The Entropy of the Square-Well Fluid

I. The Random Phase Approximation

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Abstract

The analytical expression of the entropy is obtained for the square-well fluid within the random phase approximation.

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In a general case the entropy of an equilibrium system, $S$, is (hereafter, all thermodynamic quantities are taken per atom) (see, for example, [1]):

$$ S = S_{lg} - \frac{1}{2} k_b \rho^2 \int \int g^{(2)}(\vec{r}_1,\vec{r}_2) \ln \left[ g^{(2)}(\vec{r}_1,\vec{r}_2) \right] d\vec{r}_1 d\vec{r}_2 - $$
where $S_{IG}$ is the entropy of the ideal gas (IG), $\rho$ - mean atomic density, $g(r) = g^{(2)}(|r_1 - r_2|)$ - pair correlation function, $g^{(3)}(r_1, r_2, r_3)$ - three-particle correlation function, $k_B$ - Boltzmann constant. Eq.(1) is not useful in practice.

If expressions for pressure or internal energy are known, the entropy can be found [1] by integrating one of the following relations:

$$\frac{\partial S}{\partial T} = \frac{\partial P}{\partial T} \rho,$$  \hspace{1cm} (2)

$$\frac{\partial S}{\partial T} = \frac{1}{T} \left( \frac{\partial (K + U)}{\partial T} \right) \rho,$$  \hspace{1cm} (3)

where $T$ is the absolute temperature, $P$ – pressure, $K$ - kinetic energy, $U$ - potential energy. In the pair-interaction approximation

$$U = 2\pi \rho \int_0^\infty \phi(r) g(r) r^2 \, dr,$$  \hspace{1cm} (4)

where $\phi(r)$ is the pair interatomic potential.

To obtain the IG entropy, eq.(3) can be used taking into account that $U_{IG} = 0$. For the hard-sphere (HS) model eq.(3) is not applicable since expression under integral sign is singular and therefore it is necessary to use eq.(2) to obtain an additional HS term to $S_{IG}$, $\Delta S_{HS}$. The difference between $S_{HS}$ and the entropy of the square-well (SW) fluid can be found again from eq.(3).

The SW model is determined by means the following pair potential:

$$\varphi_{SW}(r) = \begin{cases} \infty, & r < \sigma \\ \varepsilon, & \sigma \leq r < \lambda \sigma \\ 0, & r \geq \lambda \sigma \end{cases},$$ \hspace{1cm} (5)

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

In the $q$ space

$$U_{SW} = \frac{2}{3} \pi \rho \sigma^3 \varepsilon (\lambda^3 - 1) + \frac{1}{4\pi^2} \int_0^\infty [a_{SW}(q) - 1] \phi_{SW}(q) q^2 \, dq,$$ \hspace{1cm} (6)

where

$$\phi_{SW}(q) = \frac{4\pi \varepsilon}{q^3} - 4\pi \varepsilon \left[ \sin(q\lambda\sigma) - \sin(q\sigma) - q\lambda\sigma \cos(q\lambda\sigma) + q\sigma \cos(q\sigma) \right],$$ \hspace{1cm} (7)

$a_{SW}(q)$ is the structure factor of the SW system. Within the random phase approximation (RPA) [2] it is written as

$$a_{SW-RPA}(q) = \frac{1}{1 - \rho c_{HS}(q) + \beta \rho \phi_{SW}(q)},$$ \hspace{1cm} (8)
where $\beta = (k_B T)^{-1}$, $c_{HS}(r)$ is the direct correlation function of the HS fluid related to the HS structure factor as follows:

$$a_{HS}(q) = \frac{1}{1 - \rho c_{HS}(q)}.$$  

(9)

Then

$$\left(\frac{\partial U_{SW-RPA}}{\partial T}\right)_\rho = \frac{\rho k_B}{4\pi^2} \int_0^\infty \frac{\phi_{SW}^2(q)q^2 dq}{k_B(T(1 - \rho c_{HS}(q)) + \rho \phi_{SW}(q))^2},$$  

(10)

$$S_{SW-RPA} = S_{HS} + \int \frac{dT}{T} \left(\frac{\partial U_{SW-RPA}}{\partial T}\right)_\rho = S_{HS} + \frac{k_B \rho}{4\pi^2} x$$

$$\int_0^\infty \left[ -\frac{1}{\rho^2 \phi_{SW}^2(q)} \ln \frac{k_B}{a_{SW-RPA}(q)} + (1 - \rho c_{HS}(q)) a_{SW-RPA}(q) + \text{Const} \right] \phi_{SW}^2(q)q^2 dq.$$  

(11)

The integration constant is being obtained from the condition that $S_{SW} = S_{HS}$ at $a_{SW-RPA}(q) = a_{HS}(q)$:

$$\text{Const} = \frac{1}{\rho^2 \phi_{SW}^2(q)} \left( \ln \frac{k_B}{a_{HS}(q)} + 1 \right).$$  

(12)

Eq. (11) can be simplified and the final expression is

$$S_{SW-RPA} = S_{HS} + \frac{k_B}{4\pi^2} \int_0^\infty q^2 \left( \beta a_{SW-RPA}(q) \phi_{SW}(q) + \frac{1}{\rho} \ln \frac{a_{SW-RPA}(q)}{a_{HS}(q)} \right) dq.$$  

(13)

Eq.(12) can be regarded the analytical expression if to use the analytical form for $c_{HS}(q)$ obtained in [3, 4].

References


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