CRITICAL TEMPERATURE ESTIMATION OF NANOCONFINED METHANE USING VAPOUR-LIQUID SURFACE FREE ENERGY

Sudhir K Singh[1]

Abstract- Critical temperatures of nanoconfined methane is investigated using vapour–liquid surface free energy of coexistence obtained from grand-canonical transition-matrix Monte Carlo simulations using a histogram reweighting method. For a system under investigation the temperature equivalent to zero surface free energy of coexistence is the estimated critical temperature. In this investigation, methane is subjected under nanopores of varying slit width from 40 Å to 5 Å. The estimated critical temperatures have revealed nonlinear monotonic trend with inverse of nanopore width. However, in quasi-2D region of nanopore width it remained indifferent. In this work, Buckingham exponential-6 potential model is used for the interaction between methane molecules and Steele potential model is used for the interaction between confining surface and methane molecules. This investigation also reveals that the critical temperature of nanoconfined methane estimated using the vapour-liquid surface free energy of coexistence is in good agreement with that obtained using the simplified form of scaling law.
Keywords – Critical temperature, Nanoconfined methane, Coexistence, Monte Carlo

1. INTRODUCTION

The critical properties and phase equlibria has been the subject of extensive study for more than a century because of its importance in many industrial applications [1]. It has been known for a long time that the confinement introduces significant effects to many physical properties of fluids including the phase equilibria. Therefore, detailed understanding of the phase coexistence and critical properties of confined fluids is of crucial importance for the interpretation of experimental data on fluids in nanopores [2-4]. A comprehensive review on confined fluids is found in Gelb et al. [5].The fundamental scientific interest on confined fluids is to understand the new physics that results from finite size effects, varying dimensionality, and surface forces. When the pore width is of the order of the range of the intermolecular forces, a large fraction of the confined molecules will experience a reduction in the number of nearest-neighbour molecules, and we might expect this to lead to large shifts in phase coexistence curves and a lowering of any critical points. Due to difficulties in conducting experimental studies on the characterization of atomistic behaviours, molecular simulation is used to bridge the theories and the experimental outcomes. The rapid increases of computing power and new efficient algorithms have further enhanced the use of computational methods, and have made very complex problems solvable. To our best knowledge, there is only few literature report [6] with a simple square-well model, on the estimation of critical temperature using surface free energy of finite−size system and its comparison with the critical temperature obtained using simplified form of scaling law [7]. In this work, for a given slit width, the free energy barrier between vapour and liquid phases at coexistence is estimated for a given system size at various temperatures in an appropriate range using a molecular simulation technique. The surface free energy data obtained is fitted with the second degree polynomial to estimate the temperature corresponding to zero surface free energy. The temperature corresponding to the zero surface free energy represents the estimated critical temperature. In this work, we have also compared the critical temperature estimation of bulk and confined methane from two methods viz., simplified form of scaling law of density and the critical temperature estimated by the fitting of vapour−liquid surface free energy of finite−size system.

The rest of the paper is organized as follows. A short description of methodology and potential models are explained in section II. Simulation results are presented in section III. Concluding remarks are given in section IV.

2. METHODOLOGY AND POTENTIAL MODELS

2.1 Simulation Methodology

In this work, we have used grand−canonical transition−matrix Monte Carlo (GC-TMMC) simulation technique [8]. Simulations are conducted in the grand− canonical (GC) ensemble, where the chemical potential $\square$,the volume V and the temperature T are kept constant, and the number of particles N and the energy U fluctuate. GC-TMMC simulations are conducted with 30% particle displacement and 70% particle insertion/deletion moves. The macroscopic probability is calculated by summing all the microstate states at a constant number of particles. In this scheme, for each Monte Carlo move we record the acceptance probability in a matrix, regardless of whether the move is being accepted or not. Detailed methodology is described elsewhere [8]. Histogram−reweighting method [9] is utilized to obtain the coexistence chemical

---

[1] Department of Chemical Engineering, Thapar Institute of Engineering & Technology, Patiala, Punjab, India

potential. At a given coexistence chemical potential, we would observe two peaks in the macrostate probability distribution. The minimum and maximum particles numbers are set to ensure the complete sampling of both the liquid and vapour phases. The minimum particle number is set to zero and the maximum particle number is set such that the probability of observing maximum particle number at coexistence is less than a specified tolerance [10]. In the current work simulations are performed with Buckingham exp-6 model with cut-off radius, rc= 15 Å. The selection of rc= 15 Å is in accordance with the earlier investigations of phase equilibrium and interfacial properties of n-alkanes [10].

GC-TMMC simulation can also yield the surface free energy, $\Box$FL, for a finite system size with a box length L, which is determined from the   maximum probabilities in the liquid $\prod_{max}^{l}$ and vapour regions $\prod_{max}^{v}$, and   the minimum probability $\prod_{min}$ in the interface region:

$$\beta F_L = \frac{1}{2}\left(\ln\prod_{max}^{l} + \ln\prod_{max}^{v}\right) - \ln\prod_{min}$$

(1)

where, $\Box\Box$denotes the inverse temperature ($\Box$ $\Box$= 1/kT, where k is Boltzmann's factor).

In this work, the surface free energy between vapour and liquid phases, FL (FL=$\Box$ $\Box$ FL)is estimated for a given system size at various temperatures in an appropriate temperature range using GC-TMMC simulation and histogram reweighting method. The free energy data, FL, obtained with finite−size system is fitted with the second degree polynomial (T = A + BFL + CFL2, where, T and FL is temperature and non-dimensional surface free energy respectively, and A, B and C are fitting parameters) to estimate the temperature corresponding to zero FL. The temperature corresponding to zero FL is the estimated critical temperature, Tc, which is in this case, is same as the value of the fitting parameter A.

2.2 Potential Model

A united-atom approach [11] is used to model the methane molecules. Non-bonded site−site interactions are described with the modified Buckingham exponential-6 intermolecular potential of Errington and Panagiotopoulos [12], for which the pair interaction energy, U is represented as

$$U(r) = \begin{cases} \dfrac{\varepsilon}{1-\dfrac{6}{\alpha}}\left[\dfrac{6}{\alpha}\exp\left(\alpha\left[1-\dfrac{r}{r_m}\right]\right) - \left(\dfrac{r_m}{r}\right)^6\right] & \text{for} \quad r > r_{max} \\ = \infty & \text{for} \quad r < r_{max} \end{cases}$$

(2)

where $\Box$ $\Box$,r_m and α are adjustable parameters. The variable r_m is the radial distance at which $U(r)$ reaches a minimum and the cutoff distance r_{max} represent the smallest radial distance for which d[U(r)]/d(r) = 0.The radial distance for which $U(r) = 0$ is denoted by σ. The parameters ε, σ and α are 160.3 K, 3.73 Å and 15, respectively, for methane. In this work, nanopore is of slit geometry with smooth and structureless surfaces. Wall-fluid interaction is described by the 9−3 Steele potential: [13]

$$\phi_{wf}(z) = \frac{2}{3}\pi\rho_w\varepsilon_{wf}\sigma_{wf}^3\left\{\frac{2}{15}\left(\frac{\sigma_{wf}}{z}\right)^9 - \left(\frac{\sigma_{wf}}{z}\right)^3\right\}$$

(3)

where z is the distance of the fluid (methane) molecule from the wall and ρ_w, ε_{wf} and σ_{wf} are the parameters of the Steele potential, which are 0.033Å-3, 84 K, 3.92Å respectively [14], for the current study.

3. RESULTS AND DISCUSSION

In the current work, we have used non-dimensional vapour−liquid surface free energy, FL, of finite−size systems to estimate the critical temperature of nanoconfined methane in the slit pore width of 40Å to 5Å. Figure 1 presents vapour−liquid surface free energy, FL, of confined methane and second degree polynomial fitting of FL for methane confined in graphite nanopore of slit width, H = 40Å, 15 Å, 10Å and 9Å respectively. For these investigations the considered system volume and second degree polynomial fitting parameters are reported in Table 1. In the simulation, for H = 40Å, temperature is varied from 140 K to 156 K. Estimated critical temperature for H = 40Å is around 178.61 K which is very close to the bulk methane value of 178.87K. This reveals that in extremely large pores the effect of confinement is insignificant on the critical temperature. For H = 15 Å, simulation temperature is varied from 120 K to 145 K and the estimated critical temperature is around 149.62 K. For H = 10 Å, simulation temperature is varied from 106 K to 116 K and the estimated critical temperature is around 122.01 K. For H = 9 Å, simulation temperature is varied from 76 K to 90 K to estimate the corresponding FL and the estimated critical temperature is around 92.13 K. For methane confined in graphite slit pore of H = 8Å, 6 Å, and 5.0 Å the second degree polynomial fitting of FL is not shown here, which is similar to the fittings shown in the Figure. Moreover, for these investigations the considered system volume and second degree polynomial fitting parameters are reported in Table 1. In the

simulation of H = 8Å, temperature is varied from 68 K to 80 K to estimate the corresponding FL. Estimated critical temperature for H = 8Å is around 81.72 K. For H = 6 Å, and 5 Å, temperatures are varied from 68 K to 76 K and the corresponding estimated critical temperatures are around 78.8 K and 78.6 K respectively. This indicates that in quasi-2D region of pore width, (H = 6 Å–5 Å), critical temperature remains indifferent with change in H. Further, in this investigation we have compared the critical temperature, Tc of bulk and nanoconfined methane estimated using simplified form of scaling law [10] and using vapour–liquid surface free energy of finite-size systems of current work. The comparison of Tc is given in the Table 2 and also shown in the Figure 2 for better visualization of the data. In the Figure 2, Tc of bulk methane is also included, which is the case corresponding to 1/H = 0. The Tc estimated for bulk methane using using FL is around 5% lower than the Tc estimated using simplified form of scaling law.
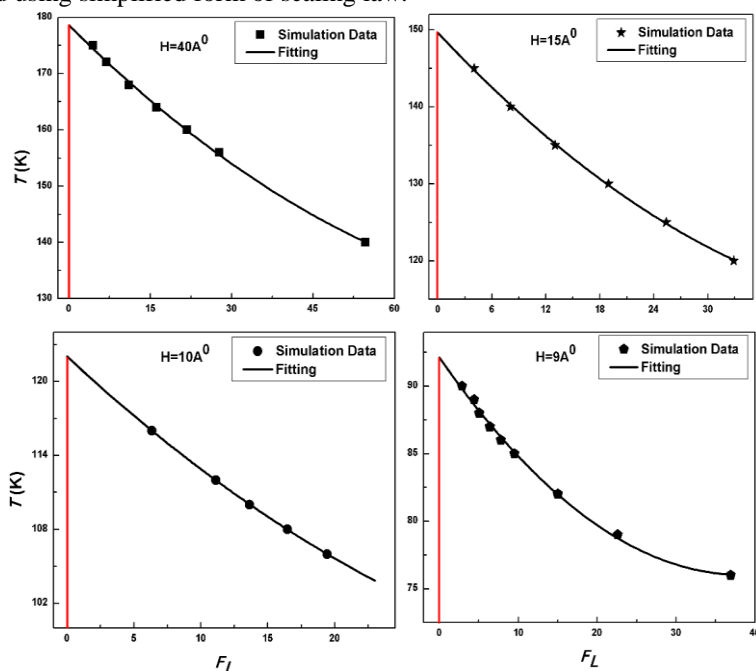
Temperature, T, vs. non-dimensional vapour-liquid surface free energy, FL is plotted and fitted with second degree polynomial for methane confined in graphite nanopore with slit width, H (Å) = 40, 15, 10 and 9. Fitting parameters are reported in Table 1. Vertical line represent zero FL.

On the other hand, Tc estimated for confined methane using FL is around 3% higher (maximum) than the Tc estimated using simplified form of scaling law [10]. Figure 2 presents the dependence of Tc of methane in graphite nanopore with inverse of slit pore width, H. This reveals that the Tc estimation using scaling law of density and the surface free energy of finite-size systems in current work are in reasonably good agreement. Moreover, critical temperature monotonically decreases with decrease of nanopore width as depicted from both the estimates. However, in the quasi-2D region of nanporepore width, where maximum possible layer in local structural behaviour is limited to one, the critical temperature becomes approximately indifferent with the change in H.
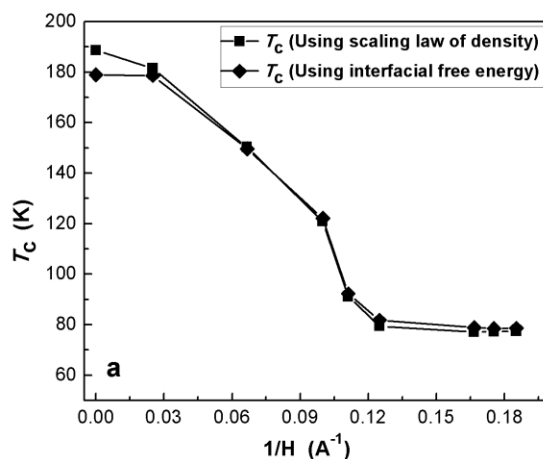
Dependence of critical temperature, Tc on the inverse slit width (1/H) is shown and compared with that obtained using simplified form of scaling law [10]. Symbols represent the estimated Tc data and lines serve as a guide to the eye. Uncertainity in each data is smaller than the symbol size.

Table -1 Simulation Result

Polynomial fitting of surface free energy, FL :				
T = A + BFL + CFL2 ; FL = 0 at T = Tc				
	V (Å3)	A=Tc	B	C
Bulk	36750	178.86532±0.9117	-0.59633±0.03253	0.00134±1.99E-04
Graphite pore, H (Å)				
40	36000	178.60521±0.51725	-0.96066±0.04718	0.00468±7.67E-04
15	37500	149.61601±0.3976	-1.24386±0.05184	0.01055±0.00138
10	36000	122.00756±0.08497	-1.00594±0.01418	0.00939±5.46E-04
9	44100	92.12544±0.22623	-0.83992±0.03418	0.01097±8.56E-04
8	51200	81.72373±0.18043	-0.9882±0.04194	0.01416±1.93E-03
6	48600	78.79909±0.21103	-0.8289±0.04724	0.01119±2.26E-03
5.0	50000	78.57246±0.06605	-0.79272±0.01471	-0.79272±0.01471

Table 1 show the critical temperature, Tc of bulk and nanoconfined methane in graphite slit pore of various slit width, H. The system volume, V, considered in each simulation and the corresponding second-degree polynomial fitting parameters A, B and C are also included.

Table -2 Simulation Result

	1/H (Å-1)	Tc (K), estimated using scaling law of density	Tc (K), estimated using FL
Bulk	0	188.582	178.86532
Graphite pore, H (Å)			
40	0.025	181.424	178.60521
15	0.066667	150.152	149.61601
10	0.1	120.87207	122.00756
9	0.111111	91.01624	92.12544
8	0.125	79.4081	81.72373
6	0.166667	77.0453	78.79909
5.0	0.2	77.122	78.57246

Table 2 shows a comparison of the estimated critical temperature, Tc of bulk and nanoconfined methane (methane confined in graphite slitpore) using two different methods.

4. CONCLUSION

We investigated, in this work, the critical temperature of nanoconfined methane using vapour−liquid interfacial free energy values of phase coexistence obtained from the GC-TMMC simulation and histogram reweighting technique. For a system under investigation, the free energy data are estimated for a given system volume and various temperatures in an appropriate range. The coexistence surface free energy values are fitted with the second-degree polynomial to estimate the temperature corresponding to zero surface free energy. In this investigation, nanopore width of confined methane is varied from 5Å to 40Å.The estimated critical temperature under nanoconfinement is found to decrease monotonically with decreasing slit width. Importantly, for extremely small pore widths, i.e., in quasi-2D region the critical temperature remains approximately indifferent with change in H. In this work, we have compared the critical temperature estimation of confined methane using two different approaches, i.e., scaling law of density and using vapour-liquid surface free energy of finite-size systems. The observed trend of critical temperature variation with inverse of nanopore width is approximately same from both estimations. Moreover, for nanoconfined methane, the critical temperature estimated using the vapour−liquid surface free energy value is differ by less than 3% than that estimated using the simplified form of scaling law. This in turn indicates that critical temperature estimated using vapour−liquid surface free energy values at coexistence is in reasonably good agreement with that obtained using simplified form of scaling law.

5. REFERENCES

[1] Vrabec J, Kedia GK, Fuchs G, Hasse H., "Comprehensive study of the vapour–liquid coexistence of the truncated and shifted Lennard–Jones fluid including planar and spherical interface properties", Mol Phys., vol. 104, pp 1509-1527, 2006.
[2] Gupta SA, Cochran HD, Cummings PT. "Shear behavior of squalane and tetracosane under extreme confinement. II. Confined film structure", J Chem Phys., vol.107, pp 10327-10334, 1997.

[3]   Bhatia S., "Adsorption of Binary Hydrocarbon Mixtures in Carbon Slit Pores: A Density Functional Theory Study", Langmuir., vol 14, pp 6231-6240, 1998.

[4]   Altwasser S., Welker C., Traa Y., Weitkamp J., "Catalytic cracking of n-octane on small-pore zeolites. Microporous Mesoporous Mater." vol. 83, pp 345-356, 2005.

[5]   Gelb LD, Gubbins KE, Radhakrishnan R, Sliwinska-Bartkowiak M., "Phase separation in confined systems. Rep Prog Phys.", vol.62, pp 1573-1659, 1999.

[6]   Singh SK., "Critical temperature estimation of bulk and confined atomic fluid using vapour−liquid interfacial free energy", Molecular Simulation, vol. 44, pp 156-163, 2018.

[7]   Singh SK, Saha AK, Singh JK. "Molecular Simulation Study of Vapor-Liquid Critical Properties of a Simple Fluid in Attractive Slit Pores: Crossover from 3D to 2D", J Phys Chem B., vol. 114, pp 4283-4292, 2010.

[8]   Errington JR., "Direct calculation of liquid–vapor phase equilibria from transition matrix Monte Carlo simulation", J Chem Phys., vol. 118, pp 9915-9925, 2003.

[9]   Ferrenberg AM, Swendsen RH, "New Monte Carlo technique for studying phase transitions", Phys Rev Lett., vol. 61, pp 2635-2638, 1988.

[10]   Singh S.K., Sinha A., Deo G., Singh J. K. Vapor-Liquid Phase Coexistence, Critical Properties, and Surface Tension of Confined Alkanes. J Phys Chem C, vol. 113, pp 7170-7180, 2009.

[11]   Ryckaert JP, Bellemans A., "Molecular dynamics of liquid n-butane near its boiling point", Chemical Physics Letters., vol.30, pp 123-125, 1975.

[12]   Errington JR, Panagiotopoulos AZ., "A New Intermolecular Potential Model for the n-Alkane Homologous Series". J Phys Chem B, vol. 103, pp 6314–6322, 1999.

[13]   Steele WA. "The physical interaction of gases with crystalline solids: I. Gas-solid energies and properties of isolated adsorbed atoms", Surf Sci., vol. 36, pp 317-352, 1973.

[14]   Porcheron F, Rousseau B, Fuchs AH, Schoen M., "Monte Carlo simulations of nanoconfined n-decane films", Phys Chem Chem Phys., vol. 1, pp. 4083-4090, 1999.