

The Entropy of the Square-Well Fluid

II. The Mean Spherical Approximation

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Abstract

The semi-analytical expression of the entropy is obtained for the square-well fluid within the mean spherical approximation.

Keywords: Entropy, square-well model, mean spherical approximation

In the first paper (I) the expression for the entropy, S , of the equilibrium square-well (SW) fluid has been obtained in the random phase approximation. Here, the expression for the SW entropy is derived by the same way in framework of the mean spherical approximation (MSA) [1] in the semi-analytical (SA) representation [2] which for the SW model is

$$c_{\text{SW-MSA(SA)}}(r) = \begin{cases} \sum_{m=0}^n b_m \left(\frac{r}{\sigma}\right)^m & r < \sigma \\ -\beta\phi_{\text{SW}}(r), & r \geq \sigma \end{cases}, \quad (1)$$

where $c(r)$ is the direct correlation function, σ - hard-core diameter, b_0, b_1, \dots, b_n - coefficients determined numerically from the condition that the pair correlation function, $g(r)$, is equal to 0 at $r < \sigma$, $\beta = (k_B T)^{-1}$, k_B - Boltzmann constant, T - absolute temperature, $\phi_{\text{SW}}(r)$ - SW pair potential at $r \geq \sigma$:

$$\phi_{\text{SW}}(r) = \begin{cases} 0, & r < \sigma \\ \varepsilon, & \sigma \leq r < \lambda\sigma \\ 0, & r \geq \lambda\sigma \end{cases}. \quad (2)$$

Here, ε and $\sigma(\lambda - 1)$ are the depth and width of the square well, respectively.

The Fourier transform of $c_{\text{SW-MSA(SA)}}(r)$ is

$$c_{\text{SW-MSA(SA)}}(q) = c_{\text{SA}}(q) - \beta\phi_{\text{SW}}(q), \quad (3)$$

where

$$c_{\text{SA}}(q) = \left(\frac{4\pi}{q^3}\right) \left\{ \sum_{m=1}^{n+2} x^{2-m} \frac{\partial^m \sin(x)}{\partial x^m} \sum_{l=0}^n b_l \prod_{k=0}^{m-2} (l+1-k) + \sum_{m=1}^{(n+1)/2} \frac{(-1)^{m+1} (2m)! b_{2m-1}}{x^{2m-1}} \right\}, \quad (4)$$

$$\phi_{\text{SW}}(q) = 4\pi\varepsilon [\sin(x\lambda) - \sin(x) - x\lambda \cos(x\lambda) + x \cos(x)] / q^3, \quad (5)$$

$x = q\sigma$.

As a result the structure factor in the approach under consideration is being written as follows:

$$a_{\text{SW-MSA(SA)}}(q) = \frac{1}{1 - \rho c_{\text{SA}}(q) + \beta\rho\phi_{\text{SW}}(q)}, \quad (6)$$

where ρ is the mean atomic density.

Then, following the method of paper I, we integrate the expression

$$\left(\frac{\partial(\Delta S_{\text{SW-MSA(SA)}})}{\partial T} \right)_{\rho} = \frac{1}{T} \left(\frac{\partial U_{\text{SW-MSA(SA)}}}{\partial T} \right)_{\rho}, \quad (7)$$

where (hereafter, per atom)

$$\Delta S_{\text{SW-MSA(SA)}} = S_{\text{SW-MSA(SA)}} - S_{\text{HS}}, \quad (8)$$

$$U_{\text{SW-MSA(SA)}} = \frac{2}{3} \pi \rho \sigma^3 \varepsilon (\lambda^3 - 1) + \frac{1}{4\pi^2} \int_0^{\infty} [a_{\text{SW-MSA(SA)}}(q) - 1] \phi_{\text{SW}}(q) q^2 dq, \quad (9)$$

S_{HS} is the entropy of the hard-sphere (HS) system.

$$\left(\frac{\partial U_{\text{SW-MSA(SA)}}}{\partial T} \right)_{\rho} = \frac{\rho k_B}{4\pi^2} \int_0^{\infty} \frac{\phi_{\text{SW}}^2(q) q^2 dq}{[k_B T (1 - \rho c_{\text{SA}}(q)) + \rho \phi_{\text{SW}}(q)]^2}, \quad (10)$$

$$S_{\text{SW-MSA(SA)}} = S_{\text{HS}} + \int \frac{dT}{T} \left(\frac{\partial U_{\text{SW-MSA(SA)}}}{\partial T} \right)_{\rho} = S_{\text{HS}} + \frac{k_B \rho}{4\pi^2} \int_0^{\infty} \left[-\frac{1}{\rho^2 \phi_{\text{SW}}^2(q)} \times \right. \\ \left. \times \left(\ln \left| \frac{k_B}{a_{\text{SW-MSA(SA)}}(q)} \right| + (1 - \rho c_{\text{SA}}(q)) a_{\text{SW-MSA(SA)}}(q) \right) + \text{Const} \right] \phi_{\text{SW}}^2(q) q^2 dq, \quad (11)$$

where

$$\text{Const} = \frac{\ln |k_B (1 - \rho c_{\text{HS}}(q))| + 1}{\rho^2 \phi_{\text{SW}}^2(q)}. \quad (12)$$

The result is

$$S_{\text{SW-MSA-SA}} = S_{\text{HS}} + \frac{k_B}{4\pi^2 \rho} \int_0^{\infty} q^2 \left(\ln |(1 - \rho c_{\text{HS}}(q)) a_{\text{SW-MSA(SA)}}(q)| - \right. \\ \left. - (1 - \rho c_{\text{SA}}(q)) a_{\text{SW-MSA(SA)}}(q) + 1 \right) dq. \quad (13)$$

It is the semi-analytical expression due to the coefficients b_m in $c_{\text{SA}}(q)$ are calculated numerically.

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