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

I. The General Consideration

Anatoliy Yuryev[1,2]

[1)] Ural Federal University, Mira st. 19, 620002 Ekaterinburg, Russia
[2)] Institute of Metallurgy of the Ural Branch of the Russian Academy of Sciences,
Amundsen st. 101, 620016 Ekaterinburg, Russia
yurev_anatolii@mail.ru

Vladimir Filippov[1,2]

[1)] Ural Federal University, Mira st. 19, 620002 Ekaterinburg, Russia
[2)] Institute of Metallurgy of the Ural Branch of the Russian Academy of Sciences,
Amundsen st. 101, 620016 Ekaterinburg, Russia
vvfilippov@mail.ru

Nikolay Dubinin[1,2]

[1)] Ural Federal University, Mira st. 19, 620002 Ekaterinburg, Russia
[2)] Institute of Metallurgy of the Ural Branch of the Russian Academy of Sciences,
Amundsen st. 101, 620016 Ekaterinburg, Russia
ned67@mail.ru

Abstract

The more simple technique is used to obtain the analytical expression of the entropy for the hard-core fluid in a general case.

Keywords: Entropy, hard-core fluid

In the previous articles [1, 2] was shown how the entropy, *S*, of an equilibrium square-well (SW) system can be found by integrating the following thermodynamic relation (hereafter, all thermodynamic quantities are taken per atom):

$$\left(\frac{\partial S}{\partial T}\right)_\rho = \frac{1}{T}\left(\frac{\partial (K+U)}{\partial T}\right)_\rho \quad , \tag{1}$$

where T is the absolute temperature, $K = \frac{3}{2}k_B T$ - kinetic energy, U - potential energy, ρ - mean atomic density, k_B - Boltzmann constant.

Here, we show a more simple way to obtain the entropy of an arbitrary system in a general case at three conditions:

1. The pair-interaction approximation for the potential energy:

$$U = 2\pi\rho\int_0^\infty \varphi(r)g(r)r^2 \mathrm{d}r \quad , \tag{2}$$

where $\varphi(r)$ is the pair interatomic potential, $g(r)$ - pair correlation function.

2. The hard-core (HC) model for the pair potential:

$$\varphi_{HC}(r) = \begin{cases} \infty, & r < \sigma \\ \phi(r), & r \geq \sigma \end{cases} \quad , \tag{3}$$

If $\phi(r) = 0$, we have the hard-sphere (HS) fluid.

3. The following expression for the Fourier transform of the direct correlation function in the HC model, $c_{HC}(r)$:

$$c_{HC}(q) = c_{IHC}(q) - \beta\phi(q), \tag{4}$$

where $c_{IHC}(q)$ is the Fourier transform of the inside-hard-core (IHC) part of the $c_{HC}(r)$.

Eq. (4) is true for example in the framework of the mean spherical approximation (MSA) [3] or the random phase approximation (RPA) [4].

From Eq. (4), the structure factor, $a_{HC}(q)$, is

$$a_{HC}(q) = \frac{1}{1 - \rho c_{IHC}(q) + \beta\rho\phi(q)} \quad , \tag{5}$$

where $\beta = (k_B T)^{-1}$.

The difference between entropy of the HS fluid, S_{HS}, and the entropy of the HC fluid, S_{HC}, can be found from eq.(1):

$$S_{HC} = S_{HS} + \frac{1}{4\pi^2}\int_0^\infty dq q^2 \phi(q) \int \frac{\mathrm{d}T}{T}\left(\frac{\partial a_{HC}(q)}{\partial T}\right)_\rho = S_{HS} + \Delta S_{HC} \tag{7}$$

For cases of RPA [1] and MSA [2] Eq. (7) was being calculated by the straightforward way.

The more simple way to calculate ΔS_{HC} is to perform integrating by parts and to change the variable T on β:

$$\Delta S_{\mathrm{HC}} = \frac{k_{\mathrm{B}}}{4\pi^2}\int_0^\infty dq q^2 \phi(q) \int d\beta\beta \frac{\partial a_{\mathrm{HC}}(q)}{\partial \beta} = \frac{k_{\mathrm{B}}}{4\pi^2}\int_0^\infty dq q^2 \phi(q) \left[\beta a_{\mathrm{HC}}(q) + \frac{\ln a_{\mathrm{HC}}(q)}{\rho\phi(q)} + \mathrm{C} \right] \tag{8}$$

The integration constant is being obtained from the condition that $S_{\mathrm{HC}} = S_{\mathrm{HS}}$ at $a_{\mathrm{HC}}(q) = a_{\mathrm{HS}}(q)$:

$$\mathrm{C} = -\frac{1}{\rho\phi(q)} \ln a_{\mathrm{HS}}(q) \quad . \tag{9}$$

Eq. (8) can be simplified and the final expression is

$$S_{\mathrm{HC}} = S_{\mathrm{HS}} + \frac{k_{\mathrm{B}}}{4\pi^2}\int_0^\infty dq q^2 \left(\beta a_{\mathrm{HC}}(q)\phi(q) + \frac{1}{\rho} \ln \frac{a_{\mathrm{HC}}(q)}{a_{\mathrm{HS}}(q)} \right) \tag{10}$$

Eq.(10) can be used if the expression for $a_{\mathrm{HC}}(q)$ is known. In the future, the method introduced here will be extended to binary mixtures.

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