\gamma}=0,$$

$$\frac{\delta\mu}{\delta u_{\alpha\gamma}}=-\beta p_{\alpha\gamma}(h_{\alpha\gamma}+1)-\rho\frac{\partial h_{\alpha\gamma}}{\partial\lambda}=0.$$

Solving for the unknown Lagrange parameters yields

$$p_{\alpha\gamma}=-\beta^{-1}\rho\frac{\partial h_{\alpha\gamma}}{\partial\lambda}(h_{\alpha\gamma}+1)^{-1},$$

$$v_{\alpha\gamma}=-\beta^{-1}\rho\frac{\partial h_{\alpha\gamma}}{\partial\lambda},$$

$$q=-\beta^{-1}.$$

As it should, q is independent of λ and $\mathbf{r}$; the same is obtained for the free energy. Upon insertion into Eq. (8) and noting from Eq. (2) that c and h scale in the same way with λ, we obtain the well-known result

$$\mu^{\mathrm{HNC}}=\beta^{-1}\rho\sum_{\alpha,\gamma}\int d\mathbf{r}\left(\frac{1}{2}h_{\alpha\gamma}^2-c_{\alpha\gamma}-\frac{1}{2}h_{\alpha\gamma}c_{\alpha\gamma}\right).\tag{9}$$

In summary, sufficient conditions for the existence of an exact differential are therefore that (a) the constrained variations of μ or A vanish nontrivially, yielding (b) a Lagrange parameter q that is independent of spatial coordinates and the coupling parameter.

Turning now to nonzero bridge functions various cases can be examined with the present formalism. For the commonly used form $B_{\alpha\gamma}=B_{\alpha\gamma}(t_{\alpha\gamma})$ we get

$$q=-\beta^{-1}(1+\partial B_{\alpha\gamma}/\partial t_{\alpha\gamma}),$$

so that the derivative should be constant for path independence, which cannot be satisfied except for the essentially unusable case of B being a linear function of t. All these closures $B_{\alpha\gamma}(t_{\alpha\gamma})$ do not lead to an exact differential and therefore imply path dependence. This result was found in a different manner by Kjellander and Sarman [10] in the path dependence analysis for simple fluids.

If the bridge function is an independent function of the coupling parameter, another Euler-Lagrange equation is necessary:

$$\frac{\delta\mu}{\delta B_{\alpha\gamma}}=p_{\alpha\gamma}(h_{\alpha\gamma}+1)=0,$$

whereby the variation becomes underdetermined and the chemical potential would trivially vanish. An exact differential therefore does not exist, entailing path dependence. Such bridge functions have been used by Du *et al.* [15] and by Kovalenko and Hirata [16] in studies of the hydration of apolar species. In Ref. [16] (and similarly in Ref. [15]) the repulsive bridge correction

$$B_{\alpha\gamma}=\ln\prod_{\eta\neq\gamma}[\omega_{\eta\gamma}\circ\exp(-\beta u^{\mathrm{rep}}_{\alpha\eta})]$$

has been used for noble gases in water where the superscript ‘‘rep’’ indicates the repulsive r^{-12} term of the Lennard-Jones potential. Although this part is clearly related to the total potential, the way the splitting is done means additional information not provided by the theory itself. Consequently, if the separate potential terms (and with them the part entering the bridge function) are scaled by $\lambda^6u^{\mathrm{attr}}$ and $\lambda^{12}u^{\mathrm{rep}}$, as in [16], the hydration free energies of Ne, Ar, Kr, and Xe are 2.97, 1.90, 1.50, and 0.99 kcal mol^{-1}, respectively. If instead $\lambda^{12}u^{\mathrm{attr}}$ and $\lambda^{12}u^{\mathrm{rep}}$ are chosen, we obtain 3.33, 3.01, 3.00, and 2.99 kcal mol^{-1}. In these cases, fitting parametrized empirical bridge functions in order to minimize the difference between integral equation prediction and experiment as in Ref. [15] is, of course, a viable route, but one has to keep in mind that the coupling path chosen acts as another empirical parameter.

The idea of the repulsive bridge correction has, of course, a sound physical basis as outlined in [15,16], which can be exploited by splitting the total chemical potential into a repulsive part under the action of the scaled bridge function and an attractive component where the bridge correction is kept constant. The latter part is simply given by subtracting the HNC-type functionals (9) supplied with the correlation functions derived from the full and only the repulsive potential. For the former, $B=B[u]$ is a functional of the now ‘‘full’’ repulsive potential. It appears hopeless to prove the existence of an exact differential for this complicated case but there is some numerical evidence. Skipping details of the derivation, if path independence were satisfied we would expect

$$\mu=(1+K)\mu^{\mathrm{HNC}}[\mathbf{h}^{\mathrm{rep}},\mathbf{c}^{\mathrm{rep}}]$$

with the constant K being possibly only a function of temperature and density and the HNC-type functional of the repulsive potential correlation functions $\mathbf{h}^{\mathrm{rep}}$ and $\mathbf{c}^{\mathrm{rep}}$. Indeed, for purely repulsive noble gases in water we obtain a fairly constant K with values in the range between -0.551 and -0.544 as derived from numerical coupling parameter integration that is apparently path independent.

A surprising result is obtained if the bridge expression is allowed to be an explicit function of the correlation functions and potential. For $B(u,h,t)$ we have (subscripts are omitted for simplicity)

$$q=-\beta^{-1}(1+\partial B/\partial t)(1-\partial B/\partial\beta u)^{-1}$$

and for $B(u,h,c)$

$$q=-\beta^{-1}(1-\partial B/\partial c)(1-\partial B/\partial\beta u)^{-1},$$

both independent of h. This means $q=-\beta^{-1}$, implying path independence for *any* function $B(t-\beta u)$, $B(c+\beta u)$, $B(h,t-\beta u)$, $B(h,c+\beta u)$, and $B(h)$, constituting a principal result of this article, again valid for both chemical potential and free energy. Since the particular function to be used can vary widely as long as the relations between t/c and u are maintained, it is in general not even possible to find a closed form expression for μ and A. In other words, these functions can lead to ‘‘hidden,’’ nonexplicit exact differentials for the chemical potential and free energy. For instance, in the case of $B(t-\beta u)$, the other Lagrange parameters for μ are

$$v=-\beta^{-1}\rho\frac{\partial h}{\partial\lambda},$$

$$p=-\beta^{-1}\rho\frac{\partial h}{\partial\lambda}(h+1)^{-1}(1-\partial B/\partial\beta u)^{-1}.$$

$\partial B/\partial\beta u$ is a function of both t and u; furthermore, defining an arbitrary path for one quantity entails a specific path for the other that may be hard to extract from the closure (4). Such an explicit expression would be needed for a closed form chemical potential obtained by inserting p into Eq. (8) and integrating. Despite the technical difficulties with these classes of bridge functions implying path independence, the renormalization idea [5] is given an important physical basis for its interpretation.

Developing model bridge functions satisfying path independence based on the results of the last paragraph is beyond the scope of this article. If the total free energy is subdivided as $A(u_1+u_2)=A_1(u_1)+\Delta A_2(u_2)$, the first part being assumed to be known and the second part being path independent, we can, however, immediately use documented functions of $t^*=t-\beta u_2$, the ICF renormalized with the long-range attractive potential u_2. In this way the free energy can be computed from a single simulation of the final state only. In addition to earlier attempts toward this end, like Baranyai’s geometric approach [17] and perturbative schemes [18], a similar idea has been pursued by Matubayasi and Nakahara [19] using an energy representation of the integral equation and the linear scaling idea for solving the coupling parameter integral.

In this work, a suitable renormalized bridge function is fitted to ‘‘exact’’ simulation data for the Lennard-Jones fluid provided by Llano-Restrepo and Chapman [20], yielding ΔA_2 from path-independent coupling parameter integration;

TABLE I. Helmholtz free energies from fitting to exact bridge functions, $A/N\varepsilon$, and from the analytic equation of state, $(A/N\varepsilon)_{\mathrm{EOS}}$, for various reduced densities ρ^* and temperatures T^*, optimal bridge parameter ζ, and hard sphere diameter d_{HS}/σ. ε and σ correspond to well depth and contact distance of the Lennard-Jones potential.

ρ^*	T^*	ζ	d_{HS}/σ	$A/N\varepsilon$	$(A/N\varepsilon)_{\mathrm{EOS}}$
0.4	1.5	0.4483	0.9984	−1.186	−1.159
0.6	1.5	0.7811	0.9984	−1.441	−1.412
0.7	1.5	0.8960	0.9984	−1.394	−1.380
0.8	1.5	0.9899	0.9984	−1.143	−1.167
0.9	1.5	1.0578	0.9984	−0.589	−0.703
0.8	1.0	0.9930	1.0139	−2.543	−2.561
0.8	0.81	1.0083	1.0214	−3.128	−3.144
0.85	0.72	1.0742	1.0254	−3.454	−3.488

A_1 is obtained from the Carnahan-Starling hard-sphere equation of state [21]. The model bridge function used here is a renormalized and parametrized variant of the Verlet function [22]

$$B(t^*) = -\frac{\zeta}{2} t^{*2} \frac{1}{1+4t^*/5}.$$

The total Lennard-Jones potential is subdivided into short- and long-range parts according to Weeks, Chandler, and Andersen [23]. The OZ equation is solved with an "exact" closure for a variety of reduced densities and temperatures, as given in [20]. The resulting indirect correlation functions are used in linear fits of the bridge parameter ζ to the exact bridge functions. With the resulting model function, the coupling parameter integration is performed numerically with the arbitrarily chosen relation $u(\lambda) = u_1 + \lambda^6 u_2$ by repeatedly solving the OZ equation for λ between 0 and 1, yielding ΔA_2. The effective hard-sphere diameter d_{HS} needed in the Carnahan-Starling equation for A_1 is determined from the simple Barker-Henderson formula [24]

$$d_{\mathrm{HS}} = \int_0^\infty dr [1 - \exp(-\beta u_1)].$$

As a reference for the total free energy, the analytical equation of state for the Lennard-Jones fluid of Johnson *et al.* [25] is chosen. The results are summarized in Table I, indicating an excellent performance of this simple strategy and emphasizing the quality of path-independent bridge models.

In conclusion, several promising options for future developments can be envisaged. The development of path-independent model bridge functions, on one hand, will be quite a challenging yet most important goal on the way to better self-contained theories of the liquid state. These attempts will benefit from the various consistency conditions found in the literature [5,26]. On the other hand, semiempirical theories could be developed by parametrizing known renormalized bridge functions to represent the structural and free energy results of molecular simulations. The "direct" approach to the computation of free energies from simulations of single states has the potential to reduce the computational burden for the determination of liquid and solution state free energies by orders of magnitude.

[1] D. Chandler and H. C. Andersen, J. Chem. Phys. **57**, 1930 (1972).

[2] D. Beglov and B. Roux, J. Phys. Chem. B **101**, 7821 (1997).

[3] A. Kovalenko and F. Hirata, Chem. Phys. Lett. **290**, 237 (1998).

[4] L. Blum and A. J. Torruella, J. Chem. Phys. **56**, 303 (1972).

[5] A. G. Vompe and G. A. Martynov, J. Chem. Phys. **100**, 5249 (1994).

[6] L. L. Lee, D. Ghonasgi, and E. Lomba, J. Chem. Phys. **104**, 8058 (1996).

[7] L. L. Lee, J. Chem. Phys. **107**, 7360 (1997).

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

[9] S. J. Singer and D. Chandler, Mol. Phys. **55**, 621 (1985).

[10] R. Kjellander and S. Sarman, J. Chem. Phys. **90**, 2768 (1989).

[11] L. L. Lee, J. Chem. Phys. **97**, 8606 (1992).

[12] N. Choudhury and S. K. Ghosh, J. Chem. Phys. **116**, 8517 (2002).

[13] I. M. Gelfand and S. V. Fomin, *Calculus of Variations* (Prentice-Hall, Englewood Cliffs, NJ, 1963).

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

[15] Q. Du, D. Beglov, and B. Roux, J. Phys. Chem. B **104**, 796 (2000).

[16] A. Kovalenko and F. Hirata, J. Chem. Phys. **113**, 2793 (2000).

[17] A. Baranyai, Phys. Rev. E **65**, 026110 (2002).

[18] S. M. Kast, Phys. Chem. Chem. Phys. **3**, 5087 (2001).

[19] N. Matubayasi and M. Nakahara, J. Chem. Phys. **117**, 3605 (2002).

[20] M. Llano-Restrepo and G. Chapman, J. Chem. Phys. **97**, 2046 (1992).

[21] N. F. Carnahan and K. E. Starling, J. Chem. Phys. **51**, 635 (1969).

[22] L. Verlet, Mol. Phys. **41**, 183 (1980).

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

[24] J. A. Barker and D. Henderson, J. Chem. Phys. **47**, 4714 (1967).

[25] J. K. Johnson, J. A. Zollweg, and K. E. Gubbins, Mol. Phys. **78**, 591 (1993).

[26] E. Lomba and L. L. Lee, Int. J. Thermophys. **17**, 663 (1996).