From adsorption to condensation: the role of adsorbed molecular clusters

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The adsorption of heptane vapour on a smooth silicon substrate with a lower temperature than the vapour is examined analytically and experimentally. An expression for the amount adsorbed under steady state conditions is derived from the molecular cluster model of the adsorbate that is similar to the one used to derive the equilibrium Zeta adsorption isotherm. The amount adsorbed in each of a series of steady experiments is measured using a UV-vis interferometer, and gives strong support to the amount predicted to be adsorbed. The cluster distribution is used to predict the subcooling temperature required for the adsorbed vapour to make a disorder–order phase transition to become an adsorbed liquid, and the subcooling temperature is found to be $2.7 \pm 0.4 \text{ K}$. The continuum approach for predicting the thickness of the adsorbed liquid film originally developed by Nusselt is compared with that measured and is found to over-predict the thickness by three-orders of magnitude.

1 Introduction

Our objective is to develop a method for predicting the conditions under which film-wise condensation is initiated: i.e. the initiation of the transition from an adsorbed vapour to an adsorbed liquid when a stagnant vapour with temperature, $T^v$, is exposed to a planar, vertically oriented, smooth substrate with a lower temperature, $T^s$. We examine the predictions using heptane adsorbing on silicon, and measure, at one position on the disk, the adsorbed film thickness using a UV-vis interferometer.

If the saturation temperature corresponding to the vapour-phase pressure, $P_{sat}^v$, is denoted $T_{sat}^v$, the continuum approach to predicting the thickness of an adsorbed liquid film assumes that a liquid film forms whenever $\Delta T$:

$$\Delta T \equiv [T_{sat}^v(T^v) - T^s]$$

is greater than zero, i.e. without subcooling. Our experiments do not support this assumption. Compared to the measurements, the continuum approach is found to strongly over-predict the liquid film thickness.

When a vapour at $T^v$ is exposed to a cooler substrate, we suppose that the adsorbate can be approximated as a collection of molecular clusters, similar to that assumed to develop the equilibrium Zeta adsorption isotherm. In both cases, the number of clusters of type $\zeta$ in the adsorbate is denoted $a_\zeta(y^{VS})$, where $\zeta$ is the number of molecules in a cluster, and the temperature function, $y^{VS}$, is defined as

$$y^{VS} \equiv \frac{P^v}{P_{sat}^v(T^s)} e^{\frac{\bar{z}}{\gamma^s}}.$$  \hspace{1cm} (2)

$\zeta$ has a maximum value of $\zeta_m$, but it is allowed values to have of $1, 2, 3, \ldots, \zeta_m$. We develop an expression for the cluster distribution $a_\zeta(y^{VS})$ in steady, thermal disequilibrium states that have an interfacial temperature discontinuity at the solid–vapour interface. From $a_\zeta(y^{VS})$, we obtain the expression for the amount adsorbed in the thermal disequilibrium, $n_{ads}(y^{VS})$.

The interfacial temperature discontinuity indicates that even though the system is in a steady state under the system constraints, there is condensation occurring on certain cluster-types, but simultaneously, others are evaporating. This has the net result that at a value of $y^{VS}$, the thickness of the adsorbate is in the steady state. This hypothesis is supported by the experimental observations.

In our experiments, a smooth silicon disk maintained at a series of progressively lower temperatures, $T^s$, is exposed to heptane vapour saturated at $301 \pm 0.2 \text{ K}$. The entropy of the adsorbate increases until a state of maximum disorder is reached. Then a disorder–order phase transition is initiated that converts the adsorbed vapour to a heterogeneous phase of adsorbed liquid and adsorbed vapour. As $T^s$ is lowered further, the entropy of the surface phase decreases, indicating that the adsorbed phase becomes more ordered as it is converted into an adsorbed liquid phase.

1.1 Basis for predicting the amount adsorbed in steady, thermal disequilibrium states

We suppose, firstly that a necessary condition for the system considered to be a thermal disequilibrium, steady state is that...
the chemical potential of the molecules in the vapour phase, \( \mu^V \), should have the same value as that of the single-molecule adsorbed “clusters”, \( \mu_{SV} \), on the solid surface at temperature \( T^S \):

\[
\mu^V_1(T^S) = \mu^V(T^S).
\]

Only clusters with one molecule are allowed to be exchanged with the vapour phase. Note that even though the chemical potentials of the molecules in the two phases are equal, there can be molecular transport between the phases, since the potentials of the molecules in the two phases are different.

Secondly, we suppose that the adsorbed vapour is in local thermodynamic equilibrium at \( T^S \), and consists of a cluster distribution that forms as a result of reactions on the surface between single-adsorbed molecules, \( A_1 \), and adsorbed, multiple-molecule clusters \( A_3, A_4, \ldots, A_m \). Symbolically then, the surface reactions may be expressed as:

\[
\begin{align*}
A_1 + A_1 &= A_2, \\
A_1 + A_2 &= A_3, \\
&\vdots \\
A_1 + A_{m-1} &= A_m.
\end{align*}
\]

For this adsorbed phase to be in local equilibrium:

\[
\begin{align*}
\mu^V_1 + \mu^V_1 &= \mu^V_2, \\
\mu^V_1 + \mu^V_2 &= \mu^V_3, \\
&\vdots \\
\mu^V_1 + \mu^V_{m-1} &= \mu^V_m,
\end{align*}
\]

or, simply

\[
\mu^V_{SV}(T^S) = \zeta \mu^V_{SV}(T^S), \quad \zeta = 1, 2, \ldots, m.
\]

Thus, the surface phase is approximated as homogeneous with possibly \( \zeta_m \) cluster-types present, but the chemical potential per molecule is uniform in the surface phase.^{3,8} We use eqn (3) and (6) as the basis for developing an analytical expression for the cluster distribution \( a_c \), and then use \( a_c \) to develop the expression for the amount adsorbed under both equilibrium and thermal disequilibrium conditions, \( \eta_{ads}(y^{VS}) \).

We emphasize that the thermal equilibrium version of eqn (3) and (6) was the basis for the derivation of the equilibrium Zeta adsorption isotherm, \( n^{SV}(x^V) \), where \( x^V \) is the pressure ratio, \( P^{V}/P_{sat}(T^S) \).\(^5\) As will be seen, under thermal disequilibrium conditions, \( \eta_{ads}(y^{VS}) \) describes the amount adsorbed, but \( \eta_{ads}(y^{VS}) \) automatically reduces to the Zeta adsorption isotherm when thermal equilibrium exists in the system, and this isotherm has significant experimental support.\(^4,15\)

In the thermal disequilibrium steady states considered, we measure the thickness of the adsorbed liquid film using a UV-vis interferometer, compare that measured with that predicted using the continuum model,\(^1\) and find that the continuum prediction is three-orders of magnitude larger than the experimental value. In addition to the assumption of no subcooling required to initiate the liquid phase, the continuum approach uses the heat transfer coefficient approximation, and assumes that the thickness of the adsorbed layer is determined by thermal conduction across the adsorbed layer. As discussed in Section 6, in the approach we propose that there is no need to introduce the heat transfer coefficient approximation.

2 Experimental apparatus and measurements

The experimental apparatus shown schematically in Fig. 1 was designed to measure the thickness of the heptane adsorbate at one position on a vertically oriented Si disk as a function of \( y^{VS} \). Inside the stainless-steel chamber, the Si disk was mounted at one end of a stainless steel cylinder that transported the cooling fluid to maintain the disk at \( T^S \). One side of the disk was polished and could be viewed through a quartz window (Kurt J. Lesker, USA) using the light source of the UV-visible interferometer (Filmetrics, USA). The interferometer light source was focused at a point 14.4 mm above the bottom of the Si disk (Fig. 1). The Si disk (Siltronix S.T., Fr) had a 18 mm diameter, a thickness of 10 mm, and a central hole of 1 mm-Dia. The disk surface had been polished using a chemical, mechanical polishing process that the manufacturer claimed provided a surface roughness of less than 1 nm.

A total of twelve thermocouples (TCs) had been implanted in the 10 mm thickness of the disk; four at each of three longitudinal depths.\(^5\) At each of these depths, the thermocouples were placed at radial depths of 1.0, 3.0, 5.0, and 7.0 mm, measured from the centreline, and were separated by 90° around the disk circumference. These thermocouples were used to determine the interfacial solid temperature, \( T^S \), during each experiment.

For cleanliness, the stainless steel chamber was evacuated using a stainless-steel turbo-molecular diffusion pump to a pressure of \( 10^{-6} \) Pa and held under this condition for over 48 hours. With the light source of the UV-visible interferometer at the position to be used subsequently, the baseline spectrum of the Si surface was recorded before the heptane was admitted to the chamber. It was found to be the standard spectrum of Si in the absence of adsorption.\(^16,17\)

A sample of the gas–vapour mixture in the chamber was drawn into a residual gas analyzer (SRS Model RGA 200) both before and after each experiment. The gas remaining in the chamber before an experiment was primarily \( N_2 \) at a partial pressure of \( 10^{-6} \) Pa. After an experiment, only heptane was detected.

The heptane that was to be introduced into the chamber was first degassed in the flask outside the chamber, as shown schematically in Fig. 1. At the end of the degassing process, the vapour-phase pressure and the temperature in the flask were measured. The vapour-phase pressure corresponded to the saturation–vapour pressure at the measured temperature, indicating that the heptane was degassed. Afterwards, the heptane was transferred from the degassing flask to the
chamber without exposure to the atmosphere using the vacuum system indicated in Fig. 1. With the heptane flowing slowly through the chamber, the cooling of the solid substrate to \( T_S \) was initiated. It was maintained constant during each experiment and ranged from 298.8 \( \pm \) 0.1 K down to 295.7 \( \pm \) 0.1 K in the different experiments. Using an independent cooling circuit, the chamber walls were maintained at 301 \( \pm \) 0.2 K. The criterion for the steady-state was that the system temperatures did not change by more than 1% in 30 minutes.

During the period required to bring the system to the steady state (approximately three hours), we assume that some heptane condensed on the 'cooled stainless steel cylinder' resulting in a shallow condensate pool, as indicated schematically in Fig. 1. When the system had reached the steady state, the interferometer was used to measure the thickness of the adsorbate. The measurements at each of the \( y^{VS} \) values are summarized in Table 1.

Once the system had reached the steady state, a second spectrum was recorded using the interferometer, and the two interferometer spectra of the Si surface were used with the software provided by the manufacturer to determine the thickness of the adsorbed film, \( \tau_m \) for each value of \( y^{VS} \). All of the experimental results are listed in Table 1. The measured values of \( \tau_m \) are also shown in Fig. 2. Note that as \( y^{VS} \) was increased from 1.12 to approximately 1.22, \( \tau_m \) reached its plateau value.

### 3 Steady state cluster distributions

In each of the experiments, the system was observed to evolve to a steady state at a given value of \( y^{VS} \). We assume that this state is reached when the two conditions listed in eqn (3) and (6) are reached, and that the vapour phase may be approximated as an ideal gas. We first show that the chemical potential of the saturated vapour, \( \mu(T^V, P_{sat}(T^V)) \), may be expressed in terms of \( y^{VS} \) and the chemical potential was evaluated at \( T_V \) and \( P_{sat}(T_S) \).

The ideal gas chemical potential, \( \mu(T, P) \), may be written as

\[
\mu(T, P) = f(T) + k_B T \ln P, \tag{8}
\]

where \( f(T) \) is an arbitrary function of temperature. We evaluate it by applying the relation at \( T^V \) and \( P_{sat}(T^V) \):

\[
f(T^V) = \mu(T^V, P_{sat}(T^V)) - k_B T^V \ln P_{sat}(T^V). \tag{9}
\]
Since the temperature function, given in eqn (7), we may obtain from eqn (11) the expression for the partition function of a cluster with \( \tau \) molecules. The possible energy levels of a degree of freedom are

\[
\epsilon_k^{(\zeta)} = \epsilon_0^{(\zeta)} + k \hbar \omega_0^{(\zeta)}; \quad \zeta = 1, 2, 3 \ldots \zeta_m; \quad k = 0, 1, 2, 3 \ldots ,
\]

where \( \epsilon_0^{(\zeta)} \) is the zero point energy of each degree of freedom of a cluster of \( \zeta \) molecules, and \( \hbar \) denotes the Planck constant divided by \( 2\pi \). The canonical ensemble and statistical thermodynamics were then applied to obtain the chemical potential expression of a cluster with \( \zeta \) molecules:

\[
\mu_{\zeta}^{SV} = k_BT^S \ln \left( \frac{a_\zeta}{a_0 a_\zeta} \right),
\]

where \( a_0 \) is the number of empty adsorption sites, and \( a_\zeta \) is the partition function of a cluster with \( \zeta \) molecules, and may be written as

\[
q_\zeta = \left( \frac{\exp \left( -\frac{-\epsilon_0^{(\zeta)}}{k_BT^S} \right)}{1 - \exp \left( -\frac{-\hbar \omega_0^{(\zeta)}}{k_BT^S} \right)} \right)^3 .
\]

This relation reduces to an identity when thermal equilibrium exists in the system.

The expression for \( \mu_{1}^{SV} \) of the adsorbed phase was constructed by Ward and Wu.\(^3\) They approximated each degree of freedom of an adsorbed cluster as a quantum mechanical, harmonic oscillator that had a fundamental frequency depending on the number of molecules in the cluster, \( \omega_0^{(\zeta)} \). We follow their procedure. The possible energy levels of a degree of freedom are

\[
\epsilon_{1,2,3}^{(\zeta)} = \epsilon_0^{(\zeta)} + k \hbar \omega_0^{(\zeta)}; \quad \zeta = 1, 2, 3 \ldots \zeta_m; \quad k = 0, 1, 2, 3 \ldots ,
\]

Table 1 Measured thicknesses of heptane films adsorbed on silicon, \( \tau_m(T^V) \) for \( T^V = 301 \pm 0.2 \)

<table>
<thead>
<tr>
<th>( T^V ) (K)</th>
<th>( P_{sat}(T^V) ) (Pa)</th>
<th>( T^S ) (K)</th>
<th>( P_{sat}(T^S) ) (Pa)</th>
<th>( \tau_m ) (nm)</th>
<th>( \Delta T ) (K)</th>
<th>( \delta_c ) (( \mu m ))</th>
<th>( \eta_l ) (m(^3) kmol(^{-1}))</th>
<th>( \tau_m ) (( \mu m )) (( \mu molm^{-2} ))</th>
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thus, for $\zeta$ equal to unity, eqn (17) gives

$$a_1 = a_0 q_1 \exp \left( \frac{\mu^V}{k_B T^S} \right),$$

or

$$a_1 = a_0 q_1 \left( \exp \left( \frac{\mu^V}{k_B T^S} \right) \right)^{T^V / T^S}.$$  \hspace{1cm} (18)

From eqn (3), (12) and (18), one finds

$$a_1 = a_0 q_1^{T^S} \left\{ \exp \left( \frac{\mu^V[T^V, P_{sat}(T^S)]}{k_B T^V} \right) \right\}^{T^V / T^S}.$$  \hspace{1cm} (19)

Recall that $a_1$ is the number of adsorbed clusters that consist of one molecule, and eqn (19) results from the condition for the steady state between the vapour phase at $T^V$ and the adsorbed phase at $T^S$, eqn (3) and (14).

When eqn (6) is combined with eqn (3), the chemical potential of a cluster with $\zeta$ molecules can be written as

$$\mu^S(T^S) = \zeta \mu^V(T^S),$$  \hspace{1cm} (20)

after making use of eqn (12), $\mu^S(T^S)$ may be written as

$$\mu^S(T^S) = \zeta \left\{ k_B T^V \ln \left( \frac{y^S}{T^S} \right) \right\} \left( \frac{\mu^V[T^V, P_{sat}(T^S)]}{k_B T^V} \right)^{T^V / T^S}.$$  \hspace{1cm} (21)

When eqn (21) is substituted in eqn (17), the result can be written as

$$a_1 = a_0 q_1 \left( \exp \left( \frac{\mu^V[T^V, P_{sat}(T^S)]}{k_B T^V} \right) \right)^{1 / T^S}.$$  \hspace{1cm} (22)

it may be simplified to:

$$a_1 = a_0 q_1 \left( \frac{T^S}{y^S} \right)^{1 / T^S} \left( \frac{\mu^V[T^V, P_{sat}(T^S)]}{k_B T^V} \right)^{T^V / T^S},$$  \hspace{1cm} (23)

and, from eqn (19) and (23), one finds

$$a_1 = a_1 \left( \frac{T^S}{y^S} \right)^{1 / T^S} \left( \frac{\mu^V[T^V, P_{sat}(T^S)]}{k_B T^V} \right)^{T^V / T^S}.$$  \hspace{1cm} (24)

This equation relates $a_1$ to conditions in the vapour phase. Even though clusters with more than one molecule are not exchanged with the vapour phase, the relation comes because $A_1$ is in local equilibrium with the other adsorbed clusters, $A_1$, and with the vapour phase as required by eqn (3) and (6).

### 3.1 Expression for the amount adsorbed in steady, thermal disequilibrium states

Since the number of clusters that have $\zeta$ molecules is denoted $a_\zeta$, the total number of molecules adsorbed in the steady thermal-disequilibrium states, $n_{ad}(y^V)$, may be expressed as

$$n_{ad}(y^V) = \sum_{\zeta=1}^{n_{oc}} \zeta a_\zeta.$$  \hspace{1cm} (25)

The expression we have established for $a_\zeta$ depends on $a_0$, eqn (17). We use the total number of adsorption sites, $M$, and the number of occupied sites, $n_{oc}$, to establish a relation that $a_0$ must satisfy.

$$M = a_0 + n_{oc},$$  \hspace{1cm} (26)

and $n_{oc}$ may be written as

$$n_{oc} = \sum_{\zeta=1}^{n_{oc}} \zeta a_\zeta;$$  \hspace{1cm} (27)

thus,

$$\frac{a_0}{M} + \sum_{\zeta=1}^{n_{oc}} \frac{a_\zeta}{M} = 1.$$  \hspace{1cm} (28)

Combining eqn (23) and (28) one finds, after summing the finite series that

$$\frac{a_0}{M} = -1 + q_1 \left( \frac{\mu^V[T^V, P_{sat}(T^S)]}{k_B T^S} \right)^{y^V / y^S} \left( \frac{T^S}{T^V} \right)^{1 / T^S}.$$  \hspace{1cm} (29)

where

$$g \equiv -1 + q_1 \left( \frac{\mu^V[T^V, P_{sat}(T^S)]}{k_B T^S} \right)^{y^V / y^S} \left( \frac{T^S}{T^V} \right)^{1 / T^S}.$$  \hspace{1cm} (30)

introduces two thermal-disequilibrium parameters $\beta_{id}$ and $\epsilon_{id}$:

$$\beta_{id}(T^V, T^S) \equiv q_1(T^S) \left( \frac{\mu^V[T^V, P_{sat}(T^S)]}{k_B T^S} \right)^{y^V / y^S}.$$  \hspace{1cm} (31)

and

$$\epsilon_{id}(T^S) \equiv q_1 \left( \frac{T^S}{T^V} \right)^{1 / T^S}.$$  \hspace{1cm} (32)

Then, $a_0/M$ can be written as

$$\frac{a_0}{M} = -1 + \beta_{id}^{y^V}.$$  \hspace{1cm} (33)

After substituting eqn (33) into eqn (23), one finds

$$a_\zeta = \frac{\beta_{id}^{y^V} - 1}{\epsilon_{id}(T^S)^{y^V - 1}} \left( \frac{T^S}{T^V} \right)^{\zeta - 1}.$$  \hspace{1cm} (34)

The expression for $a_\zeta$, given in eqn (34), may be inserted into eqn (25), and the result was summed to obtain the expression for $n_{ad}(y^V)$.
for $\eta_{id}$:

$$
\eta_{id}(y^{VS}) = \frac{M_{Cd}b_{id}(y^{VS}) \left[1 - (1 + \zeta_m)(b_{id}(y^{VS}) + s_m(b_{id}(y^{VS})) \right]}{1 - b_{id}(y^{VS}) \left[1 + (c_{id} - 1)b_{id}(y^{VS}) - c_{id}(b_{id}(y^{VS})) \right]}^{1 - \zeta_m}.
$$

In order to apply the expression for $\eta_{id}(y^{VS})$ given in eqn (35), we must determine the values of $M$, $c_{id}$, $s_m$ and $b_{id}$. Below we will use equilibrium adsorption measurements for this purpose. But we note that the fundamental assumptions made in eqn (3) and (6) are the ones used to obtain the results listed in eqn (33) to (35).

3.2 The limits of $b_{id}(y^{VS})$ approaching unity

When the expression for the cluster distribution, $a_z$, given in eqn (34), and the expression for $\eta_{id}(y^{VS})$ given in eqn (35) are examined in the limit of $b_{id}(y^{VS})$ approaching unity, the result indicates the singularities of the zero-over-zero type in both relations. But if the l’Hôpital rule is applied to each, one finds

$$
\lim_{(b_{id}(y^{VS}) \to 1)} a_z(y^{VS}) = \frac{M_{Cd}}{1 + c_{id} s_m},
$$

and

$$
\lim_{(b_{id}(y^{VS}) \to 1)} \eta_{id}(y^{VS}) = \frac{M_{Cd} s_m (1 + \zeta_m)}{(1 + c_{id} s_m)}.
$$

Since $c_{id}$ and $s_m$ are finite, there are no actual singularities in either function.

As will be seen, the steady state corresponding to $y_{id}$ equal to $b_{id}^{-1}$ is the state where the phase transition is predicted to be initiated. These relations, eqn (36) and (37), will aid in showing that the transition is a disorder-order type transition.

4 Equilibrium adsorption of heptane on a silicon nanopowder

In the equilibrium adsorption limit, $T^S$ and $y^{VS}$ have the same value, denoted $T$, and $y^{VS}$ is less than the saturation vapour pressure corresponding to this temperature, $P_{sat}(T)$. In this limit, $y^{VS}$, eqn (2) goes to

$$
\lim_{(T^S, T^V \to T, P^V < P_{sat}(T))} y^{VS} \to \chi^V,
$$

where

$$
\chi^V \equiv \frac{P^V}{P_{sat}(T)}, \quad \text{and} \quad \chi^V < 1.
$$

Finally, in view of eqn (38) to (40), in this limit $\eta_{id}(y^{VS})$, eqn (35), becomes $n^{SV}(x^V)$, the amount adsorbed under equilibrium conditions, according to the equilibrium Zeta adsorption isotherm:

$$
\lim_{(T^S, T^V \to T, P^V < P_{sat}(T))} \eta_{id}(y^{VS}) = n^{SV}(x^V)
$$

where

$$
n^{SV}(x^V) = \frac{M_{Cd} x^V \left[1 - (1 + \zeta_m)(x^V)^{1 + \zeta_m} + s_m(x^V)^{1 + \zeta_m} \right]}{(1 - x^V) \left[1 + (c - 1)x^V - c(x^V)^{1 + \zeta_m} \right]}. \quad (41)
$$

Thus, in the equilibrium adsorption limit, $\eta_{id}(y^{VS})$ reduces to the equilibrium Zeta adsorption isotherm and it contains the four isotherm constants: $M$, $c$, $\chi$ and $\zeta_m$.

4.1 Measured equilibrium adsorption of heptane on a silicon nanopowder

We now propose to use equilibrium adsorption measurements and determine the values of the Zeta adsorption isotherm constants for heptane adsorbing silicon. In eqn (41), $n^{SV}$ is the amount adsorbed per unit area. It may convert the amount adsorbed per unit mass of the substrate by replacing $M$ with

$$
M = \frac{M_g}{A_{sat}(Si)} \quad (42)
$$

where $M_g$ is the number of adsorption sites per unit mass of the adsorbent, and $A_{sat}(Si)$ is the specific surface area, and can be expressed as

$$
A_{sat}(Si) = M_g \sigma_{\text{heptane}}, \quad (43)
$$

<table>
<thead>
<tr>
<th>Table 2 Equilibrium Zeta adsorption isotherm constants at 301 K, and thermal disequilibrium parameters for heptane adsorbing on silicon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibrium</td>
</tr>
<tr>
<td>0 &lt; $x^V$ &lt; 0.95</td>
</tr>
<tr>
<td>Thermal disequilibrium</td>
</tr>
<tr>
<td>1 &lt; $y^{VS}$ &lt; 1.31</td>
</tr>
</tbody>
</table>
where $\bar{a}_{\text{heptane}}$ is the average cross-sectional area of an adsorption site. Its value was determined by Zandavi and Ward,\textsuperscript{13} and is listed in Table 2.

The value of $\zeta_m$ cannot be determined from the equilibrium adsorption measurements. Only the threshold value, $\zeta_{th}$, can be obtained from such measurements. As demonstrated by Ward and Wu,\textsuperscript{3} when a value of $\zeta_m$ is assumed that is less than $\zeta_{th}$, the agreement between the calculated equilibrium adsorption compared to that measured increases as the assumed value of $\zeta_m$ is increased, until $\zeta_{th}$ is reached. If the assumed value of $\zeta_m$ is increased above $\zeta_{th}$, the agreement does not increase further. We shall determine $\zeta_m$ from the adsorbed-film thickness measurements, Fig. 2. Provided the value of $\zeta_m$ is greater than the $\zeta_{th}$, the amount calculated to be adsorbed under equilibrium conditions will not be affected by replacing $\zeta_{th}$ with $\zeta_m$. We use the equilibrium gravimetric measurements of the adsorption and desorption isotherms of heptane vapour adsorbing on a silicon nanopowder (Sigma Aldrich) to determine the value of the equilibrium adsorption isotherm parameters. The measurement procedure used is similar to that described previously: \textsuperscript{12–15}

A sample of approximately 10 mg of the silicon nanopowder was placed in an adsorption apparatus (Surface Measurements Systems) and heated in a $\text{N}_2$ atmosphere to 423 K, and held at this temperature for four hours. After cooling to 301 K, gravimetric measurements were made with $n_{SV}$ when anhydrous, $n$-heptane (Sigma Aldrich, 99% purity) was exposed to the nanopowder sample with $x^V$ in the range of 0 $<$ $x^V$ $\leq$ 0.95. When the change in $n_{SV}$ was less than 0.02% in 20 minutes at a value of $x^V$, the system was assumed to have reached equilibrium at that value of $x^V$.

The gravimetric measurements were converted to per unit area using $A_{\text{sat}}$($\text{Si}$). The amount adsorbed per unit area as a function of $y^V$ (or $x^V$) is shown in Fig. 3. The Nonlinear Regression Package of Mathematica\textsuperscript{TM} was used to determine the values of the equilibrium adsorption isotherm parameters that are listed in Table 2. The calculated amount adsorbed using eqn (41) and the equilibrium isotherm parameters are shown as the solid line in Fig. 3. Note then for these experiments $y^V \rightarrow x^V < 1$, eqn (38).

For the thermal disequilibrium experiments shown in Fig. 4, both $y^V$ and $T^V/T^S$ are each greater than or equal to unity, but we neglect any effect of reducing $T^S$ below $T^V$ on the value of the isotherm parameters, as indicated in Table 2. This assumption will be examined further when $\eta_{\text{ad}}(y^V)$ is calculated using the thermal disequilibrium values of the parameters and compared with the measurements in Fig. 4.

5 The cluster distribution and the entropy of the adsorbate

As indicated in Section 4.1, the data shown in Fig. 3 were used with eqn (41) to determine constants appearing in Table 2 for 0 $<$ $x^V$ $<$ 0.95, and then we used the results found from the thermal equilibrium limits (eqn (39) and (40)) to justify the values of $c_{\text{ad}}(T^S)$ and $\beta_{\text{ad}}(T^O,T^S)$ listed in this table.

For $y^V$ equal to or greater than 1.22, as seen in Fig. 2, the measured film thickness, $\tau_m$, was uniform. We assume that in the uniform range, the specific volume of the adsorbed fluid may be approximated as that of saturated liquid heptane, $v_s$ at the measured solid interface temperature, $T^S$. The adsorption in this range calculated on this basis is listed in the penultimate column of Table 1. Since the parameters, other than $\zeta_m$, that appear in the expression for $\eta_{\text{ad}}(y^V)$ have been determined, and are listed in Table 2, the Nonlinear Regression Package of
Mathematica™ may be used with eqn (35) and the measured amount adsorbed, \( \tau_m (y^\text{VS}) \), to determine the value of \( \zeta_m \) that minimizes the difference between that measured and that predicted in the uniform range. The value of the \( \zeta_m \) determined by this procedure is listed in Table 2. Note that the value of \( \zeta_m \) is greater than the \( \zeta_{th} \).

### 5.1 The molecular cluster distribution indicates a phase transition

From eqn (33) and (34) and the parameters listed in Table 2, the cluster distributions \( a_0(y^\text{VS})/M \) and \( a_i(y^\text{VS})/M \) as a function of \( y^\text{VS} \) were calculated and are shown in Fig. 4(a) and (b). For \( y^\text{VS} \) much less than \( \beta_{ad}^{-1} \), the adsorption sites are mostly empty; but when \( y^\text{VS} \) is increased to 0.13, the number of occupied sites exceeds the number of unoccupied sites. For \( y^\text{VS} \) approaching \( \beta_{ad}^{-1} \), the sites are mostly occupied by single molecules, and the clusters with \( \zeta_m \) molecules occupy the smallest number of sites, but when \( y^\text{VS} \) reaches \( \beta_{ad}^{-1} \), as indicated by eqn (36) and Fig. 5, the number of each cluster-type in the adsorbate is the same. Since each cluster type would be identifiable, this means that the configuration degeneracy of the adsorbate—i.e. the number of ways the cluster-types could be distributed over the \( M \) adsorption sites—would be a maximum, as would be the disorder of the adsorbate.\(^5\,^7\)

When \( y^\text{VS} \) exceeds \( \beta_{ad}^{-1} \), clusters with the largest number of molecules, \( \zeta_m \), become the dominate cluster-type in the adsorbate. We assume that these clusters are liquid-like and that when \( y^\text{VS} \) exceeds \( \beta_{ad}^{-1} \), the adsorbed liquid phase is initiated.

This assumption is supported by the measured amount adsorbed under both thermal equilibrium and disequilibrium conditions. The measured amount adsorbed for \( y^\text{VS} \) less than or equal to unity is shown on different scales in Fig. 3 and 4. For \( y^\text{VS} \) greater than or equal to unity, \( \tau_m (y^\text{VS})/n_l \) is listed in Table 1 and shown as data points with error bars in Fig. 5. The calculated amount adsorbed obtained from eqn (35) using the parameters listed in Table 2 is shown in Fig. 5 as the solid line. Note that the calculated adsorption is within error bars of that measured.

The notion that a phase transition occurs for \( y^\text{VS} \) greater than \( \beta_{ad}^{-1} \) is supported by the measured change in the amount adsorbed, \( \delta n \), shown in Fig. 5. It is defined by

\[
\delta n \equiv \left[ \frac{\eta_{ad}(1.22) - \eta_{ad}(0.95)}{\eta_{ad}(0.95)} \right]
\]

where 0.95 is the largest value of \( y^\text{VS} \) at which we are able to measure the equilibrium amount adsorbed. The results suggest that the amount adsorbed undergoes a sudden increase to a value that is 57 times larger than the value of \( \eta_{ad} \) at 0.95, and could be characterized as a phase transition.

### 5.2 The adsorbate entropy indicates a disorder–order phase transition

We now examine the transition for \( y^\text{VS} \geq \beta_{ad}^{-1} \) from the point of view of the adsorbate entropy. At a given value of \( y^\text{VS} \) for both equilibrium and thermal disequilibrium experiments, the temperature of the solid surface is known, the solid surface area is constant, and the total number of molecules adsorbed is known. For the thermal disequilibrium experiment, the adsorbed phase has been assumed to be in local equilibrium. Thus, we may use the canonical ensemble expression for the entropy of the adsorbate, \( S^\text{SV}(y^\text{VS}) \):

\[
S^\text{SV}(y^\text{VS}) = -k_B \left[ \frac{a_0(y^\text{VS})}{M} \ln \frac{a_0(y^\text{VS})}{M} + \sum_{i=1}^{\zeta_m} \frac{a_i(y^\text{VS})}{M} \ln \frac{a_i(y^\text{VS})}{M} \right]
\]

Fig. 5 The adsorption of heptane vapour on silicon is shown for the complete range of \( y^\text{VS} \). In the phase transition indicated when \( y^\text{VS} \) exceeds \( 1/\beta_{ad} \), the value of \( \delta n \) defined in eqn (44) was 57. The solid line was calculated using eqn (35) with the parameters values listed in Table 2 with \( \zeta_m \) chosen as 356. Note that there is no measured disagreement between the calculations and either the equilibrium or thermal disequilibrium experiments.

Fig. 6 The non-dimensional entropy of the adsorbate as a function of \( y^\text{VS} \) is shown. At \( y^\text{VS} \) equal to \( \beta_{ad}^{-1} \), the entropy of the adsorbate reaches its maximum value as expected, since the number of clusters of each type, as indicated in Fig. 4 and 7, has the same value, the clusters are identifiable, and thus the quantum mechanical degeneracy of this configuration would be a maximum. As the \( y^\text{VS} \) is increased above \( \beta_{ad}^{-1} \), the entropy of the adsorbate decreases and the adsorbate becomes more ordered.
predicted to be reduced: only clusters with more than 100 molecules are predicted to be present in the adsorbate; thus the number of possible cluster-types is 356 minus 100 or 256 cluster-types in the adsorbate (see Fig. 7). When \( y^{\text{VS}} \) is increased to 1.31, only cluster-types with more than 300 molecules are predicted to be present, or 56 cluster types. As the number of cluster-types is decreased—by reducing \( T_{\text{S}} \) relative to \( y^{\text{VS}} \)—the configurational degeneracy of the adsorbate is predicted to decrease, and therefore so would its entropy or the possible disorder of the adsorbate, as seen in Fig. 6.

The phase transition that is initiated at \( y^{\text{VS}} \approx b_{\text{id}}^{-1} \) (Fig. 5) is indicated in Fig. 6 and 7 to be the disorder–order phase transition that takes place when thermal disequilibrium exists between the vapour and the adsorbate. From the known value of \( y^{\text{VS}} \) required to initiate the phase transition, the temperature of the substrate, \( T_{\text{bf}}^{\text{id}} \), can be calculated from eqn (7), and is found to be 298.3 ± 0.2 K. Since the temperature of the vapour in these experiments was 301 ± 0.2, we find that the subcooling temperature required to initiate the transition from an adsorbed vapour to adsorbed liquid is 2.7 ± 0.4 K. This result is in contrast to the assumption of the continuum model\(^1\) which assumes that no subcooling is required for the phase change.

6 Discussion

The continuum approach to predicting the thickness of the film formed on a vertically oriented surface in a gravity field when a saturated vapour at \( T_{\text{sat}}(p^{\text{VS}}) \) is in contact with a solid surface that is maintained at a \( T_{\text{S}} \) that is less than \( T_{\text{sat}}(p^{\text{VS}}) \) was originally presented by Nusselt\(^1\) in 1916 and his model is still often discussed—over 1100 citations listed on the Web of Science\(^\text{TM}\)—but we have not found any experimental confirmation of the Nusselt-based calculations.

The conditions in our experiments correspond closely to those assumed in the Nusselt model: a liquid film lies on the bottom surface of the experimental chamber during our experiments, Fig. 1, and the temperature, \( T_{\text{S}} \), was measured near the liquid–vapour interface. We take the vapour phase to be saturated at this measured temperature. The solid surface temperature, \( T_{\text{S}} \), was determined using the 12 thermocouples that were implanted in the solid substrate.\(^5\) The value of \( T_{\text{S}} \) in each experiment is listed in Table 1. In both the Nusselt model and in the approach presented herein, a steady state is assumed to exist in the system.

Both the value of \( \Delta T \), eqn (1), in each of our experiments and the corresponding value of the film thickness calculated from the Nusselt model, \( \delta_{\text{N}} \), are listed in Table 1, along with the measured values of the film thickness, \( \tau_{\text{m}} \).

Note that in each experiment, the value of \( \delta_{\text{N}} \) is at least three orders of magnitude greater than that measured. Such a large difference between measurements and model calculations often indicates the difference in conception: in the Nusselt approach the liquid film is assumed to form without the need for subcooling, and the film growth is assumed to be controlled.
by thermal energy transport. The expression for this transport was developed using the heat transfer coefficient hypothesis. The vapour was assumed to be stagnant. This reduced the heat transfer problem to a thermal conduction problem.\textsuperscript{18} Thermal equilibrium was assumed at both the liquid–vapour and solid–liquid interfaces.

Although assuming the thermal equilibrium at an interface when a phase change is occurring there has been the standard assumption, it has been challenged recently both experimentally\textsuperscript{19–22} and by simulations.\textsuperscript{4,6} We note that in the cluster approach, it was unnecessary to introduce the heat transfer coefficient or to assume thermal equilibrium at an interface where the phase change was occurring.

In the proposed approach, the basic assumptions were that for a steady state to exist the cluster distributions had to be such that eqn (3) and (6) were satisfied. These assumptions led to an expression for the amount adsorbed, $\eta_{ad}(y^V)$. As seen in Fig. 5, it was shown to be in agreement with the measured amount adsorbed under both equilibrium and thermal disequilibrium conditions.

### 7 Conclusion

The molecular cluster approach that was used to develop the Zeta adsorption isotherm for equilibrium vapour adsorption has been extended to calculate the amount of vapour adsorbed under thermal disequilibrium conditions, $\eta_{ad}(y^V)$. This approach indicates that when heptane vapour at $T^V$ is exposed to a smooth silicon substrate at a $T^S$ that is less than $T^V$, a steady state cluster distribution forms in which the adsorbate consists of molecular clusters with $\zeta$ molecules in each cluster, where $\zeta$ can be 1, 2, 3...$\zeta_m$. If thermal equilibrium exists in the system, $\eta_{ad}(y^V)$ reduces to the equilibrium Zeta adsorption isotherm, $\eta^S(y^V)$. As a result, as indicated in Fig. 4, $\eta_{ad}(y^V)$ can be used to calculate the amount adsorbed under both thermal equilibrium and thermal disequilibrium conditions.

Under thermal disequilibrium conditions, when the temperature function, $y^V_{VS}$, is increased above unity to $(\beta_{ad})^{-1}$, by lowering $T^S$ relative to $T^V$, a state of maximum disorder is reached in which the number of clusters of each type has the same concentration in the adsorbate, see Fig. 6 and 7. A further increase in the temperature function $y^V_{VS}$ is predicted to initiate an adsorbed liquid phase by a disorder–order transition, Fig. 5. The adsorbed phase then becomes progressively more uniform as the dispersion in the cluster distribution is reduced as $y^V_{VS}$ is increased further.

The continuum predictions of the thickness of an adsorbed liquid film as a function of $\Delta T$ are remarkably different from those measured using the UV-vis interferometer. The measured film thickness is in agreement with the predictions of the cluster approach, $\eta_{ad}(y^V_{VS})$ as seen in Fig. 4. This difference reflects the difference in the theoretical basis for the predictions. The continuum approach assumes that the liquid phase is initiated whenever $\Delta T$ is greater than zero, but the molecular cluster approach indicates that the adsorbed vapour does not make a transition to an adsorbed liquid until $\Delta T$ reached 2.7 K or $y^V_{VS}$ reached 1.143.

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### References