

## Free energy functions in the extended RISM approximation†

by SHERWIN J. SINGER and DAVID CHANDLER

Department of Chemistry, University of Pennsylvania,  
Philadelphia, Pennsylvania, U.S.A.

(Received 10 December 1984; accepted 28 January 1985)

It is shown that the free energies associated with the solutions of extended RISM integral equations can be obtained in closed form thus avoiding the necessity of numerical coupling parameter integrations. In addition, variational principles are deduced which provide a basis for efficient algorithms to solve extended RISM integral equations.

---

### 1. INTRODUCTION

The reference interaction site method (RISM) [1] integral equation in its extended form (i.e., with the HNC closure) [2] has been recently applied by Chiles and Rossky [3] to predict the reversible work surface for an  $S_N2$  reaction in liquid water. In their treatment, Chiles and Rossky numerically performed the coupling parameter or functional integration [1] which relates the free energy surface to the pair correlation functions computed from the integral equation theory. This procedure avoids any assumptions concerning the pair decomposability of the free energy surface. For each configuration of the solute, it requires the solution of the integral equation at many intermediate values of the coupling parameter. Chiles and Rossky demonstrated that the predictions of this method are in qualitative accord with Jorgensen's [4] Monte Carlo calculation of the same surface. This demonstration is significant since the integral equation method is not nearly as numerically intensive as the Monte Carlo procedure, and therefore many complex systems not approachable by direct numerical simulation now seem accessible to quantitative analysis.

In this note, we expand on this relative computational simplicity and point out that in the case of the extended RISM integral equation, the coupling parameter integrations for solvation as well as bulk free energy functions can be performed in closed form. Numerical calculations beyond those necessary to determine the correlation functions at a single value of the coupling parameter are not required. In particular, we express the free energy surface obtained from the functional integration of the pair correlation functions as a simple functional of the correlation functions. In light of Morita and Hiroike's [5] well known analysis of the traditional HNC theory, it is perhaps not surprising that a formula of this type

---

† This research has been supported by the National Science Foundation.

can be obtained. Along with its utility within the framework of the RISM integral equation theory, the formula may guide empirical parameterizations of free energy surfaces which build upon experimental and numerical simulation results.

Our analysis also leads to a variational principle which is equivalent to the extended RISM integral equations. The principle should be of practical use in deriving numerical solutions to those equations. Further, with the aid of the variational principle, we are able to derive a compact expression for the equation of state of polyatomic fluids in terms of extended RISM correlation functions.

## 2. FREE ENERGY OF SOLVATION

The free energy surface to which we have been referring is the excess chemical potential,  $\Delta\mu(\{\mathbf{r}^{(a)}\})$ , for a solute molecule with  $m$  interaction sites constrained to the configuration  $\{\mathbf{r}^{(a)}\} = (\mathbf{r}^{(1)}, \mathbf{r}^{(2)}, \dots, \mathbf{r}^{(m)})$ . It is related to pair correlations by the 'charging' formula [1]

$$-\beta\Delta\mu(\{\mathbf{r}^{(a)}\}) = \rho \sum_{\alpha, s} \int_0^1 d\lambda \int d\mathbf{r} [\partial f_{\alpha s}(\mathbf{r}; \lambda) / \partial \lambda] y_{\alpha s}(\mathbf{r}; \lambda). \quad (2.1)$$

Here, the Greek subscripts and the superscripts refer to the interaction sites of the solute, Roman letters label sites on the solvent molecules (which we take as a one-component system for notational simplicity),  $\rho$  is the bulk density of the solvent,  $f_{\alpha s}(\mathbf{r}; \lambda)$  is the Mayer cluster function with coupling parameter  $\lambda$ ,

$$f_{\alpha s}(\mathbf{r}; \lambda) + 1 = \exp [-\beta\lambda u_{\alpha s}(\mathbf{r})], \quad 0 \leq \lambda \leq 1, \quad (2.2)$$

where  $\beta^{-1} = k_B T$  and  $u_{\alpha s}(\mathbf{r})$  is the site-site pair potential between solute and solvent. The quantity

$$y_{\alpha s}(\mathbf{r}; \lambda) = [1 + f_{\alpha s}(\mathbf{r}; \lambda)]^{-1} g_{\alpha s}(\mathbf{r}; \lambda) \quad (2.3)$$

is the cavity distribution function evaluated as a functional of  $f_{\alpha s}(\mathbf{r}; \lambda)$  and the cluster functions of the solvent  $f_{ss}(\mathbf{r})$ , which are independent of  $\lambda$ . The coupling parameter integration serves to create the solute in the solvent.

The extended RISM equation for a single polyatomic solute in a solvent is [1, 2]

$$\rho h_{\alpha s}(\mathbf{r}) = \sum_{\gamma, s'} \omega_{\alpha\gamma} * c_{\gamma s'} * \chi_{s's}(\mathbf{r}) \quad (2.4)$$

with the closure

$$y_{\alpha s}(\mathbf{r}) = \exp [h_{\alpha s}(\mathbf{r}) - c_{\alpha s}(\mathbf{r})], \quad (2.5)$$

where  $\chi_{ss}(\mathbf{r})$  the pure solvent site density pair correlation functions, and the other symbols have their usual meaning [1].

We now observe that according to equations (2.3) and (2.5),

$$\left. \begin{aligned} (dh/d\lambda) &= \frac{d}{d\lambda} (1 + f) \exp (h - c) = (df/d\lambda)y + (1 + h) \frac{d}{d\lambda} (h - c), \\ \text{or} \quad (df/d\lambda)y &= \frac{d}{d\lambda} (c - \tfrac{1}{2}h^2) + h(dc/d\lambda) \end{aligned} \right\} \quad (2.6)$$

where we have suppressed subscripts and arguments. Further, from equation (2.4), we see that

$$\frac{\partial}{\partial \lambda} \frac{1}{2(2\pi)^3} \int d\mathbf{k} \sum_{\alpha, \gamma, s, s'} \hat{c}_{\alpha s}(k) \hat{c}_{\gamma s'}(k) \hat{\chi}_{ss'}(k) \hat{\omega}_{\alpha\gamma}(k) = \sum_{\alpha, s} \rho \int d\mathbf{r} h_{\alpha s}(r) (\partial c_{\alpha s}(r) / \partial \lambda), \quad (2.7)$$

where the carets indicate Fourier transforms. Equations (2.6) and (2.7) allow us to identify an exact differential  $d\Delta\mu(\{\mathbf{r}^{(\alpha)}\})/d\lambda$  from which we obtain with (2.1)

$$\begin{aligned} -\beta\Delta\mu(\{\mathbf{r}^{(\alpha)}\}) &= \rho \sum_{\alpha, s} \int d\mathbf{r} [c_{\alpha s}(r) - \frac{1}{2}h_{\alpha s}^2(r)] \\ &\quad + \frac{1}{2} \sum_{\alpha, \gamma, s, s'} c_{\alpha s} * \chi_{ss'} * c_{\gamma s'}(|\mathbf{r}^{(\alpha)} - \mathbf{r}^{(\gamma)}|). \end{aligned} \quad (2.8)$$

This equation is a principal result of this paper. On casual inspection, it would appear that (2.8) is a pair decomposable energy surface. However, the direct correlation functions,  $c_{\alpha s}(r)$ , obtained by solving equations (2.3)–(2.5) are nonlinear functionals of

$$\omega_{\alpha\gamma}(r) = (4\pi r^2)^{-1} \delta(r - |\mathbf{r}^{(\alpha)} - \mathbf{r}^{(\gamma)}|). \quad (2.9)$$

Therefore, the appearance is only illusory, and  $\Delta\mu(\{\mathbf{r}^{(\alpha)}\})$  as given in (2.8) is truly non-pair decomposable.

Equation (2.8) bears a striking relationship to the solvation free energy predicted from a gaussian density field theory [6]. In particular, consider the model in which the solvent density fields,  $\rho_s(\mathbf{r})$ , obey gaussian statistics with variance  $\chi_{ss'}(|\mathbf{r} - \mathbf{r}'|)$  and the solute is coupled to the solvent with the potential energy

$$-k_B T \sum_{\alpha, s} \int d\mathbf{r} c_{\alpha s}(|\mathbf{r}^{(\alpha)} - \mathbf{r}|) \rho_s(\mathbf{r}).$$

On performing the functional or path integrations over density fields, one finds that the pair correlation functions in this model are given by equation (2.4), and the solvation free energy is given very nearly by equation (2.8). The difference resides with the second term in the integral. This term,  $-(1/2)h_{\alpha s}^2(r)$ , is absent from the gaussian field theory. The integral over this term is not simply a constant since the solvent–solute pair structure,

$$g_{\alpha s}(r) = h_{\alpha s}(r) + 1, \quad (2.10)$$

depends upon  $\{\mathbf{r}^{(\alpha)}\}$  through its functional dependence on  $\omega_{\alpha\gamma}(r)$ . Thus, the distinction between equation (2.8) and the gaussian field theory might be significant for certain applications. In most liquid state calculations, however,  $c_{\alpha s}(r)$  is very large in magnitude, and the terms in equation (2.8) involving  $c_{\alpha s}(r)$  explicitly can provide the dominant contribution to the spatial variation in  $\Delta\mu(\{\mathbf{r}^{(\alpha)}\})$ . For those cases, the distinction will not be important.

Equation (2.8) can be expressed in an alternative form which leads to a variational principle. In particular, if we define

$$t_{\alpha s}(r) = h_{\alpha s}(r) - c_{\alpha s}(r), \quad (2.11)$$

then

$$\begin{aligned}
 -\beta\Delta\mu(\{\mathbf{r}^{(\alpha)}\}) &= \rho \sum_{\alpha, s} \int d\mathbf{r} \{ [1 + f_{as}(r)] \exp [t_{as}(r)] \\
 &\quad - 1 - t_{as}(r) - h_{as}(r)t_{as}(r) + \frac{1}{2}h_{as}^2(r) \} \\
 &\quad + (2\pi)^{-3} \int d\mathbf{k} \left\{ - \sum_{\alpha, s} \hat{c}_{as}(k) \rho \hat{h}_{as}(k) \right. \\
 &\quad \left. + \sum_{\alpha, \gamma, s, s'} \hat{c}_{as}(k) \hat{c}_{\gamma s'}(k) \hat{\omega}_{\alpha\gamma}(k) \hat{\chi}_{ss'}(k) \right\}. \quad (2.12)
 \end{aligned}$$

Let us regard this quantity as a functional of  $t_{as}(r)$ ,  $c_{as}(r)$  and  $h_{as}(r)$ . Variations with respect to these functions yield

$$\begin{aligned}
 -\beta\delta\Delta\mu(\{\mathbf{r}^{(\alpha)}\}) &= \rho \sum_{\alpha, s} \int d\mathbf{r} \left[ \{ [1 + f_{as}(r)] \exp [t_{as}(r)] - 1 - h_{as}(r) \} \delta t_{as}(r) \right. \\
 &\quad + \{ -t_{as}(r) + h_{as}(r) - c_{as}(r) \} \delta h_{as}(r) \\
 &\quad \left. + \{ -h_{as}(r) + \rho^{-1} \sum_{\gamma, s'} \omega_{\alpha\gamma} * c_{\gamma s'} * \chi_{ss'}(r) \} \delta c_{as}(r) \right]. \quad (2.13)
 \end{aligned}$$

With equations (2.4), (2.5) and (2.11), the terms in curly brackets vanish. Thus, the solvation energy functional (2.12) is stationary with respect to variations about the solutions that satisfy the extended RISM integral equations. This observation may be of practical value in the numerical solutions of these integral equations.

### 3. TOTAL FREE ENERGY

It is not difficult to extend the analysis of the previous section to derive the free energy functional for the solvent consistent with the extended RISM integral equation for the solvent. We omit the details of the derivation since they follow closely those of the previous section and Morita and Hiroike's analysis of the HNC theory for simple atomic fluids [5]. The result for a one-component system is

$$\begin{aligned}
 \mathcal{A} &= (\rho^2/2) \sum_{\alpha, \gamma} \int d\mathbf{r} [c_{\alpha\gamma}(r) - \frac{1}{2}h_{\alpha\gamma}^2(r)] \\
 &\quad - \frac{1}{2(2\pi)^3} \int d\mathbf{k} \{ \text{Tr } \rho \hat{\omega}(k) \hat{\mathbf{c}}(k) + \ln \det [1 - \rho \hat{\omega}(k) \hat{\mathbf{c}}(k)] \}, \quad (3.1)
 \end{aligned}$$

where  $\mathcal{A}$  is the excess Helmholtz free energy per unit volume per  $-k_B T$ , and the other symbols have their usual meaning [1]. Extensions of this formula to multi-component systems are obvious.

As in the previous section, we can rewrite the free energy functional as

$$\begin{aligned}
 \mathcal{A}[\mathbf{c}, \mathbf{h}, \mathbf{t}] &= (\rho^2/2) \sum_{\alpha, \gamma} \int d\mathbf{r} \{ [1 + f_{\alpha\gamma}(r)] \exp [t_{\alpha\gamma}(r)] - 1 - t_{\alpha\gamma}(r) \\
 &\quad - h_{\alpha\gamma}(r)t_{\alpha\gamma}(r) + \frac{1}{2}h_{\alpha\gamma}^2(r) \} - \frac{1}{2(2\pi)^3} \int d\mathbf{k} \\
 &\quad \times \{ \rho^2 \text{Tr } \hat{\mathbf{c}}(k) \hat{\mathbf{h}}(k) + \text{Tr } \rho \hat{\omega}(k) \hat{\mathbf{c}}(k) + \ln \det [\mathbf{1} - \rho \hat{\omega}(k) \hat{\mathbf{c}}(k)] \}. \quad (3.2)
 \end{aligned}$$

Variations with respect to  $\mathbf{c}$ ,  $\mathbf{t}$  and  $\mathbf{h}$  yield

$$\begin{aligned} \delta\mathcal{A} = & (\rho^2/2) \sum_{\alpha, \gamma} \int d\mathbf{r} \left[ \{[1 + f_{\alpha\gamma}(r)] \exp [t_{\alpha\gamma}(r)] \right. \\ & - 1 - h_{\alpha\gamma}(r)\} \delta t_{\alpha\gamma}(r) + \{-t_{\alpha\gamma}(r) + h_{\alpha\gamma}(r) \\ & - c_{\alpha\gamma}(r)\} \delta h_{\alpha\gamma}(r) \left. \right] + [\rho^2/2(2\pi)^3] \int d\mathbf{k} \\ & \times \{-\hat{h}_{\alpha\gamma}(k) + [\hat{\omega}(k)\hat{\mathbf{c}}(k)[\mathbf{1} - \rho\hat{\omega}(k)\hat{\mathbf{c}}(k)]^{-1}\hat{\omega}(k)]_{\alpha\gamma}\} \delta\hat{\mathbf{c}}_{\alpha\gamma}(k). \end{aligned} \quad (3.3)$$

Thus, the free energy is stationary with respect to these variations provided  $\mathbf{h}$ ,  $\mathbf{t}$  and  $\mathbf{c}$  satisfy

$$t_{\alpha\gamma}(r) = h_{\alpha\gamma}(r) - c_{\alpha\gamma}(r), \quad (3.4)$$

$$h_{\alpha\gamma}(r) = [1 + f_{\alpha\gamma}(r)] \exp [t_{\alpha\gamma}(r)] - 1, \quad (3.5)$$

and

$$\hat{\mathbf{h}}(k) = \hat{\omega}(k)\hat{\mathbf{c}}(k)[\mathbf{1} - \rho\hat{\omega}(k)\hat{\mathbf{c}}(k)]^{-1}\hat{\omega}(k). \quad (3.6)$$

These relationships are the extended RISM equations for the fluid.

This variational principle provides a basis for deriving efficient numerical algorithms for solving the extended RISM integral equations. It also provides a compact route to the equation of state. In particular, due to the stationarity, the pressure  $p$ , as given by

$$\rho[\partial(-\mathcal{A}/\rho)/\partial\rho] = (\beta p/\rho) - 1, \quad (3.7)$$

can be evaluated by differentiating only the explicit density dependence in (3.1). That is,

$$\begin{aligned} (\beta p/\rho) - 1 = & -(\rho/2) \sum_{\alpha, \gamma} \int d\mathbf{r} [c_{\alpha\gamma}(r) - \frac{1}{2}h_{\alpha\gamma}^2(r)] + \frac{1}{2(2\pi)^3} \int d\mathbf{k} \\ & \times \{\rho^{-1} \ln \det [\mathbf{1} - \rho\hat{\omega}(k)\hat{\mathbf{c}}(k)] \\ & + \text{Tr } \hat{\omega}(k)\hat{\mathbf{c}}(k)[\mathbf{1} - \rho\hat{\omega}(k)\hat{\mathbf{c}}(k)]^{-1}\}. \end{aligned} \quad (3.8)$$

#### REFERENCES

- [1] CHANDLER, D., 1982, *The Liquid State of Matter: Fluids, Simple and Complex*, edited by E. W. Montroll and J. L. Lebowitz (North Holland).
- [2] HIRATA, F., and ROSSKY, P. J., *Chem. Phys. Lett.*, **83**, 329. HIRATA, F., PETTITT, B. M., and ROSSKY, P. J., 1982, *J. chem. Phys.*, **77**, 509. PETTITT, B. M., and ROSSKY, P. J., 1982, *J. chem. Phys.*, **77**, 1451. HIRATA, F., ROSSKY, P. J., and PETTITT, B. M., 1983, *J. chem. Phys.*, **78**, 4133.
- [3] CHILES, R. A., and ROSSKY, P. J., 1984, *J. Am. chem. Soc.*, **106**, 6867.
- [4] CHANDRASEKHAR, J., SMITH, S. F., and JORGENSEN, W. L., 1984, *J. Am. chem. Soc.*, **106**, 3049.
- [5] MORITA, T., and HIROIKE, K., 1960, *Prog. theor. Phys.*, **23**, 1003.
- [6] CHANDLER, D., SINGH, Y., and RICHARDSON, D. M., 1984, *J. chem. Phys.*, **81**, 1975.