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A corresponding states principle for physisorption and deviations for quantum fluids

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RESEARCH ARTICLE

A corresponding states principle for physisorption and deviations for quantum fluids

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The principle of corresponding states has long been observed to be valid for simple fluids in the bulk state. It has recently been proposed that fluids adsorbed in a microporous sorbent also follow a form of corresponding states [D.F. Quinn, Carbon 40, 2767 (2002)]. It was observed that adsorption isotherms for several different adsorbates follow near-universal behaviour when plotted at the reduced temperature 2.36 as a function of reduced pressures, where the critical temperature and pressure are used as the reducing parameters. Significantly, Quinn noted that hydrogen manifestly does not follow the trends of the other fluids, showing much higher adsorption than any other fluid studied; this was ascribed to hydrogen being able to adsorb in very narrow pores not accessible to other adsorbates. It is shown in the current work that the anomalous behaviour of hydrogen can be described entirely by quantum effects and the relative strength of the fluid-fluid and solid-fluid potentials. Analytical and simulation methods are used to investigate the adsorption of various gases within slit and cylindrical pores. For large pore sizes, accessible to all adsorbates, corresponding states behaviour occurs for classical gases, with deviations observed for quantum gases, in agreement with experimental observations. In contrast, size-dependent selectivity (sieving) is found in small pores.

1. Introduction

The law of corresponding states [1] expresses the fact that the bulk properties of many gases exhibit remarkably similar ‘reduced’ equations of state: \( P^* = g(T^*, n^*) \). Here \( P^* = P/P_c \), the ratio of the pressure to the critical pressure. The function \( g \) is a universal function of the reduced thermodynamic variables, \( n^* = n/n_c \), the density relative to the critical density, and \( T^* = T/T_c \), the temperature relative to the critical temperature. The origin of this universal behaviour is that these systems possess a nearly identical form [2] of reduced interparticle interaction; viz, the pair potential satisfies to good approximation

\[
U(r) = \varepsilon U^*(\frac{r}{\sigma}).
\]

Here, \( \varepsilon \) is the well-depth and \( \sigma \) is the hard-core diameter of the pair potential. Insofar as the function \( U^*(r) \) is universal, then \( T_c, P_c \) and \( n_c \) are universal constants times \( \varepsilon, \varepsilon/\sigma^3 \) and \( \sigma^{-3} \) respectively. These conclusions are rigorously valid if both quantum effects and many-body interactions are negligible. For many fluids, these assumptions are valid and suffice to explain their bulk behaviour. However, weakly interacting, low molecular mass fluids exhibit deviations from universal behaviour because of quantum effects. For example, the critical temperatures of Ne, H\(_2\) and \(^4\)He are decreased (by about 7%, 40% and 60%, respectively) from their classical values by quantum effects [3–5]. Three-body effects cause very small shifts in \( T_c \) and small deviations from the ‘law of rectilinear diameters’, i.e., a symmetrical coexistence curve [6].

In the case of adsorption, no such corresponding states behaviour can be derived rigorously because adsorption involves additional length scales and energy scales associated with the adsorption potential [7]. However, since these additional parameters are related to those of the adsorbate, e.g. by ‘combining rules’ [2,8–10], one might wonder whether or not corresponding states behaviour is expected for adsorption. This article describes an exploration of this question. Although the problem is as old as the earliest studies of adsorption, the present research was stimulated by recent intriguing experimental results of Quinn [9], who found that adsorption isotherms on a variety of activated carbons exhibit a kind of universal

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behaviour, when expressed in reduced variables. Specifically, he found that the excess adsorption isotherms \(N(P^*, T^*)\) assume a nearly identical form for the gases Ar, CH\(_4\), CO, N\(_2\) and O\(_2\) at the reduced temperature \(T^* = 2.36\). Selected data from Quinn’s paper are reproduced in Figure 1. In contrast, the corresponding H\(_2\) coverage is a factor 5 to 10 times greater than that of the other gases, the ratio depending on the pressure. This can be clearly seen by examining the data in Figure 1. The behaviour seen in Figure 1 was seen for four activated carbons, representing various pore size distributions and surface chemistry, including AX21 (a ‘super activated’ carbon with a high surface area of 2500 m\(^2\)/g and wide pore size distribution) and PVDC (a polymer derived carbon with a lower surface area of 1000 m\(^2\)/g, but a pore volume made up of primarily micropores). One possible explanation for the lack of universality for H\(_2\), considered by Quinn, is that the hydrogen molecules enter smaller pores than the other gases because of their smaller size. This size-selectivity idea has been proposed often to explain observed H\(_2\) adsorption in porous hosts. The present study finds both the nearly universal behaviour of classical gases and the deviant behaviour of H\(_2\) to be consistent with model calculations based on simple assumptions about the interactions, with no need to invoke the small pore entry hypothesis. The distinct behaviour of H\(_2\) is explained in terms of its different interaction (large adsorption well-depth \(D\)) and the fact that quantum effects reduce its critical temperature, \(T_c\), thus enhancing its adsorption, compared to the other gases, at a given value of \(T^*\).

The following section describes our simulation results for both slit-shaped and cylindrical pores. Section 3 analyses the behaviour in terms of the interaction models, with some focus on the Henry’s law regime of low P adsorption. Section 4 summarizes our results.

### 2. Simulations

We have used conventional modelling and grand canonical Monte Carlo (GCMC) simulation techniques to calculate the adsorption behaviour of a number of gases within slit-shaped and cylindrical pores. Irregular porous materials are not accurately described by either geometry, but simulations with such simple geometries provide definite comparisons with experimental data and permit semiquantitative conclusions to be drawn. While it is evident that distributions of cylindrical or slit pores can provide improved comparisons with experimental data, we do not pursue that approach here. The present goal is more modest – namely, a qualitative understanding of the Quinn observations. The Quinn excess adsorption data for the various gases are plotted in Figure 1. The data have been converted to amount adsorbed per BET surface area reported by Quinn [11] rather than amount adsorbed per gram, as originally given by Quinn. The change in units was required to facilitate comparison with simulation data.

The adsorption potential \(V(r)\) used in our simulations was computed by assuming a continuum carbon substrate, within individual layers, with carbon atomic density \(n_c = 114\, \text{nm}^{-3}\), and integrating (over graphitic planes) a Lennard–Jones (LJ) pair potential, corresponding to

\[
U_{\text{LJ}}(r) = 4\varepsilon_{ac}\left(\frac{\sigma_{ac}}{r}\right)^{12} - \left(\frac{\sigma_{ac}}{r}\right)^{6}.
\]

Here, \(\varepsilon_{ac}\) and \(\sigma_{ac}\) are the well depth and diameter parameters for the atom–carbon pair interaction; these values have been deduced from conventional (but approximate [2]) Lorentz–Berthelot combining rules: \(\varepsilon_{ac} = (\varepsilon_c \varepsilon_{cc})^{1/2}\) and \(\sigma_{ac} = (\sigma_c + \sigma_{cc})/2\), using semiempirical values of the carbon parameters, \(\sigma_{cc}\) and \(\varepsilon_{cc}\). Table 1 presents values of the relevant parameters for the gases used in these simulations. We have treated H\(_2\) and CH\(_4\) as spherical ‘atoms’, with the LJ parameters in this table.

For the slit pore case, the total potential energy \(V(z)\) depends just on the distance \(z\) from one surface of the pore; it is assumed to equal a sum of two terms, one from each half-space bounding the slit:

\[
V_{\text{slit}}(z) = V_1(z) + V_1(H - z),
\]

![Figure 1. Excess adsorption as a function of reduced pressure \((P^* = P/P_c)\), at \(T^* = T/T_c = 2.36\) as determined experimentally by Quinn [11] for various classical gases: H\(_2\) (filled circles), CO (squares), CH\(_4\) (up triangles), N\(_2\) (down triangles), and O\(_2\) (diamonds). The maximum deviation from the mean observed by Quinn for adsorption of classical gases on PVDC was 33% at \(P^* = 0.15\). Similar results were obtained on three other carbon sorbents (color online).](image-url)
where $H$ is the width of the slit pore, and

$$V_1(z) = 2\pi \varepsilon_{ac} \sigma_{ac} \Delta n_c \left[ \frac{2}{3} \left( \frac{\sigma_{ac}}{z} \right)^{10} - \left( \frac{\sigma_{ac}}{z} \right)^{4} - \frac{\sigma_{ac}^4}{3\Delta (0.61\Delta + z)} \right] \quad (4)$$

This latter expression for the single surface potential, $V_1(z)$, is the so-called ‘Steele 10-4-3 potential’. It is based on a sum over planes of graphite, where $\Delta = 0.335\,\text{nm}$ is their spacing [12]. We neglect deviations from additivity in the total potential. We have used the Feynman–Hibbs approach [13,14] for approximating quantum effects for fluid–fluid and solid–fluid interactions for $\text{H}_2$ in our simulations at 77 K. Quantum effects have been shown to be non-negligible for adsorption of $\text{H}_2$ in nanopores at this temperature [15,16].

Figure 2 presents the results of the slit pore simulations for $\text{Ar}$, $\text{CH}_4$, $\text{Kr}$ and $\text{H}_2$ at a reduced temperature $T^* = 2.36$, the value chosen by Quinn for his data comparisons, as shown in Figure 1. One sees that the simulation results for large $H$ exhibit the trend seen by Quinn. That is, for $H \geq 0.94\,\text{nm}$, the results for $\text{Ar}$, $\text{CH}_4$, and $\text{Kr}$ nearly coincide, while the $\text{H}_2$ adsorption is typically a factor of 10 higher, depending on the choice of $P^*$. In contrast, for the two slightly narrower pores studied, the three classical

Table 1. Lennard–Jones potential parameters used in the GCMC simulations. Parameter values deduced from combining rules are discussed in the text [17–19].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$\text{H}_2$</th>
<th>$\text{Ar}$</th>
<th>$\text{CH}_4$</th>
<th>$\text{Kr}^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma$ (nm)</td>
<td>0.305</td>
<td>0.34</td>
<td>0.372</td>
<td>0.36</td>
</tr>
<tr>
<td>$\varepsilon/k$ (K)</td>
<td>37.0</td>
<td>120.0</td>
<td>161.35</td>
<td>171.0</td>
</tr>
<tr>
<td>$\sigma_{ac}$ (nm)</td>
<td>0.3225</td>
<td>0.34</td>
<td>0.356</td>
<td>0.35</td>
</tr>
<tr>
<td>$\varepsilon_{ac}/k$ (K)</td>
<td>32.19</td>
<td>57.97</td>
<td>67.22</td>
<td>69.2</td>
</tr>
<tr>
<td>$P_C$ (MPa)</td>
<td>1.30</td>
<td>4.87</td>
<td>4.62</td>
<td>5.50</td>
</tr>
<tr>
<td>$T_C$ (K)</td>
<td>33.0</td>
<td>150.8</td>
<td>190.6</td>
<td>209.4</td>
</tr>
</tbody>
</table>

Figure 2. Excess adsorption, $N$, in slit pores calculated from GCMC simulations as a function of reduced pressure, $P^*$, for $\text{H}_2$ (filled circles), $\text{Ar}$ (squares), $\text{CH}_4$ (triangles), $\text{Kr}$ (diamonds). The slit widths, $H$, are: (a) 0.64 nm, (b) 0.69 nm, (c) 0.94 nm, and (d) 1.34 nm. The lines are drawn as a guide to the eye (color online).
gases exhibit quite distinct behaviour; at $H = 0.64 \text{ nm}$, the Ar uptake curve departs from those of Kr and CH$_4$. This deviation from the pattern of a common behaviour, seen for larger pores, is a size effect. The origin of this behaviour can be understood from the fact that the adsorption potential, $V_{\text{slit}}(z)$, permits the smaller Ar particle to enter pores that restrict access to Kr and CH$_4$.

These general trends can be seen also in Figure 3. One observes the slit width dependence of the excess adsorption of H$_2$ relative to the other gases. The three classical gases, Ar, CH$_4$, and Kr, all exhibit a clear maximum in the amount adsorbed with respect to the slit width. The maximum occurs around $H = 0.6 \text{ nm}$, where one layer of the gas molecules will adsorb between the slits. As the slit pore becomes wider the solid–fluid potential decreases because the attractive potential overlap from the neighbouring walls of the slit pore decreases. This can be seen by the plot of the reduced solid–fluid potentials as a function of $H$ in Figure 4. We have plotted the minimum in the solid–fluid potential as a function of slit width in Figure 4 for H$_2$, Ar, CH$_4$, and Kr, and have reduced the values for each gas by the temperature of the isotherms in Figures 2 and 3 ($T^* = 2.36T_c$). Note that the magnitude of the reduced solid fluid potential is much larger for H$_2$ than for the other gases. This gives rise to the observed increase in the amount adsorbed for slit pores larger than the minimum in the potential curve at about 0.65 nm. This is largely the result of the lower effective $T_c$ of H$_2$ due to quantum effects. This will be discussed in greater detail in Section 3.

Slit pore models have been widely used to approximate adsorption on activated carbons [20–24]. Real activated carbons are not composed of parallel slit pores; more accurate models have been proposed that include structural information and pore connectivity [25]. While cylindrical pores are not good models for activated carbons, they do provide a measure of how pore geometry may affect the concept adsorption universality and deviations due to quantum effects. We have also carried out simulations of Ar, CH$_4$ and H$_2$ within a cylindrical carbon nanotube (see Figure 5). The adsorption potential was computed with the same method as that used in a number of recent publications [19,26,27].

Adsorption in the cylindrical pores is qualitatively similar to that in the slit pores. However, we note that the 0.35 nm radius tube shows strong size selectivity. This is indicative of the larger confinement in a one-dimensional cylindrical
pore, compared with the effective two dimensional slit pores.

3. Dependence of adsorption on the interactions

One of the striking features of both the theoretical and experimental isotherms is a much larger initial slope for H$_2$ than for the classical gases. This big difference can be accounted for by examining the statistical experiments, a supercritical temperature classical gases. In the simulations and the Quinn ratio is approximately in the virial coefficients; at this higher temperature, the was used, but even then there remains a big disparity experimental isotherms is a much larger initial slope. One of the striking features of both the theoretical and

For the sequence of gases He, H$_2$, Ar, N$_2$, CO, O$_2$ and CH$_4$, the values of $D^*_c$ are 37, 18, 7.3, 9.5, 9.6, 7.6 and 7.9, respectively. These values are based on well-depth observations of Quinn. He and Seaton [22] have recently examined the pore size distribution in BPL using molecular simulations. Their model indicates that very few of the pores in BPL have pore size exclusion can in fact play a role in the apparent lack of universality in adsorption isotherms for selected pore sizes. This size exclusion effect is independent of the quantum effects we have described up to this point. Given that BPL and other activated carbons posses a range of pore sizes it is worthwhile asking what roll size exclusion plays in the observations of Quinn. He and Seaton [22] have recently examined the pore size distribution in BPL using molecular simulations. Their model indicates that very few of the pores in BPL have pore

$B(T) = \int \{\exp[-\beta V_{slit}(z)] - 1\}\,dz.$

At low $T$, this integral is dominated by the exponential, resulting in a simple activated form for the adsorption, which may be written

$B(T) \propto \exp(D^*).$  \hspace{1cm} (7)

Here, $D^* = \beta D$ and the condition $\exp(D^*) \gg 1$ is assumed to be valid, as confirmed below. We first evaluate the value $D^*_c$ of $D$ at the critical temperature. For the sequence of gases He, H$_2$, Ar, N$_2$, CO, O$_2$ and CH$_4$, the values of $D^*_c$ are 37, 18, 7.3, 9.5, 9.6, 7.6 and 7.9, respectively. These values are based on well-depth values for these gases’ interactions with graphite, empirically determined from thermodynamic measurements or scattering data [28]. Note that the H$_2$ value of $D^*_c$ is more than a factor of two larger than that of the other classical gases, whose values of $D^*_c$ are rather similar. When $D^*_c$ is exponentiated, there results a value of $B(T_c)$ for H$_2$ that is much greater than that of the classical gases. In the simulations and the Quinn experiments, a supercritical temperature $T = 2.36 \ T_c$ was used, but even then there remains a big disparity in the viral coefficients; at this higher temperature, the ratio is approximately

$\frac{B_{H_2}}{B_{\text{classical}}} \sim 40.$ \hspace{1cm} (8)

This argument thus explains the huge disparity in initial slopes between H$_2$ and the classical gases. If He were used instead of H$_2$, incidentally, because its value of $D^*_c$ is so much larger (twice that of H$_2$), the adsorption ratio would be even larger: $B_{11c}/B_{\text{classical}} \sim 10^5$.

The preceding discussion leaves open the question: why is $D^*_c$ so different for these quantum gases than for the classical gases? There are several reasons, which we mention for the H$_2$ case. One is that quantum effects depress the critical temperature of H$_2$ by more than 30% relative to what its value would be if it were classical. We define a ‘constant’ $k_{\text{quant}}$ through the relation

$k_{\text{quant}} \approx 1.33 \text{ for classical gases and } 0.89 \text{ for H}_2.$ There is also a ‘combining rule’ effect. The geometric combining rule for well depths says that the two-body (pair) interaction parameter $\varepsilon_{\text{GC}}$ is the geometric mean of $\varepsilon_{\text{CC}}$ and $\varepsilon$. Then $\varepsilon_{\text{GC},\varepsilon} = [\varepsilon_{\text{CC},\varepsilon}]^{1/2}$. Forgetting other factors entering into $D$, one can then conclude that $D^*_c$ is particularly large for H$_2$ because its value of $\varepsilon$ is so small. To quantify this connection, we define another constant $k_{\text{int}}$ through the relation

$k_{\text{quant}} \approx \frac{k_{\text{int}} (\varepsilon_{\text{CC}},\varepsilon)^{1/2}}{\varepsilon}.$

Temporarily, let us assume that the $k$ ratio is the same for H$_2$ as for the other gases. The $\varepsilon$ value for H$_2$ is about 1/3 of the other gases. Then, the rightmost factor causes an increase in value of $D^*_c$ for H$_2$ by a relative factor $3^{1/2} \approx 1.7$. An additional factor of about 1.5 comes from the smaller value (mentioned above) of $k_{\text{quant}}$ for H$_2$. This leads to a combined factor of about 2.5, meaning that $D^*_c$ is expected to be 2.5 times larger for H$_2$ than for the other gases. That estimate is about right, as indicated in the empirical values cited above.

Is it clear from the data in Figures 2 and 5 that pore size exclusion is also an important factor? It certainly seems to be the case that BPL have pore sizes that are much smaller than those of other adsorbents. This suggests that the pore size distribution in BPL is more important than in other adsorbents. However, it is also possible that the pore size distribution in BPL is less important than in other adsorbents. This suggests that the pore size distribution in BPL is more important than in other adsorbents. However, it is also possible that the pore size distribution in BPL is less important than in other adsorbents.
widths smaller than about 0.7 nm. Hence, the largest contribution to the adsorption isotherms comes from pores where no size exclusion takes place. This observation lends credibility to our conclusion that pore size exclusion is not needed to adequately explain the results of Quinn.

4. Summary and conclusions
This paper has addressed the intriguing problem of why adsorption on activated carbons exhibits a common behaviour for classical gases, but quite distinct behaviour for H2. Our explanation invokes two features to explain these properties. One is ‘chemical’: the gas–surface interaction for H2 is much more attractive, relative to the fluid–fluid interaction, than that of the other gases. The other is quantum: the critical temperature of H2 is reduced by quantum effects so that a comparison of various gases’ adsorption isotherms at $T = 2.36T_c$ corresponds to a lower effective temperature for H2 (and so greater relative adsorption).

There are numerous alternative model potentials that might be considered for these adsorption systems. Because of the plausibility of the arguments made in the preceding paragraph, however, we believe that other ‘reasonable’ adsorption potentials will exhibit the same trends.

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