A Simple Way for Obtaining the Expression for the Entropy of Fluid

III. The Mean Spherical Approximation

Vladimir Filippov
Ural Federal University, Mira st. 19, 620002 Ekaterinburg, Russia
vvfilippov@mail.ru

Anatoliy Yuryev
Ural Federal University, Mira st. 19, 620002 Ekaterinburg, Russia
yurev_anatolii@mail.ru

Nikolay Dubinin
Ural Federal University, Mira st. 19, 620002 Ekaterinburg, Russia
ned67@mail.ru

Copyright © 2013 Vladimir Filippov et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Abstract

The more simple technique is used to obtain the analytical expression of the entropy for the square-well fluid in the mean spherical approximation.

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

In the previous article (I) was shown a more simple way to obtain the entropy, $S$, of an equilibrium arbitrary fluid with the hard-core (HC) pair potential.

Here, we apply this way to the square-well (SW) model within the mean spherical approximation (MSA) [1].

The SW pair potential is
\[
\varphi_{\text{SW}}(r) = \begin{cases} 
\infty, & r < \sigma \\
\varepsilon, & \sigma \leq r < \lambda \sigma \\
0, & r \geq \lambda \sigma
\end{cases}
\] (1)

where \(\varepsilon, \lambda\) and \(\sigma\) are the SW parameters.

The Fourier transform of the attractive part of \(\varphi_{\text{SW}}(r)\) is
\[
\phi_{\text{SW}}(q) = \frac{4\pi\varepsilon}{q} \left[ \sin(q\lambda\sigma) - \sin(q\sigma) - q\lambda\sigma \cos(q\lambda\sigma) + q\sigma \cos(q\sigma) \right].
\] (2)

The expression for the Fourier transform of the direct correlation function, \(c(r)\), in the SW-MSA approach we represent as
\[
c_{\text{SW-MSA}}(q) = c_{\text{SA}}(q) - \beta \phi_{\text{SW}}(q),
\] (3)

where \(\beta = (k_B T)^{-1}\), \(T\) is the absolute temperature, \(k_B\) - Boltzmann constant, \(c_{\text{SA}}(q)\) - the semi-analitical (SA) expression obtained in [2]:
\[
c_{\text{SA}}(q) = \left( \frac{4\pi}{q^2} \right) \left[ \sum_{m=1}^{\infty} x^{2m} \sum_{l=0}^{m} b_l \sum_{k=0}^{m/2} (-1)^{(n+1)/2} \frac{(2m)!}{x^{2m-1}} \right].
\] (4)

Here, the coefficients \(b_m\) are calculated numerically from the condition, that the radial distribution function is equal to zero inside the HC; \(x = q\sigma\).

The structure factor, \(a(q)\), of the SW system within the MSA(SA) is written as
\[
a_{\text{SW-MSA(SA)}}(q) = \frac{1}{1 - \rho c_{\text{SA}}(q) + \beta \rho \phi_{\text{SW}}(q)}. \] (5)

Finally, using Eq.(10) from (I) we have the following expression for the entropy:
\[
S_{\text{SW-MSA(SA)}} = S_{\text{HS}} + \frac{k_B}{4\pi^2} \int_0^\infty dq q^3 \left[ \beta a_{\text{SW-MSA(SA)}}(q) \phi_{\text{SW}}(q) + \frac{1}{\rho} \ln \frac{a_{\text{SW-MSA(SA)}}(q)}{a_{\text{HS}}(q)} \right].
\] (6)

Here, \(a_{\text{HS}}(q)\) is the hard-sphere (HS) \(a(q)\), taken in the analytical form [3], \(\rho\) - mean atomic density. Eq.(6) can be transformed exactly to Eq.(13) obtained in [4].

**References**


**Received:** April 30, 2013