

Unusual Entropy of Adsorbed Methane on Zeolite-Templated Carbon

Supporting Information

Part 2: Statistical Mechanical Model

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S1. Introduction

We present a simple description of adsorbed methane on a hypothetical carbon surface using basic statistical mechanics, that can also be easily extended to other adsorptive fluids and/or sorbent materials. A standard approach in deriving the thermodynamic properties of a single component polyatomic molecular phase is followed: determine the relevant contributing sources of entropy of the adsorbed phase, derive their canonical partition functions, and subsequently their contributions to entropy, and finally sum over the components to arrive at the total absolute entropy of the adsorbed phase. The goal of this approach is to estimate the entropy of the adsorbed phase for comparison with the equivalent quantity which can be extracted from the measured adsorption data in an experimental system. The approach roughly follows that for the treatment of a (pure) polyatomic molecular gas phase, e.g. as described by McQuarrie¹, with additional considerations to account for its two-dimensional nature, and has been specifically defined for the adsorbed phase in the presence of a unit gram of sorbent material.

We consider an adsorbed phase that is in thermodynamic equilibrium with a gas phase of the same composition: pure methane. The surface of adsorption is considered to be pure carbon, and its properties are unaffected by the presence or lack of the adsorbed phase. The surface is divided into a finite number of methane adsorption sites that is fixed by the total surface area divided by the area of a single methane adsorption site. The most significant components of entropy of the adsorbed phase in this simplified model are: configurational, translational, rotational, surface vibrational, and internal vibrational. There are various ways to account for the fact that configurational, translational, and surface vibrational quantities are inherently related. In this work, we have considered the case of a two-dimensional lattice gas with fixed adsorption site locations, therefore diminishing the contribution from translational entropy (since each adsorbed molecule only explores the small area within a site) which is recovered by accounting for configurational entropy. Each adsorbed molecule is considered to “fill” the area of its site like a spreading liquid, and therefore the vibrations of the molecule parallel to the surface have not been considered. Other models could also have been chosen, e.g. a bulk two-dimensional spreading layer (a liquid), where specific site configurations are not taken into consideration but where translational entropy imparts a significantly larger contribution. Typically, the differences in the final results between these different simple models are small, if appropriate care is taken in deriving the correct partition functions and all sources of entropy are accounted for.

Note: the model described in this work does not account for interactions between adsorbed molecules.

S2. Individual Partition Functions

Configurations and Translations

The configurational component of entropy arises from the existence of a finite number of adsorption sites within a unit quantity of material, N_{total} , and the number of different configurations that are possible for a given quantity of adsorbed methane, N_a , within those sites. The expression for the total system configurational partition function, Z_{config} , is simply the number of unique configurations, Ω , assuming indistinguishability of the adsorbed species and sites:

$$Z_{config} = \Omega = \frac{N_{total}!}{N_a! (N_{total} - N_a)!}$$

The translational motion of an adsorbed molecule on the surface of the sorbent material gives rise to the second component of entropy, translational entropy, for which the single molecule partition function is the two-dimensional analog to that of an ideal gas in three dimensions:

$$z_{trans} = \frac{A_{trans}}{\Lambda^2}$$

$$\Lambda = \frac{h}{\sqrt{2\pi M k_B T}}$$

In this model, the area available to the adsorbed molecule for translation is the area of a single adsorption site:

$$A_{trans} = A_{site} = \frac{A_{total}}{N_{total}}$$

The values for A_{total} and N_{total} in the adsorbate/sorbent system of interest can be determined in numerous ways. Ideally, we should choose values that are obtained independently from the measured methane adsorption data to achieve the most relevant eventual comparison with the experimental data. In this work we use the BET specific surface area of the sorbent, measured by N₂ adsorption at 77 K, as a measure of A_{total} . The minimum cross-sectional area of a single molecule of adsorbed methane can be used to estimate the maximum number of sites; numerous methods (e.g., the TraPPE model²) suggest a value of $A_{site} = \sim 0.139 \text{ nm}^2$. The molecular mass of the adsorbate, M , is known. This gives an expression dependent only on temperature:

$$z_{trans} = \frac{A_{site} 2\pi M k_B T}{h^2}$$

Internal and External Vibrations

The standard partition function¹ corresponding to vibrational motion, z_{vib} , is given by:

$$z_{vib} = \frac{e^{-\frac{\vartheta}{2T}}}{1 - e^{-\frac{\vartheta}{T}}}$$

For simplification, the characteristic vibration is expressed in terms of a vibrational temperature, ϑ (having units of K), which is related to the characteristic vibrational frequency, ν (in units of s⁻¹), by:

$$\vartheta = \frac{h\nu}{k_B}$$

In this way, the partition functions corresponding to each internal molecular vibrational mode of a polyatomic molecule, indexed by i , may be written as:

$$z_{intvib,i} = \frac{e^{-\frac{\vartheta_i}{2T}}}{1 - e^{-\frac{\vartheta_i}{T}}}$$

The internal vibrational modes and their corresponding temperatures are well tabulated for most common adsorptive molecules, including methane. The vibrational temperatures of the nine internal vibrational modes of methane are shown in Table S1. We make the simplifying assumption that an adsorbed molecule has the same internal vibrational properties as the same molecule in the gas phase. The total internal vibrational partition function for a single molecule is the product of each of the individual internal vibrational partition functions:

$$Z_{intvib} = \prod_i \frac{e^{-\frac{\theta_i}{2T}}}{1 - e^{-\frac{\theta_i}{T}}}$$

External vibrations of the adsorbate molecule perpendicular to the surface of the sorbent are also a significant contribution to the total entropy of the adsorbed phase. The form of the external vibrational partition function is the same as that for internal vibrations (above), but the characteristic vibrational temperature of this external mode must be derived. The adsorbed molecule can be simply modeled as a harmonic oscillator in a one-dimensional potential well. The frequency of a harmonic oscillator is given as:

$$\nu_{harmonic} = \frac{1}{2\pi} \sqrt{\frac{K}{M}}$$

The frequency of vibration of a harmonically oscillating adsorbed molecule depends on the force constant of interaction, K , and the molecular mass of the adsorbate, M . To derive the force constant between the molecule and the surface, we must choose a functional form for the potential. Numerous well-known examples of fluid-surface potentials exist: e.g., the Lennard-Jones 9-3 and 10-4 potentials³, and the celebrated Steele 10-4-3 potential⁴. For simplicity, a Lennard-Jones 10-4 potential (corresponding to the interaction between one molecule of methane and a single infinite sheet of graphene) is used in this work since more sophisticated potentials were not found to give significantly different results. This potential is obtained by integrating a standard molecule-molecule Lennard-Jones 12-6 potential over two additional surface dimensions, giving:

$$U = \frac{4\pi}{A_c} \varepsilon \sigma^2 \left(\frac{1}{5} \left(\frac{\sigma}{z} \right)^{10} - \frac{1}{2} \left(\frac{\sigma}{z} \right)^4 \right)$$

Here, A_c is the surface area per carbon atom in a single graphene sheet (2.613 \AA^2), ε is the depth of the graphene-methane potential well, and σ is the equilibrium distance of interaction corresponding to the well minimum. The corresponding 11-5 force is:

$$F = \frac{8\pi}{A_c} \varepsilon \sigma^2 \left(- \left(\frac{\sigma^{10}}{z^{11}} \right) + \left(\frac{\sigma^4}{z^5} \right) \right)$$

The force constant can be approximated by performing a Taylor series expansion of the 11-5 force around σ :

$$F = \frac{8\pi}{A_C} \varepsilon \sigma^2 \left[-\left(\frac{\sigma^{10}}{\sigma^{11}}\right) + \left(\frac{\sigma^4}{\sigma^5}\right) + \left(11\left(\frac{\sigma^{10}}{\sigma^{12}}\right) - 5\left(\frac{\sigma^4}{\sigma^6}\right)\right)(z - \sigma) + \dots \right]$$

$$F \approx \frac{8\pi}{A_C} \varepsilon \sigma^2 \left[\frac{6}{\sigma^2} (z - \sigma) \right]$$

$$K \approx \frac{48\pi \varepsilon}{A_C}$$

The characteristic frequency, and subsequently the vibrational temperature, of external vibrations in the adsorbed phase may then be expressed as:

$$\nu_{ext} = \frac{1}{2\pi} \sqrt{\frac{48\pi \varepsilon}{M A_C}}$$

$$\vartheta_{ext} = \frac{1}{2\pi k_B} \sqrt{\frac{48\pi \varepsilon}{M A_C}}$$

To obtain the effective Lennard-Jones parameters between a methane molecule and a single graphene sheet, Lorentz-Berthelot mixing rules may be applied on the pure component Lennard-Jones parameters⁵; the values used are given in Table S2. The resulting partition function for the surface vibrations of a single adsorbed molecule, Z_{extvib} , is then:

$$Z_{extvib} = \frac{e^{-\frac{\vartheta_{ext}}{2T}}}{1 - e^{-\frac{\vartheta_{ext}}{T}}}$$

Molecular Rotations

Lastly, the contribution to entropy by rotational motions within the adsorbed phase must be considered. The partition function corresponding to a spherical top in the high-temperature approximation, Z_{rot} , is:

$$Z_{rot} = \frac{\sqrt{\pi}}{\varphi} \prod_j \sqrt{\frac{T}{\vartheta_j}}$$

Again, we make the simplifying assumption in the case of rotations that the contribution to total entropy in the adsorbed phase may be taken as the same as that of the gas phase. The index j counts over the three principal moments of inertia: xx , yy , and zz . The high-temperature approximation is valid as long as each $\vartheta_j \ll T$, which is well satisfied within this study. The symmetry number, φ , is the number of ways that the adsorbed molecule can be rotated into a configuration indistinguishable from the original. For methane, the rotational symmetry number is 12. The characteristic rotational temperatures, ϑ_j , are tabulated for most common adsorptive gases. Table S4 lists the characteristic rotational temperatures for each of the principal moments of inertia for methane; they are identical since methane is a spherical top.

Table S1: Internal vibrational temperatures of methane.

Vibrational Mode	$\tilde{\omega}_{\text{vib}}$ (cm ⁻¹)	ϑ_{vib} (K)	Degeneracy
A1 Stretching (symmetric)	2972	4276	1
E Bending (symmetric)	1508	2170	2
F2 Stretching (asymmetric)	3087	4442	3
F2 Bending (asymmetric)	1285	1849	3

Table S2: Lennard-Jones parameters for CH₄—C interaction pairs.

Pair	ϵ (J mol ⁻¹)	ϵ k _B ⁻¹ (K)	σ (Å)
CH ₄ —CH ₄ *	1231	148	3.75
C—C **	233	28	3.4
CH ₄ —C ***	535	64.4	3.58

* calculated by GCMC methods⁵

** from Steele^{3a}

*** employing standard Lorentz-Berthelot mixing rules⁵

Table S3: External vibrational temperature of methane adsorbed on carbon.

Pair	$\tilde{\omega}_{\text{vib}}$ (cm ⁻¹)	ϑ_{ext} (K)
CH ₄ —C	73.5	106

Table S4: Rotational temperatures of methane.

Principal Moment of Inertia	B (cm ⁻¹)	ϑ_{rot} (K)
xx	5.25	7.54
yy	5.25	7.54
zz	5.25	7.54

S3. Total Partition Function

The total system partition function at the fixed quantity of absolute adsorption, N_a , is simply the product:

$$Z_x = z_x^{N_a}$$

Finally, the complete partition function of the adsorbed phase, Z , is simply:

$$Z = Z_{config} Z_{trans} Z_{intvib} Z_{extvib} Z_{rot}$$

We note once again that this is the partition function for the system at absolute adsorbed amount N_a and temperature T , for a unit gram of sorbent material.

S4. Adsorbed Phase Entropy

By definition, the Helmholtz free energy, A , is related to the total partition function as:

$$A = U - TS = -k_B T \ln Z$$

Therefore, the absolute entropy of the adsorbed phase, S , elsewhere denoted S_a , is:

$$S = S_a = -\frac{dA}{dT} = \frac{d}{dT}(k_B T \ln Z)$$

$$S_a = S_{config} + S_{trans} + S_{intvib} + S_{extvib} + S_{rot}$$

The following is a list of the individual entropy contributions from the partition functions derived in Section S2. The configurational entropy (via Stirling's approximation):

$$S_{config} = \frac{d}{dT} \left(k_B T \ln \left(\frac{N_{total}!}{N_a! (N_{total} - N_a)!} \right) \right)$$

$$S_{config} = k_B \ln \left(\frac{N_{total}!}{N_a! (N_{total} - N_a)!} \right)$$

$$S_{config} \approx k_B [N_{total} \ln N_{total} - N_{total} - N_a \ln N_a + N_a - (N_{total} - N_a) \ln(N_{total} - N_a) + N_{total} - N_a]$$

$$S_{config} \approx k_B [N_{total} \ln N_{total} - N_a \ln N_a - (N_{total} - N_a) \ln(N_{total} - N_a)]$$

The translational entropy:

$$S_{trans} = \frac{d}{dT} \left(k_B T \ln \left(\left(\frac{A_{total} 2\pi M k_B T}{N_{total} h^2} \right)^{N_a} \right) \right)$$

$$S_{trans} = \frac{d}{dT} \left(N_a k_B T \ln \left(\frac{A_{total} 2\pi M k_B T}{N_{total} h^2} \right) \right)$$

$$S_{trans} = N_a k_B \left[T \frac{d}{dT} \left(\ln \left(\frac{A_{total} 2\pi M k_B T}{N_{total} h^2} \right) \right) + \ln \left(\frac{A_{total} 2\pi M k_B T}{N_{total} h^2} \right) \right]$$

$$S_{trans} = N_a k_B \left[T \left(\frac{A_{total} 2\pi M k_B T}{N_{total} h^2} \right)^{-1} \frac{d}{dT} \left(\frac{A_{total} 2\pi M k_B T}{N_{total} h^2} \right) + \ln \left(\frac{A_{total} 2\pi M k_B T}{N_{total} h^2} \right) \right]$$

$$S_{trans} = N_a k_B \left[1 + \ln \left(\frac{A_{total} 2\pi M k_B T}{N_{total} h^2} \right) \right]$$

The external vibrational entropy:

$$S_{extvib} = \frac{d}{dT} \left(k_B T \ln \left(\left(\frac{e^{-\frac{\vartheta_{ext}}{2T}}}{1 - e^{-\frac{\vartheta_{ext}}{T}}} \right)^{N_a} \right) \right)$$

$$S_{extvib} = N_a k_B \left[\ln \left(\frac{e^{-\frac{\vartheta_{ext}}{2T}}}{1 - e^{-\frac{\vartheta_{ext}}{T}}} \right) + T \frac{d}{dT} \left(\ln \left(\frac{e^{-\frac{\vartheta_{ext}}{2T}}}{1 - e^{-\frac{\vartheta_{ext}}{T}}} \right) \right) \right]$$

$$S_{extvib} = N_a k_B \left[\ln \left(\frac{e^{-\frac{\vartheta_{ext}}{2T}}}{1 - e^{-\frac{\vartheta_{ext}}{T}}} \right) + T \frac{1 - e^{-\frac{\vartheta_{ext}}{T}}}{e^{-\frac{\vartheta_{ext}}{2T}}} \frac{d}{dT} \left(\frac{e^{-\frac{\vartheta_{ext}}{2T}}}{1 - e^{-\frac{\vartheta_{ext}}{T}}} \right) \right]$$

$$S_{extvib} = N_a k_B \left[\ln \left(\frac{e^{-\frac{\vartheta_{ext}}{2T}}}{1 - e^{-\frac{\vartheta_{ext}}{T}}} \right) + T \frac{1 - e^{-\frac{\vartheta_{ext}}{T}}}{e^{-\frac{\vartheta_{ext}}{2T}}} \left((1 - e^{-\frac{\vartheta_{ext}}{T}})^{-1} \frac{d}{dT} (e^{-\frac{\vartheta_{ext}}{2T}}) + e^{-\frac{\vartheta_{ext}}{2T}} \frac{d}{dT} \left(\frac{1}{1 - e^{-\frac{\vartheta_{ext}}{T}}} \right) \right) \right]$$

$$S_{extvib} = N_a k_B \left[\ln \left(\frac{e^{-\frac{\vartheta_{ext}}{2T}}}{1 - e^{-\frac{\vartheta_{ext}}{T}}} \right) + T \left(\frac{e^{-\frac{\vartheta_{ext}}{2T}} \frac{d}{dT} \left(-\frac{\vartheta_{ext}}{2T} \right)}{e^{-\frac{\vartheta_{ext}}{2T}}} + (1 - e^{-\frac{\vartheta_{ext}}{T}}) \frac{-1}{(1 - e^{-\frac{\vartheta_{ext}}{T}})^2} \frac{d}{dT} \left(-e^{-\frac{\vartheta_{ext}}{T}} \right) \right) \right]$$

$$S_{extvib} = N_a k_B \left[\ln \left(\frac{e^{-\frac{\vartheta_{ext}}{2T}}}{1 - e^{-\frac{\vartheta_{ext}}{T}}} \right) + T \left(\frac{\vartheta_{ext}}{2T^2} + \frac{e^{-\frac{\vartheta_{ext}}{T}}}{1 - e^{-\frac{\vartheta_{ext}}{T}}} \frac{d}{dT} \left(-\frac{\vartheta_{ext}}{T} \right) \right) \right]$$

$$S_{extvib} = N_a k_B \left[\ln \left(e^{-\frac{\vartheta_{ext}}{2T}} \right) - \ln \left(1 - e^{-\frac{\vartheta_{ext}}{T}} \right) + T \left(\frac{\vartheta_{ext}}{2T^2} + \frac{e^{-\frac{\vartheta_{ext}}{T}}}{1 - e^{-\frac{\vartheta_{ext}}{T}}} \left(\frac{\vartheta_{ext}}{T^2} \right) \right) \right]$$

$$S_{extvib} = N_a k_B \left[-\frac{\vartheta_{ext}}{2T} - \ln \left(1 - e^{-\frac{\vartheta_{ext}}{T}} \right) + \frac{\vartheta_{ext}}{2T} \left(1 + 2 \frac{e^{-\frac{\vartheta_{ext}}{T}}}{1 - e^{-\frac{\vartheta_{ext}}{T}}} \right) \right]$$

$$S_{extvib} = N_a k_B \left[-\ln \left(1 - e^{-\frac{\vartheta_{ext}}{T}} \right) + \frac{\vartheta_{ext}}{T} \left(\frac{e^{-\frac{\vartheta_{ext}}{T}}}{1 - e^{-\frac{\vartheta_{ext}}{T}}} \right) \right]$$

Likewise, each component of internal vibrational entropy:

$$S_{intvib,i} = N_a k_B \left[-\ln \left(1 - e^{-\frac{\vartheta_i}{T}} \right) + \frac{\vartheta_i}{T} \left(\frac{e^{-\frac{\vartheta_i}{T}}}{1 - e^{-\frac{\vartheta_i}{T}}} \right) \right]$$

The rotational entropy (for methane, where $\vartheta_1 = \vartheta_2 = \vartheta_3 = \vartheta_{rot}$):

$$S_{rot} = \frac{d}{dT} \left(k_B T \ln \left(\left(\frac{\sqrt{\pi}}{\varphi} \prod_j \sqrt{\frac{T}{\vartheta_j}} \right)^{N_a} \right) \right)$$

$$S_{rot} = N_a k_B \left[\frac{d}{dT} \left(T \ln \left(\frac{\sqrt{\pi}}{\varphi} \right) + \frac{3}{2} T \ln \left(\frac{T}{\vartheta_{rot}} \right) \right) \right]$$

$$S_{rot} = N_a k_B \left[\ln \left(\frac{\sqrt{\pi}}{\varphi} \right) + \frac{3}{2} \ln \left(\frac{T}{\vartheta_{rot}} \right) + \frac{3}{2} T \frac{\vartheta_{rot}}{T} \frac{1}{\vartheta_{rot}} \right]$$

$$S_{rot} = N_a k_B \left[\ln \left(\frac{\sqrt{\pi}}{\varphi} \left(\frac{T}{\vartheta_{rot}} \right)^{\frac{3}{2}} \right) + \frac{3}{2} \right]$$

S5. Remarks

It should be noted that in this approach, there have been no considerations of intermolecular interactions.

S6. Nomenclature

The following nomenclature are used in the above derivation of the statistical mechanical model of entropy in the adsorbed phase of methane on the surface of activated carbon.

Table S5: Nomenclature.

Quantity	Symbol	Typical Units
Potential Energy	U	kJ
Helmholtz Free Energy	A	kJ

Entropy	S	J K^{-1}
Single Molecule Partition Function	z	-
Total System Partition Function	Z	-
Number of Configurations	Ω	-
Force	F	kg m s^{-2}
Force Constant	K	kg s^{-2}
Vibrational Frequency	ν	s^{-1}
Vibrational Temperature	θ_i	K
Rotational Temperature	θ_j	K
Rotational Symmetry Number	ϕ	-
Surface Occupancy	ϑ	-
Absolute Adsorbed Quantity	N_a	-
Molar Absolute Adsorbed Quantity	n_a	mol
Total Number of Surface Sites	N_{total}	-
Surface Area	A_{total}	m^2
Surface Area of a Single Adsorption Site	A_{site}	\AA^2
Surface Area of a Single Carbon Atom	A_C	\AA^2
Distance from Surface	z	\AA
Molecular Mass	M	Da
Lennard-Jones Bond Length	σ	\AA
Lennard-Jones Interaction Strength	ε	K k_B^{-1}
Thermal deBroglie Wavelength	Λ	m
Planck's Constant	h	J s
Boltzmann's Constant	k_B	J K^{-1}

Note: all specific quantities taken per gram of sorbent material

S7. References

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