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Addendum to "Free energies from integral equation theories: Enforcing path independence"

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The variational formalism developed for the analysis of the path dependence of free energies from integral equation theories [S. M. Kast, Phys. Rev. E **67**, 041203 (2003)] is extended in order to allow for the three-dimensional treatment of arbitrarily shaped solutes.

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Recently, the free-energy-path-dependence problem within certain integral equation theories was addressed by employing a variational formalism [1]. In this context, the reference interaction site model (RISM) integral equation component of the total chemical-potential functional in the three-dimensional (3D) case, $Q^{3\mathrm{D}}$, last equation in the left column of page 041203-2, reflects only the special case of solute-solvent potentials with spherical symmetry, reducing essentially to the one-dimensional (1D) situation. In the more general 3D case, however, the Fourier transforms of direct and total correlation function (denoted by carets) can be complex numbers to be accounted for in the chemical-potential functional that has to be real itself. Since the Lagrange parameters are real numbers as well, a correspondingly more general, real-valued expression for $Q^{3\mathrm{D}}$ is

$$Q^{3\mathrm{D}} = \frac{1}{2}\left(\sum_{\gamma,\gamma'} \hat{c}_{\gamma}^{*} \frac{\partial \hat{c}_{\gamma'}}{\partial \lambda} \hat{\chi}_{\gamma\gamma'} + \sum_{\gamma,\gamma'} \hat{c}_{\gamma} \frac{\partial \hat{c}_{\gamma'}^{*}}{\partial \lambda} \hat{\chi}_{\gamma\gamma'} \right.$$
$$\left. - \sum_{\gamma} \frac{\partial \hat{c}_{\gamma}^{*}}{\partial \lambda} \rho \hat{h}_{\gamma} - \sum_{\gamma} \frac{\partial \hat{c}_{\gamma}}{\partial \lambda} \rho \hat{h}_{\gamma}^{*} \right),$$

where the star indicates the complex conjugate. The solvent susceptibility in the 3D-RISM theory is always real. This modified $Q^{3\mathrm{D}}$ contains the same information as the original version, which can be shown by functional differentiation of the updated chemical potential functional: the forward Fourier transform of a real-valued function $f(\mathbf{r},\lambda)$ can be written in a general form appropriate for differentiation of the functional defined over the domain of spatial and coupling coordinates as

$$\hat{f}(\mathbf{k},\lambda') = \int_0^1 d\lambda \int d\mathbf{r}\, e^{-i\mathbf{k}\cdot\mathbf{r}} f(\mathbf{r},\lambda)\, \delta(\lambda - \lambda'),$$

$$\hat{f}^{*}(\mathbf{k},\lambda') = \int_0^1 d\lambda \int d\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r}} f(\mathbf{r},\lambda)\, \delta(\lambda - \lambda'),$$

which defines Hermitian symmetry, $\hat{f}^{*}(\mathbf{k},\lambda) = \hat{f}(-\mathbf{k},\lambda)$, for c and h. Application of the functional chain rule within the Euler–Lagrange equations, given here exemplarily for a component of the first term in the $Q^{3\mathrm{D}}$ functional, yields

$$\frac{\delta}{\delta c(\mathbf{r},\lambda)} \int_0^1 d\lambda' \int d\mathbf{k}\, \hat{c}^{*}(\mathbf{k},\lambda') \frac{\partial \hat{c}(\mathbf{k},\lambda')}{\partial \lambda} \hat{\chi}(\mathbf{k})$$
$$= \int_0^1 d\lambda' \int d\mathbf{k}\, e^{i\mathbf{k}\cdot\mathbf{r}} \frac{\partial \hat{c}(\mathbf{k},\lambda')}{\partial \lambda} \hat{\chi}(\mathbf{k})\, \delta(\lambda - \lambda')$$
$$- \frac{\partial}{\partial \lambda} \int_0^1 d\lambda' \int d\mathbf{k}\, e^{-i\mathbf{k}\cdot\mathbf{r}} \hat{c}^{*}(\mathbf{k},\lambda') \hat{\chi}(\mathbf{k})\, \delta(\lambda - \lambda')$$
$$= (2\pi)^3 \left[\frac{\partial c(\mathbf{r},\lambda)}{\partial \lambda} \circ \chi(\mathbf{r}) - \frac{\partial}{\partial \lambda} \big(c(\mathbf{r},\lambda) \circ \chi(\mathbf{r}) \big) \right] = 0,$$

where additionally the relation $\hat{\chi}(\mathbf{k}) = \hat{\chi}(-\mathbf{k}) = \hat{\chi}(k)$ (spherical symmetry) has been used. With comparable functional derivatives for the other terms in $Q^{3\mathrm{D}}$ we directly obtain Eq. (8) again such that the remainder and the conclusions of the paper are unchanged. For the six-dimensional (6D) molecular Ornstein–Zernike equation a similar formalism using generalized Fourier transforms would be needed, which will be described elsewhere.

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[1] S. M. Kast, Phys. Rev. E **67**, 041203 (2003).

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