Estrutura de líquidos

g(r) e relações entre séries – equação de Ornstein-Zernike

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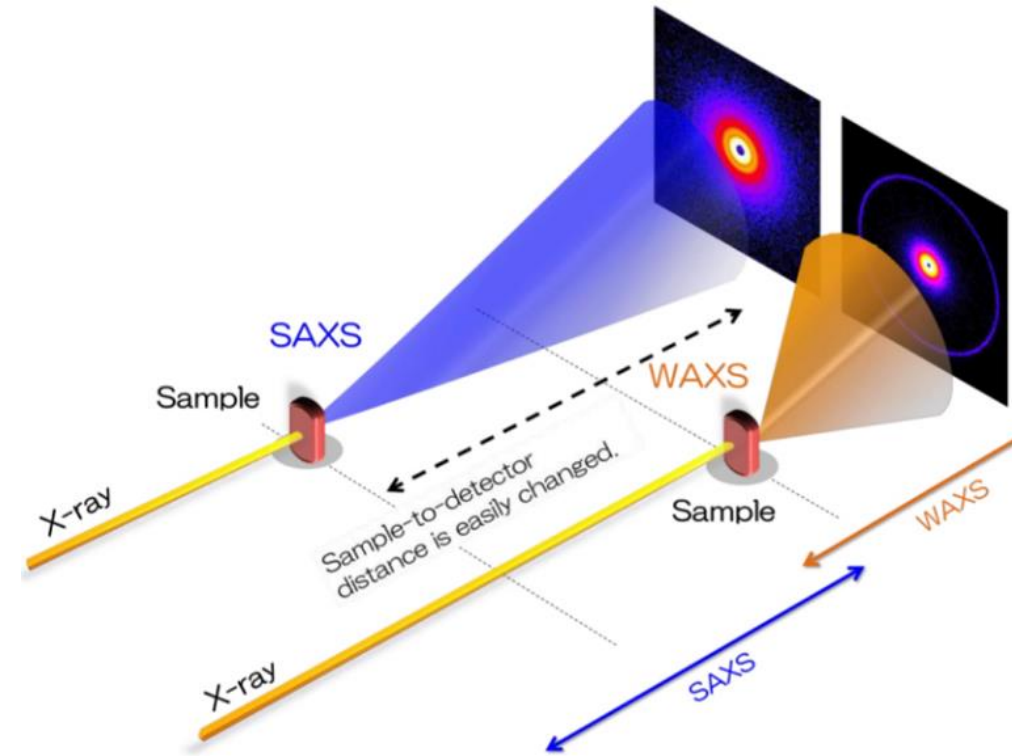
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Experimento e teoria

espalhamento

$$S(q) = 1 + \frac{N}{V} \int_V d\vec{r}\, g(r)\, e^{i\vec{q}\cdot\vec{r}}$$

experimento   teoria

termodinâmica

$$\frac{P}{k_B T} = n - n^2 \frac{1}{6k_B T} \int_0^\infty dr\, 4\pi r^2 r \frac{\partial U}{\partial r} g(r)$$

experimento   teoria

Solvation Thermodynamics of Organic Molecules by the Molecular Integral Equation Theory: Approaching Chemical Accuracy

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2015

The integral equation theory (IET) of molecular liquids has been an active area of academic research in theoretical and computational physical chemistry for over 40 years because it provides a *consistent* theoretical framework to describe the structural and thermodynamic properties of liquid-phase solutions. The theory can describe pure and mixed solvent systems (including *anisotropic* and *nonequilibrium* systems) and has already been used for theoretical studies of a vast range of problems in chemical physics / physical chemistry, molecular biology, colloids, soft matter, and electrochemistry. A considerable advantage of IET is that it can be used to study specific solute–solvent interactions, unlike continuum solvent models, but yet it requires considerably less computational expense than explicit solvent simulations.

However, until recently this area of research (although active) was mostly considered as an outlier compared to molecular simulation methods. Among other reasons for this we would like to highlight the following: (i) due to several problems with bridge functionals (see below), the theory has traditionally been considered to be too inaccurate for widespread use in practical applications such as research in the biomedical and environmental sciences; (ii) a lack of stable implementations of the IET algorithms in user-friendly software prevented researchers with noncomputational backgrounds from using these methods.

The situation has changed during the past decade. Recent developments in theoretical and computational aspects of IET have made it possible to make accurate calculations of thermodynamic and structural properties of solvation across multiple classes of molecular systems at relatively low computational expense.[1−9] IET methods have been implemented in several open-source and proprietary pieces of computational chemistry
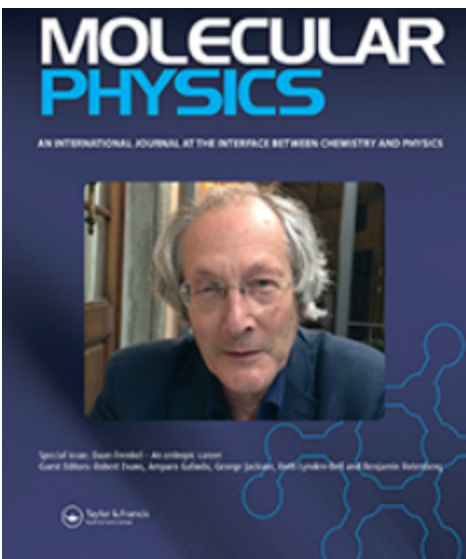
2018

Finite-size integral equations in the theory of liquids and the thermodynamic limit in computer simulations

M. Heidari, K. Kremer, R. Potestio & R. Cortes-Huerto
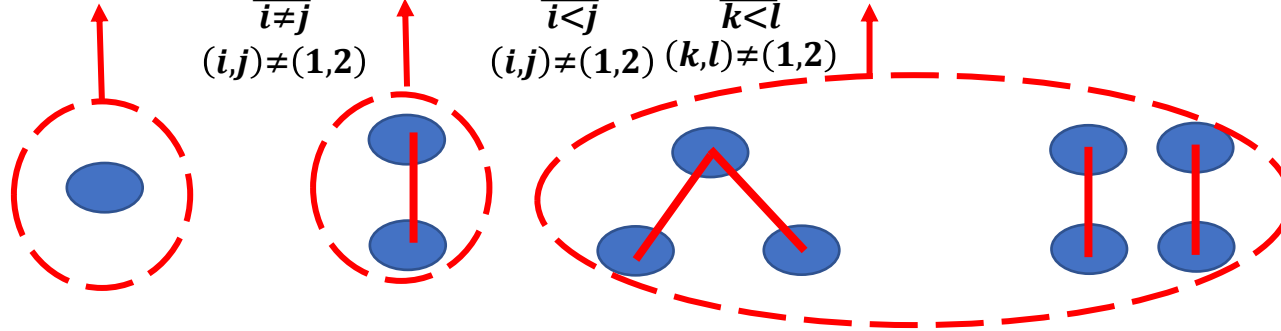
ABSTRACT

We present an efficient method to obtain bulk isothermal compressibilities (κ_T) and Kirkwood–Buff (KB) integrals of single- and multicomponent liquids using fluctuations of the number of molecules obtained from small-sized molecular dynamics simulations. We write finite-size versions of the Ornstein–Zernike and the KB integral equations and include there finite size effects related to the statistical ensemble and the finite integration volumes required in computer simulations. Consequently, we obtain analytical expressions connecting κ_T and the KB integrals in the thermodynamic limit (TL) with density fluctuations in the simulated system. We validate the method by calculating various thermodynamic quantities, including the chemical potentials of SPC/E water as a function of the density, and of aqueous urea solutions as a function of the mole fraction. The reported results are in excellent agreement with calculations obtained by using the best computational methods available, thus validating the method as a tool to compute the chemical potentials of dense molecular liquids and mixtures. Furthermore, the present method identifies conditions in which computer simulations can be effectively considered in the TL.

G(r) e somas de séries na densidade

$$e^{-\beta u(r_{ij})} = 1 + f(r_{ij})$$

$$g(r) = V^2 e^{-\beta u(r)} \int\limits_V d\vec{R}_{31} \ldots . \int\limits_V d\vec{R}_{N1} \; \frac{\prod_{i,j=3}^{N} [1 + f(r_{ij})]}{Z(T,V,N)}$$

$$g(r)\, e^{\beta u(r)} = V^2 \int\limits_V d\vec{r}_3 \,.... \int\limits_V d\vec{r}_N \left\{ 1 + \sum_{\substack{i \neq j \\ (i,j) \neq (1,2)}} f_{ij} + \sum_{\substack{i < j \\ (i,j) \neq (1,2)}} \sum_{\substack{k < l \\ (k,l) \neq (1,2)}} f_{ij}\, f_{kl} + o(f^3) \right\}$$

$$g(r)e^{\beta u(r)} = \left\{ \left(\underbrace{\text{soma sobre configurações de N-2 partículas}} \right) + \left(S \text{ sobre } N\text{-3 partículas} \right) + \left(S \text{ sobre } N\text{-4} \right) \right.$$

$$\left. + \left(S \text{ sobre } N\text{-4} \right) + \cdots \left(S \text{ sobre } N\text{-6} \right) + \left(S \text{ sobre } N\text{-6} \right) + \cdots \right\} \frac{V^2}{Q_N}$$

$$g(r)e^{\beta u(r)} = \left\{ \left(\begin{array}{c} \text{① ②} \\ \text{soma sobre} \\ \text{configurações} \\ \text{de N-2} \\ \text{partículas} \end{array} \right) + \left(\begin{array}{c} \text{S sobre} \\ \text{N-3 partículas} \end{array} \right) + \left(\begin{array}{c} \text{S sobre} \\ \text{N-4} \end{array} \right) + \left(\begin{array}{c} \text{S sobre} \\ \text{N-4} \end{array} \right) + \cdots \left(\begin{array}{c} \text{S sobre} \\ \text{N-6} \end{array} \right) + \left(\begin{array}{c} \text{S sobre} \\ \text{N-6} \end{array} \right) + \cdots \right\} \frac{V^2}{Q_N}$$

agregados de $L + 2$ partículas

Z_{N-L-2}

$$\boldsymbol{g(r)}\, e^{\beta\mu(r)} = \frac{V^2}{\boldsymbol{Z_N}} \sum_{L=0} \Omega(L+2, N) \left(\begin{array}{c} \text{aglomerados de} \\ L+2 \ \text{partículas} \\ \text{que incluem} \\ 1 \ e \ 2 \end{array} \right) \left(\begin{array}{c} \text{soma sobre} \\ \text{configurações de} \\ N - L - 2 \ \text{partículas} \end{array} \right)$$

ℓ_1 ℓ_2 ℓ_3 ℓ_4 ℓ_5 ℓ_6 ℓ_7

k partículas

$$g(r)\, e^{\beta\mu(r)} = \frac{V^2}{Z_N} \sum_{L=0} \Omega(L+2,N) \begin{pmatrix} \text{aglomerados de} \\ L+2 \ \text{partículas} \\ \text{que incluem} \\ 1\ e\ 2 \end{pmatrix} \begin{pmatrix} \text{soma sobre} \\ \text{configurações de} \\ N-L-2 \ \text{partículas} \end{pmatrix}$$

Z_{N-L-2}

ℓ_1 ℓ_3 ℓ_4 ℓ_5 ℓ_6 ℓ_7 $\ell 8!\, b_{\ell 8}$ ℓ_2

k partículas
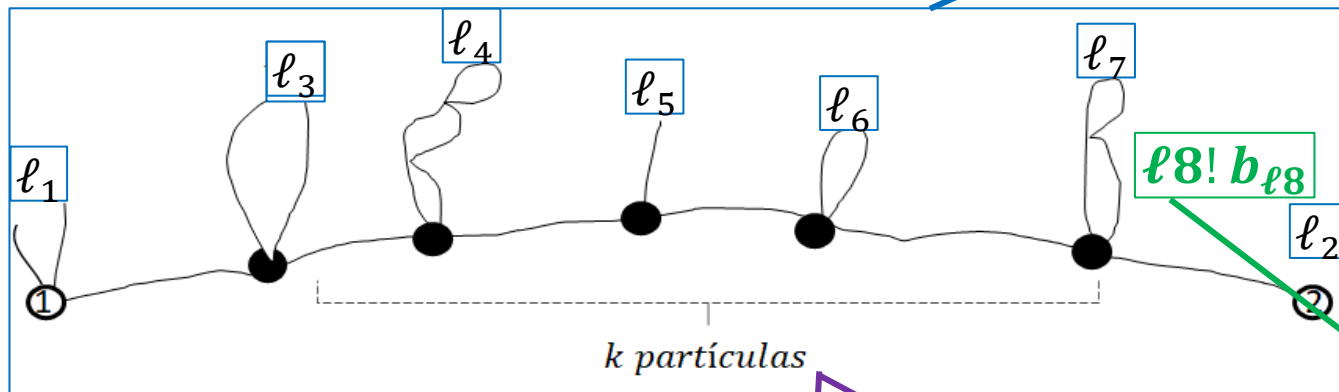
$k!\, \delta_k(r_{12})$

$$2 + L = 2 + k + \sum_{k=0}^{k+2} \ell_{k+1}$$

$$g(r) e^{\beta\mu(r)} = V^2 \sum_{k=0} \frac{(N-2)!}{(N-L-2)!\, k! \displaystyle\prod_{n=1}^{k+2} l_n!} \; k!\, \delta_k \sum_{\{l_n\}} \prod_{r=1}^{k+2} (l_n+1)!\, b_{l_{n+1}} \frac{Z_{N-L-2}}{Z_N}$$

$$g(r)e^{\beta u(r)} = 1 + (\,\circ\!\!\!-\!\!\!\overset{\bullet}{\diagdown}\!\!\!-\!\!\!\circ\,)\,n + \left(\vphantom{\begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \end{array}} \right. \; \begin{array}{c} \text{[diagrams]} \end{array} \; \left. \vphantom{\begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \end{array}} \right) n^2 + \; \ldots$$
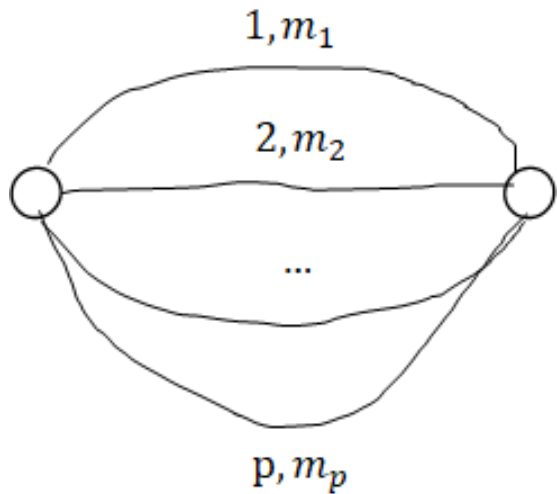
$$g(r)e^{\beta u(r)} = 1 + S(r;n) + P(r;n) + \prod(r;n)$$

NÃO CONDUTORES não dependem de $|\vec{r}_{12}|$	CONDUTORES dependem de $|\vec{r}_{12}|$	
	redutíveis	**irredutíveis**
apêndices $$\int d\vec{r}_{53} \int d\vec{r}_{43} f_{34} \, f_{45} f_{53}$$ $$\int d\vec{r}_{62} \int d\vec{r}_{72} f_{26} \, f_{67} f_{72}$$	**paralelos (Π)** $$\int d\vec{r}_{31} \int d\vec{r}_{41} f_{13} \, f_{32} f_{24} f_{41} =$$ $$\left[\int d\vec{r}_{31} f_{13} \, f_{32} (\vec{r}_{31} - \vec{r}_{21})\right]\left[\int d\vec{r}_{41} f_{41} \, f_{24} (\vec{r}_{41} - \vec{r}_{21})\right]$$ $$= \left[\int d\vec{r}_{31} f_{13} \, f_{32} (\vec{r}_{31} - \vec{r}_{21})\right]^2$$	**em série (S)** diagramas com nós – toda corrente de $1\rightarrow 2$ passa pelo nó $$\int d\vec{r}_{31} \int d\vec{r}_{41} f_{13} \, f_{34} f_{14} f_{42}$$
aglomerados independentes		**em ponte (P)** diagramas sem nó

Deixando apenas diagramas irredutíveis: série e ponte

$$g(r)e^{\beta u(r)} = 1 + S(r;n) + P(r;n) + \prod(r;n)$$

$$\prod(r;n) = \sum_{i,j} S^i(r;n)P^j(r;n)$$
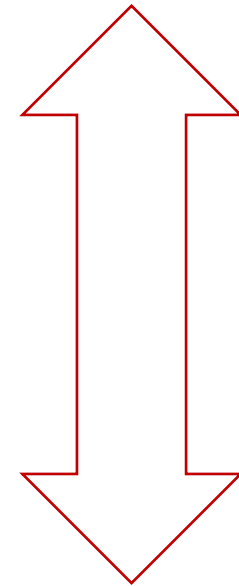
$$g(r)e^{\beta u(r)} = \exp\{S(r;n) + P(r;n) +\}$$

A função de correlação direta $C(r)$

$$\boxed{g(r) = e^{-\beta u(r)}\{1 + S(r;n) + P(r;n) + \prod(r;n)\}}$$

$$= [1 + f(r)]\{1 + S(r;n) + P(r;n) + \prod(r;n)\}$$
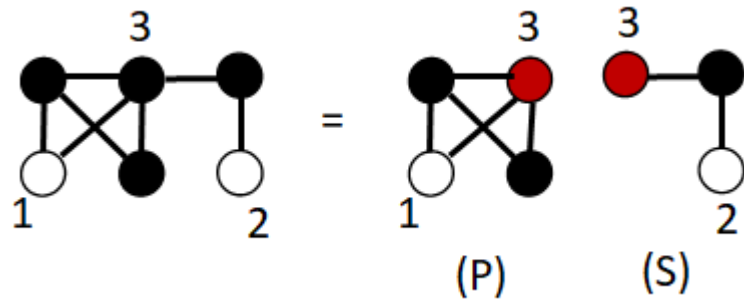
$$= 1 + S(r;n) +$$

$$[f(r) + P(r;n) + \prod(r;n) + f(r) + f(r)S(r;n)$$
$$+ f(r)P(r;n) + f(r)\prod(r;n)]$$

diagramas
com nó:
$S(r)$

diagramas sem nó: $C(r)$

Uma relação entre a série com nós $S(r)$ e a série sem nós $C(r)$

$$g(r) = 1 + S(r;n) + C(r;n)$$

(P)   (S)

Todo diagrama com nó (série) é o "produto" de um diagrama sem nó (correlação direta) e qualquer outro tipo de diagrama

$$S(r_{12}) = n \int d\vec{r}_j \, C(\vec{r}_{1j}) \, [C(\vec{r}_{j2}) \quad OU \quad S(\vec{r}_{j2})]$$

$$g(r) = 1 + S(r;n) + C(r;n) + \int d\vec{r}' \, C(r')[g(\vec{r} - \vec{r}') - 1]$$