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NOTE

Thermodynamic Interpretation of the Fragmentation Phenomenon in Nanopores

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Based on the new van der Waals equation of state for confined fluids in nanopores, an interesting thermodynamic interpretation has been made for the fragmentation phenomenon of the confined fluids in the nanopores such as carbon nanotubes. The new concept of anisotropic fugacity has been introduced in this work.

Key Words: **Thermodynamic, Fragmentation, Nanopores.**

In recent years, the concepts of nanothermodynamics have been examined in the study of small systems[1–4]. For the study of small systems, one has to improve the basic equations of the conventional (macro) thermodynamics. Although the fundamental concepts of nanothermodynamics have been introduced by Hill[5,6] in the early 1960s, yet there are serious challenges in defining the environmental variables in nanosystems such as temperature and pressure. Parallel to nanothermodynamics many efforts have been made by using the concepts of nonextensive statistical mechanics and thermodynamics. Following the pioneering work of Tsallis[7,8] it has been shown that there is a close relation between nanothermodynamics and non-extensive thermodynamics *via* the fundamental parameters in two disciplines[9] and simulation data could determine the basic entropic parameter of non-extensive small systems by using the method of molecular dynamics[10]. Recently, it has been shown that thermodynamic equations for a confined fluid at nanometric scale may be different from their counterparts in macrothermodynamics[11]. On the other hand, critical shift of a confined fluid in a nanopore has been seen regarding to the critical properties of a fluid in a nanopore[12]. For the study of pressure-volume-temperature (P-V-T) behaviour of the confined fluids in a small pore (nanopore), Zarragoicoechea and Kuz[13] have improved the van der Waals equation of state considering the tensorial nature of the pressure in the nanopores. In this work by using the modified form of van der Waals equation of state some thermodynamic properties have been obtained to interpret the complex phenomenon of phase change or fragmentation of the confined fluids in the nanopores.

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Theory and Discussion

Following the pioneering work of Landau and Lifshitz[14] on the assumption of pressure as a diagonal tensor, Zarragoicoechea and Kuz[13] proposed the following equations of state for a confined fluid in a long nanotube with the nanosized diameter:

$$p_{xx} = p_{yy} = \frac{NkT}{V - Nb} - \frac{N^2}{V^2}\left[a - \varepsilon\sigma^3\left(3\frac{c_1}{\sqrt{A}} + 4\frac{c_2}{A}\right)\right] \quad (1)$$

$$p_{zz} = \frac{NkT}{V - Nb} - \frac{N^2}{V^2}\left[a - 2\varepsilon\sigma^3\left(\frac{c_1}{\sqrt{A}} + \frac{c_2}{A}\right)\right] \quad (2)$$

$$c_1 = 4.6571 \quad (3)$$

$$c_2 = -2.1185 \quad (4)$$

where a and b are the van der Waals equation of state bulk parameters, ε and σ are energy and size parameters of the Lennard-Jones potential parameters and A the cross-sectional area of the nanopore. These equations recover the conventional van der Waals equation of state (in bulk) when the cross-sectional area goes to infinity[13] and we have

$$p_{xx} = p_{yy} = p_{zz} \quad (5)$$

By using equations (1) and (2) we can use the equilibrium criterion through the calculation of fugacity of the confined fluid in different directions. We may use the general definition of the fugacity which may be read as[15]

$$f = p \exp\left(\int_0^p (Z - 1)\frac{dp}{p}\right) \quad (6)$$

Considering the various components of the pressure tensor in different directions, we can write the following direction dependent equations for fugacity:

$$f_{xx} = f_{yy} = p_{xx} \exp\left(\int_0^{p_{xx}} (Z_{xx} - 1)\frac{dp_{xx}}{p_{xx}}\right) = p_{yy} \exp\left(\int_0^{p_{yy}} (Z_{yy} - 1)\frac{dp_{yy}}{p_{yy}}\right) \quad (7)$$

and

$$f_{zz} = p_{zz} \exp\left(\int_0^{p_{zz}} (Z_{zz} - 1)\frac{dp_{zz}}{p_{zz}}\right) \quad (8)$$

where Z_{xx}, Z_{yy} and Z_{zz} could be obtained by multiplication of V/RT group to both sides of eqns. (1) and (2). After obtaining the relevant equations for the compressibility factors we can use eqns. (7) and (8) to derive the fugacity of a confined fluid in a nanopore for each direction. The results may be written as follows:

$$\ln f_{xx} = \ln\frac{V - Nb}{V} - \frac{N}{kTV}\left[a - \varepsilon\sigma^3\left(3\frac{c_1}{\sqrt{A}} + 4\frac{c_2}{A}\right)\right] + Z_{xx} - 1 + \ln\frac{NkT}{V} \quad (9)$$

$$\ln f_{yy} = \ln\frac{V - Nb}{V} - \frac{N}{kTV}\left[a - \varepsilon\sigma^3\left(3\frac{c_1}{\sqrt{A}} + 4\frac{c_2}{A}\right)\right] + Z_{yy} - 1 + \ln\frac{NkT}{V} \quad (10)$$

and

$$\ln f_{zz} = \ln \frac{V - Nb}{V} - \frac{N}{kTV}\left[a - 2\varepsilon\sigma^3\left(\frac{c_1}{\sqrt{A}} + \frac{c_2}{A}\right)\right] + Z_{zz} - 1 + \ln \frac{NkT}{V} \tag{11}$$

In the above equations Z_{xx}, Z_{yy} and Z_{zz} may be written as

$$Z_{xx} = Z_{yy} = \frac{V}{V - Nb} - \frac{N}{VkT}\left[a - \varepsilon\sigma^3\left(3\frac{c_1}{\sqrt{A}} + 4\frac{c_2}{A}\right)\right] \tag{12}$$

$$Z_{zz} = \frac{V}{V - Nb} - \frac{N}{VkT}\left[a - 2\varepsilon\sigma^3\left(\frac{c_1}{\sqrt{A}} + \frac{c_2}{A}\right)\right] \tag{13}$$

As can be seen from eqns. (9)–(11), the fugacity of a confined fluid in a nanopore is an anisotropy property dependent on the geometrical direction. On the other hand, this property is applied as a criterion for fluid phase equilibria. Therefore, we can conclude that there are different phases in the x-y direction from the z-direction in a long nanosized tube such as a carbon nanotube. This fact has been confirmed in the experimental observations of the fragmentation phenomenon of the confined water in long nanotubes.

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