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A Generalized Law of Corresponding States for the Physisorption of Classical Gases with Cooperative Adsorbate-Adsorbate Interactions

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Abstract

The Law of Corresponding States for classical gases is well established. Recent attempts at developing an analogous Law of Corresponding States for gas physisorption, however, have had limited success, in part due to the omission of relevant adsorption considerations such as the adsorbate volume and cooperative adsorbate-adsorbate interactions. In this work, we modify a prior Law of Corresponding States for gas physisorption to account for adsorbate volume, and test it with experimental data and a generalized theoretical approach. Furthermore, we account for the recently-reported cooperative adsorbate-adsorbate interactions on the surface of zeolite-templated carbon (ZTC) with an Ising-type model, and in doing so, show that the Law of Corresponding States for gas physisorption remains valid even in the presence of atypically enhanced adsorbate-adsorbate interactions.

1. Introduction

Gas physisorption on microporous carbons has been extensively explored for a variety of applications ranging from improved gas storage to efficient gas separation. At high pressures, nonideal effects can significantly influence both the gaseous and adsorbed phases. In bulk gases, the Law of Corresponding States generalizes the gas nonideality and provides a simplified equation of state. According to this law, nonideal gases behave similarly and have similar compressibility factors at corresponding conditions (i.e., when the conditions of the gases relative to the critical point are equal). The Law of Corresponding States has been shown to be highly accurate for bulk gases through a number of studies[1,2].

In 2002 Quinn hypothesized an extension to the Law of Corresponding States for gas physisorption, based on empirical evidence.[3] Quinn posited that gases have approximately equal excess adsorption uptake quantities (n_e) at corresponding conditions on the same adsorbent, which we call "Quinn's hypothesis of corresponding states." Quinn provided evidence to support this hypothesis by comparing argon, carbon monoxide, methane, nitrogen, and oxygen physisorption on four microporous carbons. Quinn found general agreement among the corresponding excess adsorption uptake quantities, although discrepancies often exceeded 50%. Hydrogen physisorption did not follow the trend, a fact that was initially attributed to hydrogen being able to better penetrate the adsorbent micropores, but later explained more satisfactorily as a quantum effect.[4] Recently, others have expanded Quinn's hypothesis to include gate-opening MOFs and have noted deviations for larger molecules,[5] but to date this issue has not been resolved. In this work we present a novel Law of Corresponding States for gas physisorption that includes adsorbate volume considerations. It builds upon previous work but is more successful, especially for larger molecules such as ethane.

2. Quinn's Hypothesis of Corresponding States

Excess adsorption uptake of methane, krypton and ethane on three microporous carbons are compared at corresponding conditions in Figure 1 using values from Ref. [6,7,8] along with new measurements. These three carbons (ZTC, MSC-30 and CNS-201) have significant differences in synthesis, specific surface area, and pore-size distribution, but all contain predominantly micropores (see Supporting Information, S1). For each adsorbent, experimentally measured isotherms of the three gases are compared at reduced temperatures (T^R) of 1.25 ± 0.02 and 1.38 ± 0.03 and at corresponding reduced pressures (P^R), which are defined as

$$T^R = \frac{T}{T_c} \tag{1}$$

$$P^R = \frac{P}{P_c} \tag{2}$$

$$V^R = \frac{V}{V_c} \tag{3}$$

Here T, P and V are the system temperature, bulk phase pressure and bulk phase molar volume, and T_c, P_c, and V_c are the critical temperature, pressure, and molar volume of the bulk fluid.

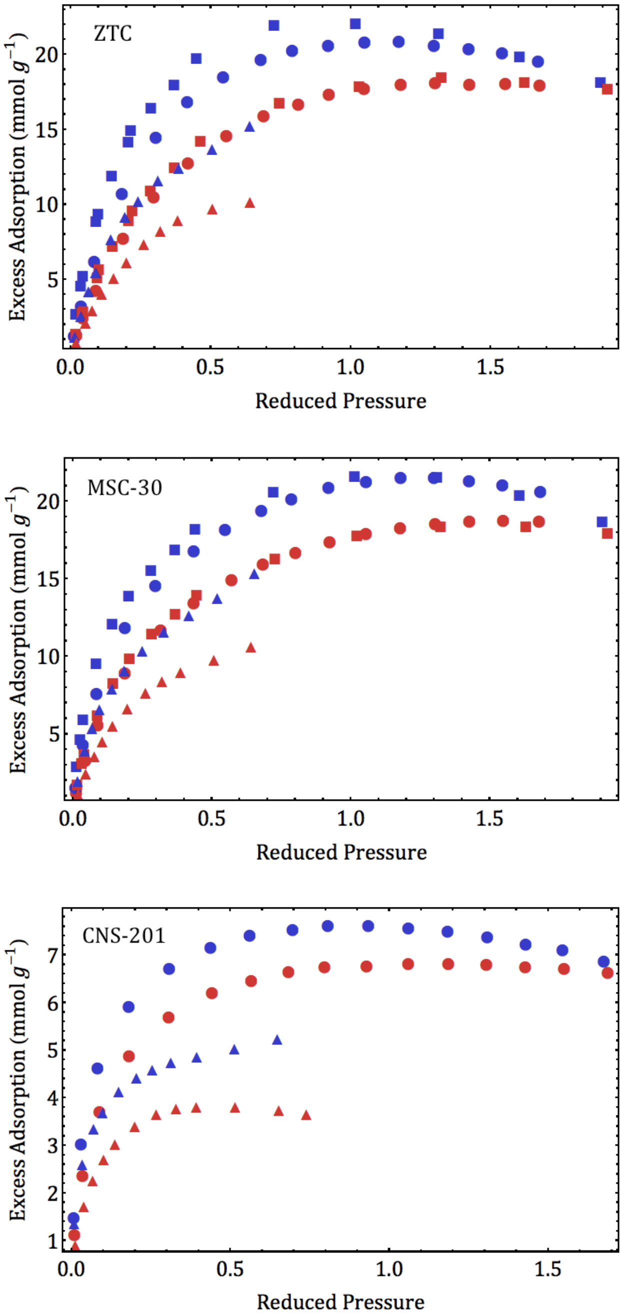


Figure 1. Comparison of methane (squares), krypton (circles), and ethane (triangles) excess adsorption at corresponding conditions as per Quinn's hypothesis (at reduced temperatures of 1.25±0.02 (blue) and 1.38±0.03 (red)).

As seen in Figure 1, there is good agreement between the measured methane and krypton isotherms using Quinn's hypothesis of corresponding states, with only moderate discrepancies (less than 25%). The ethane isotherms, however, deviate significantly from those of the other gases, with discrepancies of ~50%.

It is notable that all of the adsorptive species used for empirical support of Quinn's hypothesis of corresponding states (argon, carbon monoxide, methane, nitrogen, and oxygen) have similar molecular size. This is seen by comparing their 12-6 Lennard-Jones parameters, σ, which serve as proxies for excluded-volume diameters (see Table 1). Argon, carbon monoxide, methane, nitrogen, oxygen, and krypton all have σ values that are within 5% of their group average, 0.3560 nm. Ethane, however, is a significantly larger molecule with a σ that is 26% larger than the group average. Accordingly, ethane does not adhere to Quinn's hypothesis of corresponding states.

Table 1. Lennard-Jones σ Parameters of Relevant Gases

gas	Lennard-Jones σ (nm)
argon	0.3405[9]
carbon monoxide	0.3661[9]
methane	0.3737[9]
nitrogen	0.3613[9]
oxygen	0.3382[9]
krypton	0.3636[9]
ethane	0.4480[10]

3. Law of Corresponding States Comparing Fractional Occupancy

In this work, we define fractional occupancy (θ) as the ratio of the absolute adsorbed amount (n_a) to the maximum possible quantity of adsorption for the adsorbent at any temperature or pressure (n_{max}):

$$\theta = \frac{n_a}{n_{max}} \tag{4}$$

By comparing fractional occupancies instead of excess adsorption, we develop a Law of Corresponding States for the physisorption of classical gases interacting through London dispersion forces that better fits empirical data:

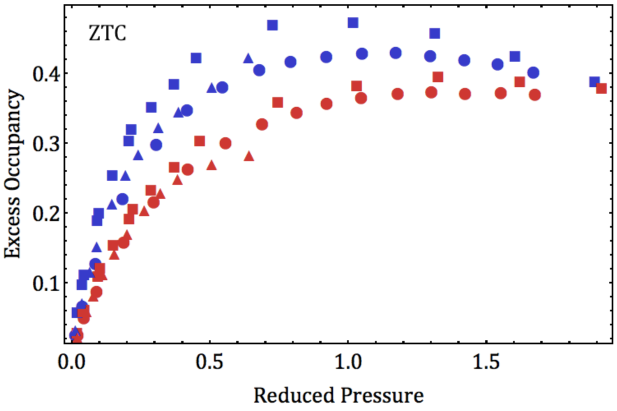
> "At corresponding conditions on the same adsorbent, classical adsorbed gases have the same fractional occupancy."

Unfortunately, absolute adsorption and hence fractional occupancy are not easily accessible through experimentation. Consequently we also define a proxy metric, the excess occupancy (θ_e):

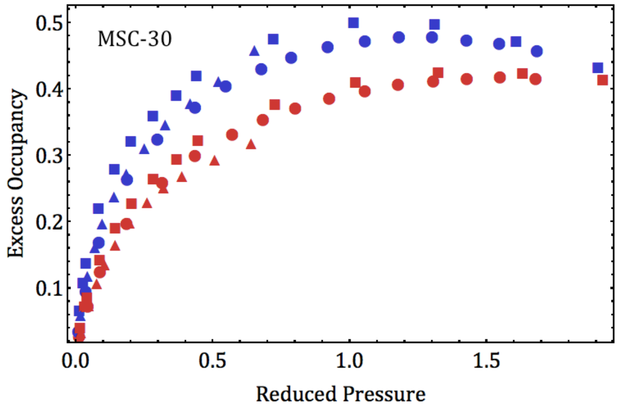
$$\theta_e = \frac{n_e}{n_{max}} \tag{5}$$

At low gas densities, the excess occupancy well approximates the fractional occupancy, but excess occupancies are more easily obtained by experiment. For this reason, here, we compare excess occupancies instead of the more fundamental fractional occupancies, which must be determined indirectly. For completeness, we also extrapolate fractional occupancies using a fitting procedure and compare these values at corresponding conditions in the Supporting Information (S3). The maximum adsorption quantity was estimated by multiplying the liquid molar density of the adsorptive species at its triple point by the measured micropore volume of the adsorbent (see Supporting Information S2).

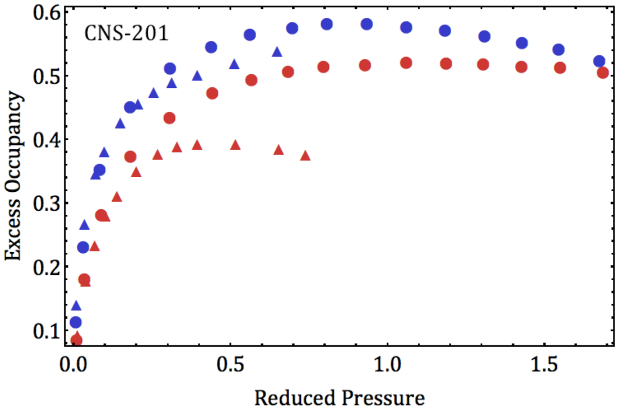
The experimentally-derived excess occupancies of methane, krypton and ethane on ZTC, MSC-30 and CNS-201 are compared at reduced temperatures of 1.25±0.02 and 1.38±0.03 (Figure 2, A-C). Using a robust fitting technique described in detail elsewhere[11], ethane excess occupancies have been extrapolated to higher reduced temperatures of 1.43±0.01, 1.80±0.02 and 2.07±0.05 and compared to experimentally measured methane and krypton data at corresponding conditions (Figure 2, D-E).


ZTC
Excess Occupancy
0.1
0.2
0.3
0.4
Reduced Pressure
0.0
0.5
1.0
1.5

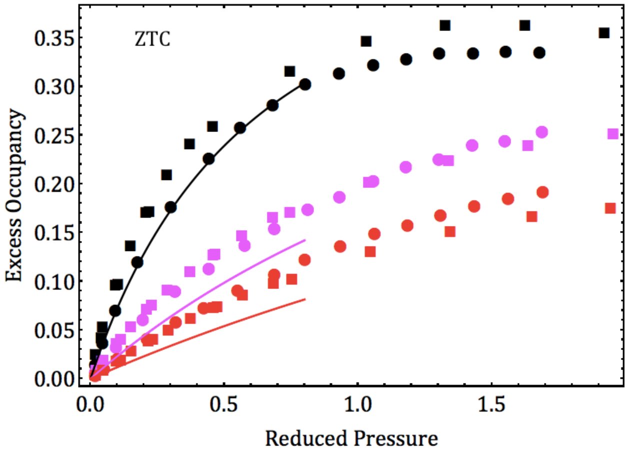
A.


MSC-30
Excess Occupancy
0.1
0.2
0.3
0.4
0.5
Reduced Pressure
0.0
0.5
1.0
1.5

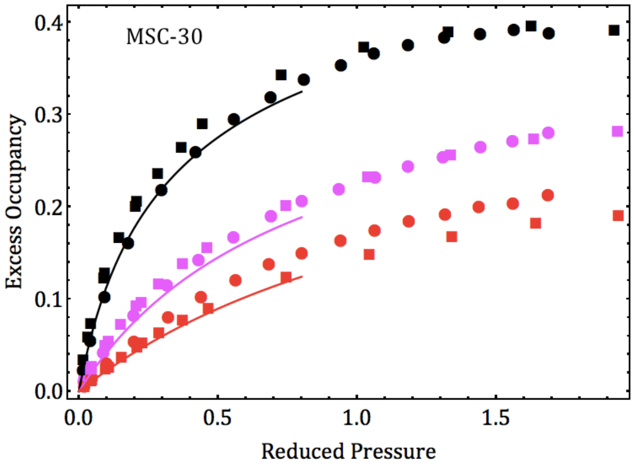
B.


CNS-201
Excess Occupancy
0.1
0.2
0.3
0.4
0.5
0.6
Reduced Pressure
0.0
0.5
1.0
1.5

C.



D.



E.

Figure 2. Comparison of excess occupancies at corresponding conditions for methane (squares), krypton (circles), and ethane (triangles) adsorption. The data in A-C are at reduced temperatures of 1.25±0.02 (blue) and 1.38±0.03 (red). The data in D-E are at reduced temperatures of 1.43±0.01 (black), 1.80±0.02 (magenta), and 2.07±0.05 (red). The lines indicate extrapolated ethane results, calculated from the fit parameters obtained by fitting experimental data with a superposition of Langmuir isotherms.

Figure 2, which presents the experimentally-derived excess occupancies of methane, krypton, and ethane at corresponding conditions, shows good correspondence between the curves, with discrepancies of less than 25%, except for ethane at high temperatures on CNS-201. This may result from a rotational hindrance of the ethane molecules within the very small pores of CNS-201 (as small as ~0.54 nm in width). This comparison of excess occupancies instead of excess uptake gives a significant improvement over Quinn's hypothesis of corresponding states where discrepancies of ~50% can be found with the same experimental data. Likewise, the extrapolated excess occupancies of ethane on MSC-30 are in reasonable agreement (discrepancies of less than 25%) with the experimentally derived excess occupancies of methane and krypton at reduced temperatures of 1.43±0.01, 1.80±0.02, and 2.07±0.05. On ZTC, deviations between the experimental and the extrapolated isotherms are larger and likely derive from small fitting inaccuracies magnified over the huge extrapolation range (>220K). The fitting and extrapolation procedure was not applied to ethane on CNS-201 due to an insufficient number of available isotherms.

4. Law of Corresponding States for Physisorption

There are two fundamentally distinct approaches to understanding gas-solid physisorption: the mono and multi-layer adsorption models developed by Langmuir, Brunauer, Emmett, Teller and others[12], and the pore-filling model developed by Euken, Polanyi, Dubinin, and others[12]. Each model successfully treats relevant physisorption phenomenon under differing conditions and both have widespread use. Here the Law of Corresponding States for physisorption is justified in the context of each model.

4.1 Monolayer Adsorption Model

Adsorbed molecules form a densified layer near the adsorbent surface, in a dynamic equilibrium with the gas phase. The significant decrease in the molar entropy of the adsorptive species upon adsorption is offset by a commensurate decrease in the molar enthalpy. At equilibrium

$$\frac{\Delta H_{ads}}{T} = \Delta S_{ads} \tag{6}$$

$$\Delta H_{ads} = H_a - H_g \tag{7}$$

$$\Delta S_{ads} = S_a - S_g \tag{8}$$

where ΔH_{ads} is the isosteric enthalpy of adsorption and ΔS_{ads} is the isosteric entropy of adsorption. It should be possible to predict the fractional occupancy of the adsorbed species at a fixed temperature and gas pressure with knowledge of the gas-phase enthalpy (H_g) and entropy (S_g), and knowledge of the constant-coverage, adsorbed-phase enthalpy (H_a) and entropy (S_a) (and how they change with fractional occupancy at a fixed temperature).

The gas-phase molar entropy, S_g, (in reference to the boiling-point liquid molar entropy, S_{L1}), of monatomic gases with similar critical volumes is well approximated by a function that depends only on reduced quantities, $f(T^R, V^R)$ (Supporting Information, S4). We assume that the molar entropy of the adsorbed phase (S_a) is given by the molar entropy of the liquid phase (S_{L1}) with the addition of a θ-dependent entropy of configurations of the adsorbate molecules on the adsorbent, $f(\theta)$.[13]

$$S_a = S_{L1} + f(\theta) \tag{9}$$

The S_g (in reference to S_{L1}) is approximated by $f(T^R, P^R)$,

$$-\Delta S_{ads} = f(T^R, P^R) - f(\theta) \tag{10}$$

For a monatomic gas, the right-hand side of Equation 6 (ΔS_{ads}) depends only on fractional occupancy and reduced quantities. Although polyatomic gases have additional degrees of freedom from internal vibrational and rotational modes, for many adsorbate-adsorbent systems, these internal vibrational and rotational modes are only negligibly altered upon physisorption[13,14] and do not significantly contribute to ΔS_{ads}. The assumption that rotational modes remain largely unchanged upon physisorption may break down in special circumstances, particularly in pores small enough to inhibit rotational modes.

The left-hand side of Equation 6 depends on the isosteric enthalpy of adsorption, a proxy metric of the physisorption binding-site energies. We first consider an idealized adsorbent with completely homogeneous binding-site energies and no adsorbate-adsorbate interactions. Under these assumptions, ΔH_{ads} is a constant for an ideal gas-adsorbent system, independent of pressure, or fractional occupancy at a fixed reduced temperature. These assumptions are later relaxed.

To begin, we assume that the isosteric enthalpy of adsorption is proportional to the critical temperature of the adsorptive species,[5] as detailed in the Supporting Information (S5, S6).

$$\Delta H_{ads} = c_1 T_c \tag{11}$$

Here c_1 is an undetermined (adsorbent specific) coefficient and the left-hand side of Equation 6 becomes

$$\frac{\Delta H_{ads}}{T} = \frac{c_1 T_c}{T} \qquad (12)$$

By substituting Equation 1 into Equation 12

$$\frac{\Delta H_{ads}}{T} = \frac{c_1}{T^R} \qquad (13)$$

Hence under the idealized assumptions above, the left-hand side of Equation 6 only depends on reduced quantities. Since both sides of Equation 6 only depend on reduced quantities and fractional occupancy, the fractional occupancy of distinct gases individually adsorbed on a specific idealized adsorbent must be equal at corresponding conditions.

4.2 Heterogeneities and Adsorbate-Adsorbate Interactions

Real adsorbents typically exhibit a heterogeneous distribution of binding sites. Such a distribution of binding-site energies leads to an isosteric heat ($-\Delta H_{ads}$) that decreases as a function of fractional occupancy as the most favorable sites are filled first. The distribution of binding sites is unique to the adsorbent and depends on pore-size distribution, surface structure, and chemical homogeneity. One may posit that each adsorbent has a characteristic binding-site energy distribution that varies with fractional occupancy and is proportional to the critical temperature of the adsorptive species, but is otherwise independent of the adsorptive species at corresponding conditions (see Supporting Information, S5, S6). In this approximation, c_1 is no longer a constant in Equation 11. Instead c_1 becomes a function of fractional occupancy that is unique to each adsorbent, but independent of the adsorptive species at corresponding conditions.

Furthermore, cooperative adsorbate-adsorbate interactions are important in some physisorptive systems. In these systems, favorable interactions can lead to an isosteric heat that increases as a function of fractional occupancy[6,7]. The contribution of these interactions is assumed to be proportional to the product of the critical temperature, T_c, and a function that depends only on fractional occupancy, $f(\theta)$, at a fixed reduced temperature (see Supporting Information, S7). The expression for ΔH_{ads} in Equation 11 is thus modified by adding a term that is proportional to $f(\theta)T_c$:

$$\frac{\Delta H_{ads}}{T} = \frac{c_1(\theta)T_c + c_2 f(\theta)T_c}{T} \qquad (14)$$

Here c_2 is an undetermined coefficient that is independent of the adsorptive species at corresponding conditions. By substitution

$$\frac{\Delta H_{ads}}{T} = \frac{c_1(\theta)+c_2 f(\theta)}{T^R} \qquad (15)$$

The left-hand side of Equation 6 remains approximately independent of the adsorptive species, even upon taking into account binding-site heterogeneity and adsorbate-adsorbate interactions (Equation 15). Consequently, Equation 6 only depends on reduced quantities and the fractional occupancy, consistent with the proposed Law of Corresponding States for gas physisorption.

4.3 BET Model

A simple extension of the Langmuir model to incorporate multiple layers of adsorption was worked out by Brunauer, Emmett, and Teller and is known as BET Theory[15]. This theory is widely used to determine the surface area of porous materials and gives the fractional occupancy (θ) as a function of pressure (P), saturation pressure (P_0), and a parameter, c_{BET}.

$$\theta = \frac{c_{BET}\frac{P}{P_O}}{\left(1-\frac{P}{P_O}\right)\left(1-\frac{P}{P_O}+c_{BET}\frac{P}{P_O}\right)} \tag{16}$$

$$c_{BET} = e^{\frac{(-\Delta H_{ads}-H_l)}{RT}} \tag{17}$$

The parameter c_{BET} depends on the heat of adsorption for the first layer, $-\Delta H_{ads}$, the heat of liquefaction of the adsorbate, H_l, and the temperature, T. The assumption that ΔH_{ads} is proportional to T_c has been previously justified. We may similarly assume that H_l is proportional to T_c (see Supporting Information, Section S10). Finally, we assume that for a given gas, P_0 is proportional to P_c, allowing Equation 16 to be reduced as:

$$\theta \propto \frac{\left(e^{\frac{c_3}{RT^R}}\right)(P^R)}{(1-P^R)\left(1-P^R+\left(e^{\frac{c_3}{RT^R}}\right)(P^R)\right)} \tag{18}$$

In this expression, c_3 is the factor relating the heat of adsorption and the heat of liquefaction. Equation 18 gives the fractional occupancy in terms of only reduced parameters, consistent with the Law of Corresponding States for physisorption.

4.4 Pore-Filling Model

The similarity between the Law of Corresponding States and Dubinin-Polanyi theory was recently noted by Sircar et al.[5] Here we further develop this insight to show the importance of fractional occupancy to the Law of Corresponding States for physisorption.

Specifically, we consider a pore-filling model of adsorption in the form of the Dubinin-Astakhov equation:[16]

$$\theta = e^{-\left(\frac{RTln(\frac{P_o}{P})}{E}\right)^{\chi}} \tag{19}$$

In this equation, T is the temperature, P is the pressure, P_0 is the equilibrium vapor pressure, E is the characteristic binding energy, and χ is an adsorbent-specific heterogeneity parameter.

$$E = \beta E_o \tag{20}$$

$$\beta = \frac{\alpha}{\alpha_o} \tag{21}$$

The affinity coefficient (β) relates the characteristic binding energy of a sample adsorbate (E) to that of the standard adsorbate (E_0) and depends on the ratio of their static polarizabilities, α and α_{O}, respectively. The adsorbate polarizability is assumed to be proportional to the critical temperature of the adsorptive species (see Supporting Information, S5).

Equation 19 then reduces to:

$$\frac{(-\ln(\theta))^{\frac{1}{\chi}}}{R} = \frac{Tln(\frac{P_o^R}{P^R})}{c_4T_c} = \frac{T^R ln(\frac{P_o^R}{P^R})}{c_4} \tag{22}$$

where

$$P_o^R = \frac{P_o}{P_c} \tag{23}$$

The undetermined constant, c_4, is derived from the polarizability and characteristic binding energy of the standard adsorbate. Both sides of Equation 22 are independent of the adsorptive species at corresponding conditions, consistent with the Law of Corresponding States for gas physisorption.

5. Anomalous Surface Thermodynamics

As we previously reported, both methane and krypton physisorption on ZTC yield anomalous surface thermodynamics at supercritical temperatures.[11,6,7] Methane and krypton isotherms were fitted with a superposition of Langmuir isotherms to extract thermodynamic quantities[11,6,7]. This yields analytically differentiable fits that are useful in determining the absolute adsorption, and the isosteric enthalpy of adsorption.[11,6,7] On ZTC, the isosteric heats of methane and krypton adsorption increase with fractional occupancy, a property that is attributed to enhanced adsorbate-adsorbate interactions within the uniquely nanostructured pores.

From Equation 7, the molar enthalpy of the adsorbed phase, H_a, (as a function of absolute adsorption) was determined by adding the isosteric enthalpy of adsorption (ΔH_{ads}) to the gas-phase enthalpy values (H_g) at the same conditions (obtained from REFPROP[17]). On ZTC, enhanced adsorbate-adsorbate interactions cause the low-temperature adsorbed-phase enthalpies to decrease toward minimum, most favorable values, which are reached at moderate fractional occupancies (Figure 3).

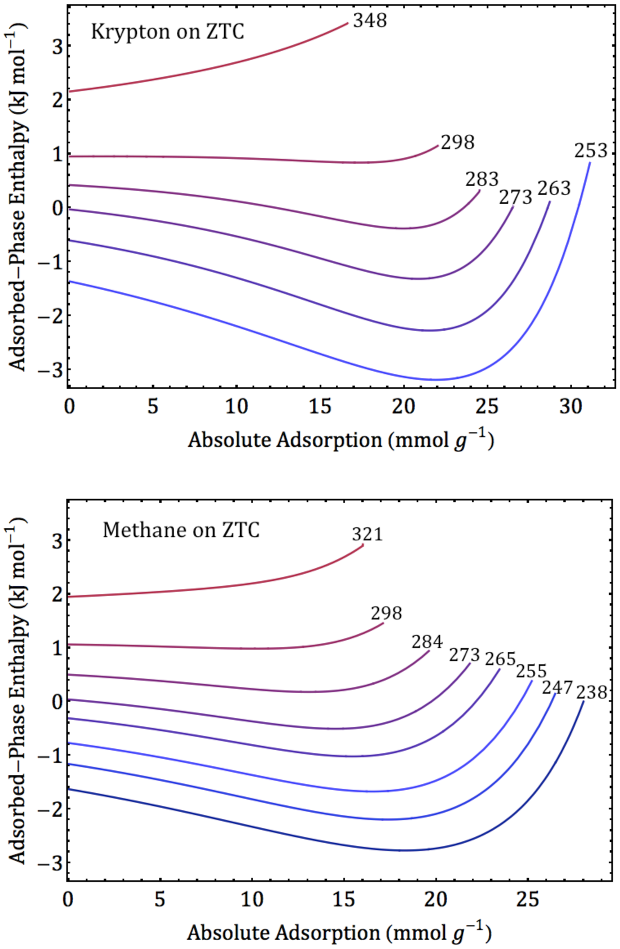


Figure 3. Adsorbed-phase enthalpies of krypton and methane on ZTC. Labels are temperatures in K.

The adsorbed-phase enthalpies may also be plotted as a function of the average intermolecular spacing in the adsorbed phase (x_{avg}) (Figure 4). Here x_{avg} was estimated by dividing the micropore volume of ZTC (V_{mic}), as measured by the Dubinin-Radushkevich method[18,19]), by the quantity of absolute adsorption (n_a) and taking the cube root.[7]

$$x_{avg} = \left(\frac{V_{mic}}{n_a}\right)^{\frac{1}{3}} \tag{24}$$

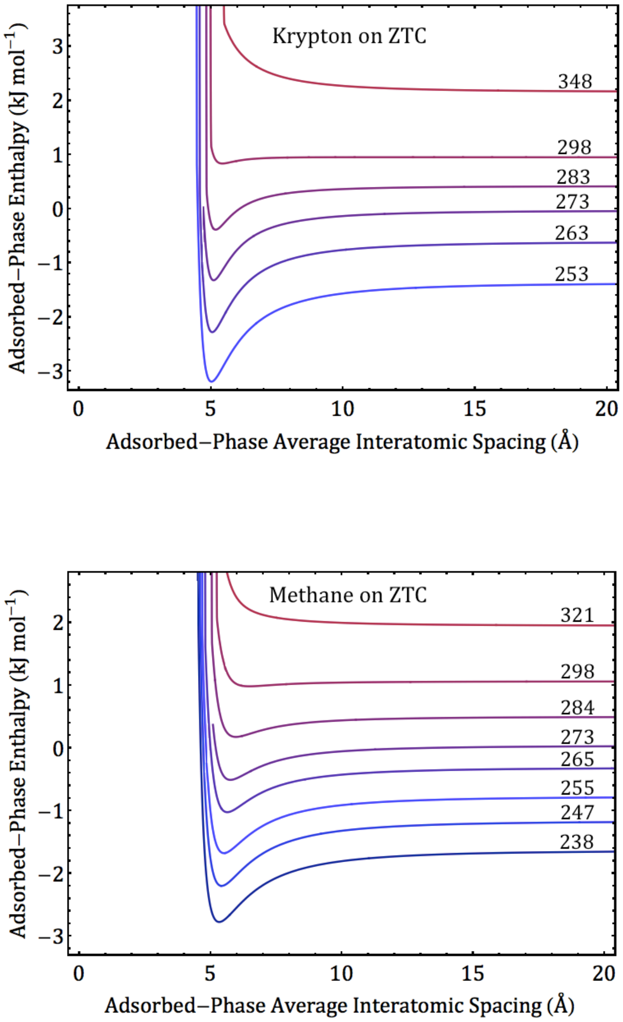


Figure 4. Adsorbed-phase enthalpies of methane and krypton on ZTC, as a function of x_{avg}. Labels are temperatures in K.

As shown in Figure 4, the adsorbed-phase enthalpies (as a function of x_{avg}) change with temperature and resemble a 12-6 Lennard-Jones potential. The deepest "potential wells" are observed at the lowest temperatures. The significant temperature dependence shows that the enhanced adsorbate-adsorbate interactions are disrupted by thermal motion, and suggests that they may be modeled with a cooperative interaction model such as the Ising model. The heat capacity of the adsorbed phase at constant pressure (C_P) is determined from the adsorbed-phase enthalpy (Figure 5).

$$C_P = \left.\frac{dH_a}{dT}\right|_P \tag{25}$$

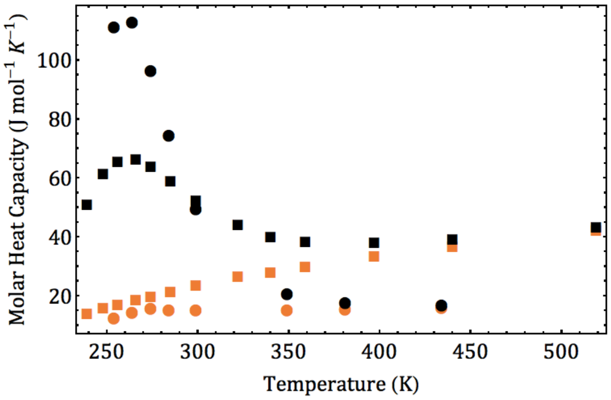


Figure 5. Constant pressure heat capacities of methane (squares) and krypton (circles) adsorbed phases on ZTC (black) and MSC-30 (orange) at an example pressure of 2 MPa.

For both methane and krypton there is good agreement between adsorbed-phase heat capacities at high temperatures for both ZTC and MSC-30. In the case of krypton, a monatomic gas, the C_P on ZTC at high temperatures and the C_P on MSC-30 at all temperatures are in good agreement with the C_P for an ideal two-dimensional gas (16.6 J mol^{-1} K^{-1}). At low temperatures, however, the C_P of both gases are significantly larger on ZTC than on MSC-30, with values that exceed even the liquid-phase heat capacities (methane~55.7 J

mol^{-1} K^{-1} and krypton~44.7 J mol^{-1} K^{-1})[17]. These unexpectedly large adsorbed-phase heat capacities may be attributed to a phase transition in the adsorbed phase on the surface of ZTC.

6. Model for Cooperative Interactions

As temperature is increased, the effects of adsorbate-adsorbate interactions decrease, and disappear as the slopes in Figure 3 go to zero at a critical temperature (T_0) of ~300 K. Figure 5 indicates the presence of a phase transition (in the adsorbed phase) around 270 K. We assume that below T_0, two phases arise: a vacancy-rich phase with a low concentration of occupied sites (α'), and an adsorbate-rich phase with a high concentration of occupied sites (α'') and more adsorbate-adsorbate interactions. We expect an unmixing phase diagram where the concentration of occupied sites in the α' and α'' phases are temperature dependent. The simplest phase diagram is symmetric, so these concentrations, $c_{\alpha'}$ and $c_{\alpha''}$, are related by

$$c_{\alpha'} = 1 - c_{\alpha''} \tag{26}$$

The average adsorbate-adsorbate interaction energy per adsorbed molecule (U_{avg}) should be dominated by the interactions in the adsorbate-rich α'' phase, with phase fraction $F_{\alpha''}$

$$F_{\alpha''} = \frac{\theta + c_{\alpha''} - 1}{2c_{\alpha''} - 1} \tag{27}$$

For simplicity we consider the case when θ=0.5 and thus equal phase fractions of 0.5 for all temperatures. If we assume (as in the point approximation) that the arrangement of molecules within the "clustered" α" phase is random and that each nearest-neighbor pair has an interaction strength of ε (from the Lennard-Jones potential)[9], then for θ=0.5

$$U_{avg} = \frac{z\varepsilon c_{\alpha''}{}^2}{2} \tag{28}$$

With the following definitions

$$L = 2c_{\alpha''} - 1 \tag{29}$$

$$\frac{1+L}{1-L} = \mathrm{e}^{\left(\frac{2T_0 L}{T}\right)} \tag{30}$$

the unmixing problem is transformed to the Bragg-Williams ordering problem with one order parameter, L.[20] By substitution

$$U_{avg} = \frac{z\varepsilon(\frac{L+1}{2})^2}{2} \tag{31}$$

In the context of this model, cooperative adsorbate-adsorbate interactions on ZTC at temperatures below T_0 are consistent with the Law of Corresponding States for physisorption as explained in Section 4.2 and elaborated on in the Supporting Information, Section S7.

For experimental comparison, for each measured temperature, we determined the difference between the minimum enthalpy (θ≈0.5) and the low coverage enthalpy (θ≈0) (in Figure 3) as a proxy measure of U_{avg}. These "potential well" depths were then normalized by $\frac{z\varepsilon}{2}$ so they could be compared directly to $(\frac{L+1}{2})^2$ in Figure 6, per Equation 31. In Figure 6, we set T_0=300 K and assume z=4 (square-lattice).

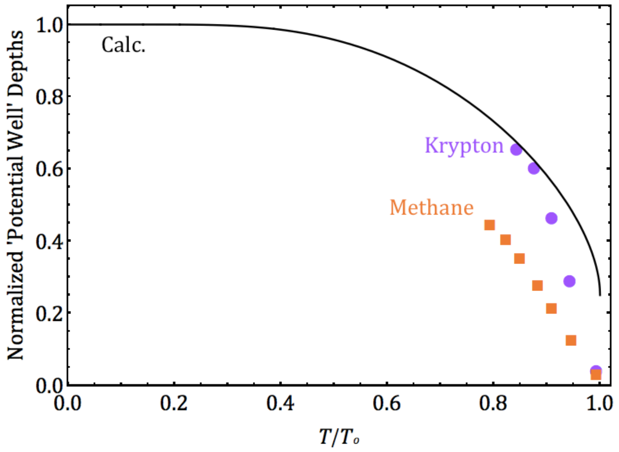


Figure 6. Normalized "potential well" depths of methane and krypton on ZTC, compared to calculated $(\frac{L+1}{2})^2$.

Figure 6 compares the measured adsorbate-adsorbate interaction enthalpies to thermal trends from the Ising model. Qualitative similarities between the measured and modeled temperature dependence support the hypothesis of cooperative adsorbate-adsorbate interactions on ZTC. The observed deviations are not surprising for such a simple model and uncertainty in the n_{max}, T_0 and z parameters.

7. Conclusions

The principle that distinct gases have similar adsorptive fractional occupancies at corresponding conditions on the same adsorbent is established as a novel Law of Corresponding States for gas physisorption. This principle is tested empirically using measurements of methane, krypton, and ethane physisorption on ZTC, MSC-30, and CNS-201 at reduced temperatures of 1.25±0.02 and 1.38±0.03. Reasonable agreement is found across different size gases with discrepancies of less than 25%. Accordingly this principle is useful for estimating pure gas isotherms, though should not be considered a replacement for experimental isotherm data. Further support is obtained from statistical mechanics wherein the validity of this principle as a first approximation is established for a number of conditions. The principle of corresponding states proves successful even in the presence of cooperative adsorbate-adsorbate interactions, which were modeled using the Ising model in a low-level approximation.

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