Density functional study of separation for hydrogen-carbon monoxide mixture

in carbon nanotube

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In this work, we report an investigation by means of density functional theory (DFT) of the separation of hydrogen-carbon monoxide mixture in an isolated single-walled carbon nanotube. In density functional theory, the equilibrium behavior of a system can be represented by a system grand potential, which is expressed as

$$\Omega = F + \sum_{i=1}^{K} \int dr \rho_i(r)(\psi(r) - \mu_i) \qquad (1)$$

where $\rho_i(r)$ and μ_i are the number density and chemical potential of bulk species i, respectively. Ω and F are the grand potential functional and the intrinsic Helmholtz free energy functional. $\psi(r)$ represents the external potential.

The Helmholtz free energy described in our model can be split into two parts, $F = F_{id} + F_{ex}$. F_{id} is the ideal gas contribution, and the excess Helmholtz free energy, F_{ex}, is constructed by a hard-sphere part and a soft attraction part, therefore,

$$\beta F_{ex} = \int \phi(r) dr + \beta F_{att} \qquad (2)$$

where, the reduced excess Helmholtz density ϕ is represented by a modified fundamental measure theory (MFMT)[1]. In MFMT, the excess free energy density was based on BMCSL equation of state[2], which was proved to give a better prediction of the contact value than PY equation[3] for nonuniform hard fluids.

Consequently, the reformulated excess free energy density consists of a scalar and a vector contributions:

$$\phi = \phi^S + \phi^V \qquad (3)$$

where,

$$\phi^S = -n_0 \ln(1 - n_3) + \frac{n_1 n_2}{1 - n_3} +$$

$$\left[\frac{1}{36\pi n_3^2} \ln(1 - n_3) + \frac{1}{36\pi n_3 (1 - n_3)^2} \right] n_2^3 \qquad (4)$$

$$\phi^V = -\frac{n_{V_1} n_{V_2}}{1 - n_3} - \left[\frac{1}{12\pi n_3^2} \ln(1 - n_3) \right.$$

$$\left. + \frac{1}{12\pi n_3 (1 - n_3)^2} \right] n_2 n_{V_1} n_{V_2} \qquad (5)$$

where n_0, n_1, n_2, n_3 and n_{V_1}, n_{V_2} denote six weight factor.

In equation (2), the soft attraction part, βF_{att}, can be evaluated by WCA[4] perturbation theory. In equilibrium condition, the equilibrium density distribution of binary gases in carbon nanotube satisfies the stationary condition:

$$\frac{\delta \Omega}{\delta \rho_i(r)} = 0 \qquad (6)$$

where $\rho_i(r)$ is the equilibrium density.

Minimization of the grand potential with respect to the density profiles yields the following Euler-Langrange equation:

$$\rho(r) = \exp \left\{ -\int dr' \left[\sum \frac{\partial \phi}{\partial n_\alpha} W^{(\alpha)}(r - r') \right. \right.$$

$$\left. \left. + \rho(r') \phi_{att}(|r - r'|) \right] + \beta [\mu - \psi(r)] \right\} \qquad (7)$$

Picard-type iteration is used to solve eq. (7) with an initial value of bulk density. In order to test the validity, our GCMC simulation[5] has been also performed to calculate the density distributions of hydrogen-carbon monoxide mixture confined inside an isolated single-walled carbon nanotube.

Fig 1 show the comparison of density profiles of hydrogen and carbon monoxide in a (30,30) tube calculated by DFT and GCMC in this work. The results show that good agreements are obtained between two methods.
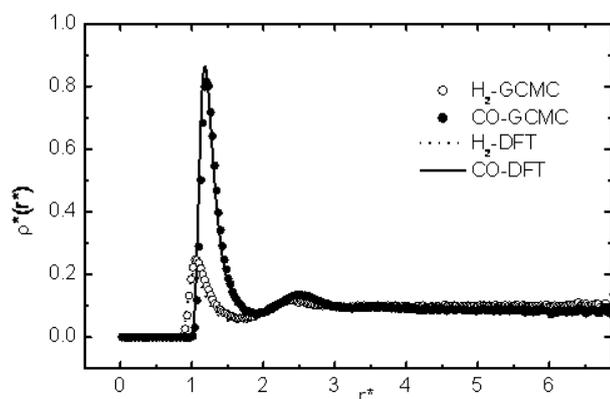

Fig.1. Density profiles for hydrogen-carbon monoxide mixture absorbed in (30,30) armchair tube at 300K with a reduced bulk density of 0.5.

The excess adsorption of each components of H_2-CO mixture in tube with various sizes are plotted in Fig.2. The excess adsorption Γ_{ex} is calculated by

$$\Gamma_{ex} = \frac{2\int_0^R \left(\rho(r) - \rho_{bulk}\right) r dr}{R^2} \qquad (8)$$

Where ρ_{bulk} is the bulk density and R is the radius of the tube.

Fig.2. demonstrates that the competitive absorption of hydrogen and carbon monoxide is affected by both the energy and the size factors. The energy factor can be qualitatively explained by the difference of the interaction potential between the two kinds of particles and the wall of tube. In high-pressure situation, the size factor becomes dominant, which makes the smaller hydrogen molecule more likely to penetrate into the pore than the bigger carbon monoxide molecule. Therefore, with a certain tube size, the selectivity of carbon monoxide decreases with the increase of pressure.
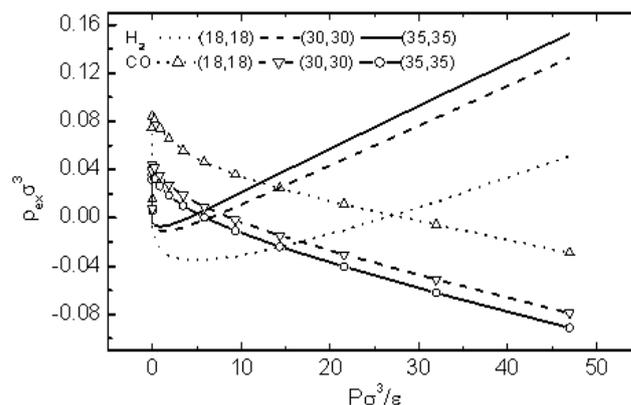

Fig.2. Prediction from DFT for excess adsorption of H_2-CO mixture: line plus symbols denotes the adsorption of CO, while lines are those of H_2. Solid lines are for (35, 35) tube, dashed lines are for (30, 30) tube and dotted lines are for (18, 18) tube.

References

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