Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

To explore the impacts of the atomistic structure of methane model and the corrugation of graphite model on adsorption over the temperature range studied, we calculated the theoretical Henry constants for the one-site and five-site molecular model of methane at a homogeneous and an energetically corrugated surface, for a much wider range of temperatures. The Henry constant between a methane molecule and the graphite surface can be calculated by integrating the Boltzmann factor over the accessible volume and over all possible orientations of the molecule (only for five-site model)[1]:

$$K_\alpha = \iint_\Omega \exp\left[-\beta\varphi(r,\omega)\right] dr d\omega - \iint_\Omega H\left[-\beta\varphi(r,\omega)\right] dr d\omega \qquad (1)$$

Where Ω is the domain accessible to an adsorbate molecule, $\beta = 1/k_B T$, φ is the potential energy of interaction between a methane molecule at position r and orientation ω with the graphite surface, and H is a Heaviside function. K_α has the unit of a volume (nm^3). The results of Henry constant are shown in *Fig.* S1.

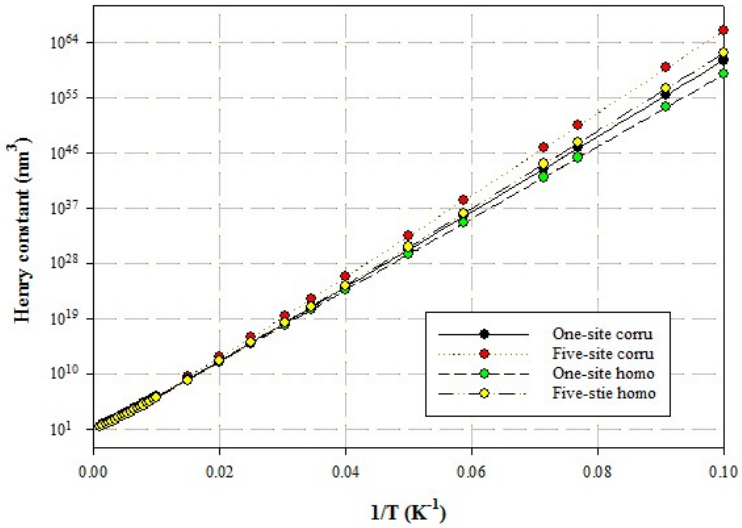

Fig. S1. The theoretical Henry constants of one-site and five-site methane models at homogeneous and corrugated surfaces at temperatures from 10K to 1000K.

Fig. S1, shows that the Henry constants of one-site and five-site methane models are virtually the same at temperatures greater than 50K, indicating that, the atomistic structure of methane and the corrugation of graphite are insignificant for adsorption in the temperature range studied in this paper.

The molecular parameters for methane models are listed in Table S1. The corrugation in the graphite was calculated as a Fourier series in the *x* and *y* directions (see Steele, 1974[2]).

Table S1. Molecular Parameters for Methane

Model	**Site**	***x* (nm)**	***y* (nm)**	***z* (nm)**	***σ* (nm)**	***ε* (K)**	***q/e***
One-site[3]					0.373	148	0
Five-site[4]	C	0	0	0	0.34	55.055	-0.66
	H1	0	0.1028	-0.0363	0.265	7.901	0.165
	H2	-0.089	-0.0514	-0.0363	0.265	7.901	0.165
	H3	0.089	-0.0514	-0.0363	0.265	7.901	0.165
	H4	0	0	0.109	0.265	7.901	0.165

Reference

1. D. Do, D. Nicholson and H. Do, *J. Colloid Interface Sci.*, 2008, **324**, 15-24.
2. W. A. Steele, *The Interaction of Gases with Solid Surfaces*, London, Pergamon, 1974; Section 4.9.
3. J. Vrabec, J. Stoll and H. Hasse, *J. Phys. Chem. B*, 2001, **105**, 12126-12133.
4. Y. Sun, D. Spellmeyer, D. A. Pearlman and P. Kollman, *J. Am. Chem. Soc.*, 1992, **114**, 6798-6801.