A solvation-free-energy functional: A reference-modified density-functional formulation

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Supporting Information

An approximation of the intrinsic free-energy functional for ideal polyatomic molecular gas

The site-density distribution functions for ideal polyatomic molecular gas under arbitrary external fields $\{U_\lambda^{IM}(\mathbf{r})\}$ are given by[1,2]

$$n_\alpha^{IM}\left(\mathbf{r}\middle|\{U_\lambda^{IM}\}\right) = n_0 \exp\left(-\beta U_\alpha^{IM}(\mathbf{r})\right)$$
$$\times \int \left\{\prod_{a=1}^{P} d\mathbf{r}_1^a\right\} \delta\left(\mathbf{r}-\mathbf{r}_1^\alpha\right) \left\{\prod_{a<b}^{P} s_{ab}\left(\left|\mathbf{r}_1^a-\mathbf{r}_1^b\right|\right)\right\} \left\{\prod_{a=1}^{P} \exp\left(-\beta U_a^{IM}\left(\mathbf{r}_1^a\right)\right)\right\}, \qquad \text{(A1)}$$

where P is the number of sites, n_0 is the number density of the ideal polyatomic molecular gas, and $s_{ab}(r) = \delta(r-L_{ab})/4\pi L_{ab}$ is the intramolecular bonding function between sites a and b. As pointed out by Chandler *et al.*[3], the external fields $\{U_\lambda^{IM}(\mathbf{r})\}$ are not obtained as a simple functional of the site-density distributions because of the nonlinear inverse problem of $\{U_\lambda^{IM}(\mathbf{r})\}$ in Eq. (A1). As a result, we cannot obtain the exact intrinsic free-energy functional for ideal polyatomic molecular gas $F_{IM}\left[\{n_\lambda^{IM}\}\right]$, since we cannot perform the functional integral of the Euler-Lagrange equation defined by

$$\left.\frac{\delta F_{IM}\left[\left\{n_\lambda^{IM}\right\}\right]}{\delta n_\alpha^{IM}\left(\mathbf{r}\left|\left\{U_\lambda^{IM}\right\}\right.\right)}\right|_{T,V} = \mu_\alpha^{IM} - U_\alpha^{IM}(\mathbf{r}), \tag{A2}$$

where μ_α^{IM} is the chemical potential for site α of ideal polyatomic molecular gas. In order to avoid the functional integral of Eq. (A2) with respect to the density functional of $\left\{U_\lambda^{IM}(\mathbf{r})\right\}$, we can alternatively apply the reference-modified density-functional theory (RMDFT) to the derivation of an approximate functional for $F_{IM}\left[\left\{n_\lambda^{IM}\right\}\right]$, where ideal multicomponent gas is employed as the reference system of RMDFT. The Euler-Lagrange equation for the ideal multicomponent gas is give by

$$\left.\frac{\delta F_{IG}\left[\left\{n_\lambda^{IG}\right\}\right]}{\delta n_\alpha^{IG}\left(\mathbf{r}\left|\left\{U_\lambda^{IG}\right\}\right.\right)}\right|_{T,V} = \mu_\alpha^{IG} - U_\alpha^{IG}(\mathbf{r}), \tag{A3}$$

where $F_{IG}\left[\left\{n_\lambda^{IG}\right\}\right]$ is the intrinsic free energy functional of the ideal multicomponent gas, and $U_\alpha^{IG}(\mathbf{r})$ and μ_α^{IG} are the external field and chemical potential for component α of the ideal multicomponent gas. The external fields for the ideal multicomponent gas $\left\{U_\lambda^{IG}(\mathbf{r})\right\}$ are defined so that

$$n_a^{IG}\left(\mathbf{r}\left|\left\{U_\lambda^{IG}\right\}\right.\right) = n_a^{IM}\left(\mathbf{r}\left|\left\{U_\lambda^{IM}\right\}\right.\right). \qquad (a=1,2,\cdots,P) \tag{A4}$$

Here, we introduce the excess intrinsic free-energy functional for $F_{IM}\left[\left\{n_\lambda^{IM}\right\}\right]$ and the excess chemical potential for μ_α^{IM} that are defined as the differences from reference ideal multicomponent gas as follows:

$$F_{IM}^{ex}\left[\left\{n_\lambda^{IM}\right\}\right] = F_{IM}\left[\left\{n_\lambda^{IM}\right\}\right] - F_{IG}\left[\left\{n_\lambda^{IM}\right\}\right], \tag{A5}$$

$$\mu_\alpha^{exIM} = \mu_\alpha^{IM} - \mu_\alpha^{IG}. \tag{A6}$$

From Eqs. (A2)-(A6), we obtain

$$U_\alpha^{IG}(\mathbf{r}) = U_\alpha^{IM}(\mathbf{r}) + \left.\frac{\delta F_{IM}^{ex}\left[\left\{n_\lambda^{IM}\right\}\right]}{\delta n_\alpha^{IM}\left(\mathbf{r}\left|\left\{U_\lambda^{IM}\right\}\right.\right)}\right|_{T,V} - \mu_\alpha^{exIM}.$$

(A7)

$F_{IM}^{ex}\left[\left\{n_\lambda^{IM}\right\}\right]$ is approximately obtained by using the second-order density-functional Taylor expansion as follows:

$$F_{IM}^{ex}\left[\left\{n_\lambda^{IM}\right\}\right] = F_{IM}^{ex}\left[\left\{n_0\right\}\right] + \sum_{a=1}^{P}\int d\mathbf{r}_1^a \mu_a^{exIM}\left[n_a^{IM}\left(\mathbf{r}_1^a\left|\left\{U_\lambda^{IM}\right\}\right.\right) - n_0\right]$$
$$-\frac{1}{2\beta}\sum_{a=1}^{P}\sum_{b=1}^{P}\int d\mathbf{r}_1^a d\mathbf{r}_1^b C_{ab}^{IM}\left(\left|\mathbf{r}_1^a - \mathbf{r}_1^b\right|\right)\left[n_a^{IM}\left(\mathbf{r}_1^a\left|\left\{U_\lambda^{IM}\right\}\right.\right) - n_0\right]\left[n_b^{IM}\left(\mathbf{r}_1^b\left|\left\{U_\lambda^{IM}\right\}\right.\right) - n_0\right]$$

.(A8)

In this equation, we use

$$\mu_\alpha^{exIM} \equiv \left.\frac{\delta F_{IM}^{ex}\left[\left\{n_\lambda^{IM}\right\}\right]}{\delta n_\alpha^{IM}\left(\mathbf{r}\left|\left\{U_\lambda^{IM}\right\}\right.\right)}\right|_{n_\lambda^{IM}=n_0},$$

(A9)

that is given by Eq. (A7) and the definition of the intramolecular direct correlation function,[4]

$$C_{\alpha\beta}^{IM}\left(\left|\mathbf{r}-\mathbf{r}'\right|\right) \equiv -\beta\left.\frac{\delta^2 F_{IM}^{ex}\left[\left\{n_\lambda^{IM}\right\}\right]}{\delta n_\alpha^{IM}\left(\mathbf{r}\left|\left\{U_\lambda^{IM}\right\}\right.\right)\delta n_\beta^{IM}\left(\mathbf{r}'\left|\left\{U_\lambda^{IM}\right\}\right.\right)}\right|_{n_\lambda^{IM}=n_0}$$
$$= \left.\frac{\delta\left[-\beta U_\alpha^{IG}(\mathbf{r})\right]}{\delta n_\beta^{IG}\left(\mathbf{r}'\left|U_\beta^{IG}\right.\right)}\right|_{n_\lambda^{IG}=n_0} - \left.\frac{\delta\left[-\beta U_\alpha^{IM}(\mathbf{r})\right]}{\delta n_\beta^{IM}\left(\mathbf{r}'\left|\left\{U_\lambda^{IG}\right\}\right.\right)}\right|_{n_\lambda^{IM}=n_0}.$$

(A10)

Equation (A10) is equal to Eq. (31) in the text. Equation (A7) is approximately expressed by using Eq. (A8) as follows:

$$U_\alpha^{IG}(\mathbf{r}) = U_\alpha^{IM}(\mathbf{r}) - \frac{1}{\beta}\sum_{a=1}^{P}\int d\mathbf{r}_1^a C_{\alpha a}^{IM}\left(\left|\mathbf{r}-\mathbf{r}_1^a\right|\right)\left[n_a^{IM}\left(\mathbf{r}_1^a\left|\left\{U_\lambda^{IM}\right\}\right.\right) - n_0\right].$$

(A11)

Using Eqs. (A8), (A11) and $F_{IG}\left[\left\{n_\lambda^{IM}\right\}\right]$ that is provided by Eq. (19) in the text, $F_{IM}\left[\left\{n_\lambda^{IM}\right\}\right]$ in Eq. (A5) is finally obtained as follows:

$$F_{IM}\left[\left\{n_\lambda^{IM}\right\}\right]=F_{IM}\left[\left\{n_0\right\}\right]-\frac{1}{\beta}\sum_{a=1}^{P}d\mathbf{r}_1^a\left[n_a^{IM}\left(\mathbf{r}_1^a\middle|\left\{U_\lambda^{IM}\right\}\right)-n_0\right]$$

$$+\sum_{a=1}^{P}\mu_a^{exIM}d\mathbf{r}_1^a\left[n_a^{IM}\left(\mathbf{r}_1^a\middle|\left\{U_\lambda^{IM}\right\}\right)-n_0\right]-\sum_{a=1}^{P}d\mathbf{r}_1^a U_a^{IM}\left(\mathbf{r}_1^a\right)n_a^{IM}\left(\mathbf{r}_1^a\middle|\left\{U_\lambda^{IM}\right\}\right)$$

$$+\frac{n_0}{\beta}\sum_{a=1}^{P}\sum_{b=1}^{P}\int d\mathbf{r}_1^a d\mathbf{r}_1^b C_{ab}^{IM}\left(\left|\mathbf{r}_1^a-\mathbf{r}_1^b\right|\right)\left[n_b^{IM}\left(\mathbf{r}_1^b\middle|\left\{U_\lambda^{IM}\right\}\right)-n_0\right]$$

$$+\frac{1}{2\beta}\sum_{a=1}^{P}\sum_{b=1}^{P}\int d\mathbf{r}_1^a d\mathbf{r}_1^b C_{ab}^{IM}\left(\left|\mathbf{r}_1^a-\mathbf{r}_1^b\right|\right)\left[n_a^{IM}\left(\mathbf{r}_1^a\middle|\left\{U_\lambda^{IM}\right\}\right)-n_0\right]\left[n_b^{IM}\left(\mathbf{r}_1^b\middle|\left\{U_\lambda^{IM}\right\}\right)-n_0\right]$$
,(A12)

where

$$F_{IM}\left[\left\{n_0\right\}\right]=-\frac{PN}{\beta}+\sum_{a=1}^{P}\mu_a^{exIM}N\,.$$
(A13)

This equation is regarded as the hypernetted-chain-type approximation for the intrinsic free-energy functional of ideal polyatomic molecular gas.

3D-RISM calculation

We need the site-density distribution functions $n_\alpha\left(\mathbf{r}\middle|\left\{U_\lambda^{PR}\right\}\right)$ to calculate SFE using Eq. (40). In the study presented here, we employed three-dimensional reference-interaction-site-model (3D-RISM) theory[5,6] to calculate $n_\alpha\left(\mathbf{r}\middle|\left\{U_\lambda^{PR}\right\}\right)$.

The 3D-RISM theory is an integral equation theory that is used to obtain the solvent distribution functions from intermolecular potential functions and the thermodynamic conditions (i.e., temperature and density). It produces the distribution functions of solvent molecule around solute molecule. The theoretical procedure of the methods has two steps. The first step is to calculate the pair correlation functions in the aqueous solution based on the solvent-solvent 1D-RISM theory,[7,8] which represents the microscopic structure of the distribution of water molecules. In the second step, we immerse a solute molecule into the solvent and calculate the 3D distribution functions of solvent

molecule using the 3D-RISM integral equations.

At infinite dilution in the solvent mixture, the solute-solvent 3D-RISM integral equations can be written as

$$\hat{h}_\gamma(\mathbf{k}) = \sum_{a=1}^{p} \hat{c}_a(\mathbf{k}) * \hat{\sigma}_{a\gamma}(k) + n_0 \sum_{a=1}^{p} \hat{c}_a(\mathbf{k}) * \hat{H}_{a\gamma}(k). \tag{A14}$$

Here, $\hat{h}_\gamma(\mathbf{k})$ and $\hat{c}_\gamma(\mathbf{k})$ are the Fourier transforms of $h_\gamma(\mathbf{r})$ and $c_\gamma(\mathbf{r})$, which are the solute-solvent total and direct correlation functions between solute molecule and solvent site γ. We mention that Eq. (A14) contains solvent-solvent total correlation function $H_{\alpha\gamma}(r)$ defined by Eq. (34) in the text. Thus we need to solve Eq. (34) before solving Eq. (A14). We can calculate $n_\alpha\left(\mathbf{r}\middle|\left\{U_\lambda^{PR}\right\}\right)$ form $h_\gamma(r)$ using the Percus' relation $n_\alpha\left(\mathbf{r}\middle|\left\{U_\lambda^{PR}\right\}\right) = n_0(h_\alpha(\mathbf{r})+1).$[12]

Equations (34) and (A14) have an unknown function of two each, the total and direct correlation functions, then one more equations are required to solve. We employed partially linearized HNC (PLHNC) equations,[5] which are called Kovalenko-Hirata (KH),[6] as the closure equations,

$$H_{\alpha\gamma}(r) = \begin{cases} \exp(\chi_{\alpha\gamma}(r)) & \chi_{\alpha\gamma}(r) < 1 \\ \chi_{\alpha\gamma}(r) - 1 & \chi_{\alpha\gamma}(r) \geq 1 \end{cases}, \tag{A15}$$
$$\chi_{\alpha\gamma}(r) = -\beta v_{\alpha\gamma}(r) + H_{\alpha\gamma}(r) - C_{\alpha\gamma}(r)$$

and

$$h_\gamma(\mathbf{r}) = \begin{cases} \exp(\chi_\gamma(\mathbf{r})) & \chi_\gamma(\mathbf{r}) < 1 \\ \chi_\gamma(\mathbf{r}) - 1 & \chi_\gamma(\mathbf{r}) \geq 1 \end{cases}, \tag{A16}$$
$$\chi_\gamma(\mathbf{r}) = -\beta U_\gamma^{PR}\left(\mathbf{r}\middle|\left\{\mathbf{r}_1^\lambda\right\}\right) + h_\gamma(\mathbf{r}) - c_\gamma(\mathbf{r})$$

where $v_{\alpha\gamma}(r)$ is the intermolecular interaction potential between sites α and γ on solvent

molecule, and $U_\gamma^{PR}\left(\mathbf{r}\big|\{\mathbf{r}_1^\lambda\}\right)$ is given by Eq. (35) in the text. We used Eqs. (34) and (A15) for the

first step, and Eqs. (A14) and (A16) for the second step. To solve the 1D-RISM and 3D-RISM

integral equations, we respectively introduce the difference functions,

$$T_{\alpha\gamma}(r) = H_{\alpha\gamma}(r) - C_{\alpha\gamma}(r) \tag{A17}$$

and

$$t_\gamma(\mathbf{r}) = h_\gamma(\mathbf{r}) - c_\gamma(\mathbf{r}). \tag{A18}$$

The numerical procedure for the first/second step is briefly summarized as follows.

1. Calculate $u_{\alpha\gamma}(r) / U_\gamma^{PR}\left(\mathbf{r}\big|\{\mathbf{r}_1^\lambda\}\right)$ at each 1D/3D grid point.

2. Initialize $T_{\alpha\gamma}(r) / t_\gamma(\mathbf{r})$ to zero.

3. Calculate $H_{\alpha\gamma}(r) / h_\gamma(\mathbf{r})$ using Eq. A14/A15.

4. Calculate $C_{\alpha\gamma}(r) / c_\gamma(\mathbf{r})$ from $C_{\alpha\gamma}(r) = H_{\alpha\gamma}(r) - T_{\alpha\gamma}(r) / c_\gamma(\mathbf{r}) = h_\gamma(\mathbf{r}) - t_\gamma(\mathbf{r})$.

5. Transform $C_{\alpha\gamma}(r) / c_\gamma(\mathbf{r})$ to $\hat{C}_{\alpha\gamma}(k) / \hat{c}_\gamma(\mathbf{k})$ using the 1D/3D fast Fourier transform

(1D-FFT/3D-FFT).

6. Calculate $\hat{H}_{\alpha\gamma}(k) / \hat{h}_\gamma(\mathbf{k})$ using Eq. 34/A14.

7. Invert $\hat{H}_{\alpha\gamma}(k) / \hat{h}_\gamma(\mathbf{k})$ to $H_{\alpha\gamma}(r) / h_\gamma(\mathbf{r})$ using the 1D-FFT/3D-FFT.

8. Calculate $T_{\alpha\gamma}(r) / t_\gamma(\mathbf{r})$ using Eq. A17/A18.

9. Calculate new $T_{\alpha\gamma}(r) / t_\gamma(\mathbf{r})$ from $T_{\alpha\gamma}(r) / t_\gamma(\mathbf{r})$ and its history with an acceleration method.

10. Repeat steps 3-9 until the input and output functions become identical within convergence

tolerance.

Here some acceleration methods for integral equation theories have been proposed for quick

convergence of the iteration process. We employed the modified Anderson method in this study.[9]

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