Calculations of heat capacities of adsorbates

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The phonon contribution to the heat capacity has been calculated for ^{4}He on Xe; for Ne on Ar, Kr, and Xe; for Ar on Kr and Xe; and for Kr on Xe. These are, to our knowledge, the first such calculations for real systems. In each case, a model was taken in which the substrate has a perfect (100) surface and the adsorbate goes down as a solid monolayer in registry with the substrate. The quasiharmonic approximation was used, and the results for Ne adsorbates were considerably different from those obtained in the harmonic approximation, because the large zero-point vibrations of the Ne atoms produce a substantial expansion normal to the surface. We find that the quasiharmonic approximation does not even exist for He on Ne, Ar, and Kr, or for ^{3}He on Xe, just as it does not for bulk ^{3}He or ^{4}He. For several cases, including ^{4}He on Xe, the calculated heat capacity becomes slightly negative at low temperatures.

I. INTRODUCTION

There have been many heat-capacity measurements for ^{3}He and ^{4}He adsorbed on various substrates,[1-4] and several measurements for Ne and other noble-gas or molecular adsorbates.[5-8] Here we report calculations of adsorbate heat capacities for seven systems involving one noble gas on the surface of another.

We begin by listing the limitations of our treatment: First, it is assumed that the adsorbate (as well as the substrate) is a solid, in which the atoms vibrate about fixed positions, and only the phonon contribution to the specific heat is considered. Second, it is assumed that the substrate has a perfect (100) surface. Third, it is assumed that the adsorbed atoms go down as a monolayer, in perfect registry with the substrate (and with the same positions parallel to the surface that an extra layer of substrate atoms would have). Fourth, we make the quasiharmonic approximation, in which the atoms are assumed to vibrate with small amplitudes about their mean positions. Since the expansion due to the zero-point vibrations is taken into account in this approximation, we expect it to be rather accurate for the heavier adsorbates (Ar and Kr) at low temperatures, semiquantitative for Ne, and only qualitatively valid in the case of ^{4}He on Xe. Finally, we take the atoms to interact through Lennard-Jones potentials, $\phi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, with the ϵ and σ for adsorbate-substrate interactions given by $\epsilon_{AS} = (\epsilon_A \epsilon_S)^{1/2}$, $\sigma_{AS} = \frac{1}{2}(\sigma_A + \sigma_S)$. Here ϵ_A, σ_A and ϵ_S, σ_S are, respectively, the potential parameters for adsorbate and substrate. This form for the interaction between atoms is traditional and probably not terribly inaccurate.

In the next two sections, we describe our method of calculation and the results.

II. METHOD OF CALCULATION

Our method is straightforward: First, the positions of the adsorbate atoms are determined by minimizing the zero-point energy. Then the vibrational frequencies and heat capacity are calculated for the system of adsorbate plus substrate. Finally, the heat capacity for the substrate alone is calculated, and is subtracted off to give the heat capacity associated with the deposition of the adsorbate.

In the quasiharmonic approximation, the zero-point energy per particle is given by

$$U = \Phi + \frac{1}{N} \sum_\omega \tfrac{1}{2}\hbar\omega , \qquad (2.1)$$

where Φ is the static energy, N is the number of particles, and ω is a vibrational frequency. If

$$\omega^* = \omega(M_S \sigma_S^2/\epsilon_S)^{1/2} \qquad (2.2)$$

then

$$U/\epsilon = \Phi/\epsilon + \tfrac{3}{2}\Lambda_S \langle\omega^*\rangle , \qquad (2.3)$$

where $\langle\omega^*\rangle$ is the average vibrational frequency and $\Lambda_S \equiv \hbar/(M_S\epsilon_S)^{1/2}\sigma_S$ is the de Boer parameter for the substrate.

In order to find the positions of the adsorbate atoms, we varied the spacing d between these atoms and the last plane of substrate atoms. For a given value of d, we determined the normal mode frequencies in the standard way[9] for a coarse mesh of planar wave vectors $\vec{q} = (q_x, q_y)$ with six values in the irreducible one-eighth of the surface Brillouin zone. (Our notation is explained in Ref. 9.) We searched for a minimum in the expression (2.3) as d was varied, until we were satisfied that our value of d was correct to three places. The results for d/a, where $\sqrt{2}\,a$

is the nearest-neighbor spacing in the substrate, are given in Table I.

Next we carried out a more accurate calculation of the vibrational frequencies at the correct value of d, using a mesh with 45 $\bar{q}$ values in the irreducible element. (In the full surface Brillouin zone, the $\bar{q}$ values lay on a uniformly spaced 17 ×17 grid.) These values of ω were used to determine the heat capacity at constant volume C_v according to the standard expression

$$\frac{C_v}{k_B} = \sum_{\omega} \frac{e^x x^2}{(e^x - 1)^2} , \tag{2.4}$$

$$x \equiv \omega^*/T^* , \tag{2.5}$$

$$T^* \equiv T(k_B/\hbar)(M_S \sigma_S^2/\epsilon_S)^{1/2} . \tag{2.6}$$

Here, as in the determination of d, our calculations of the normal mode frequencies were for an 11-layer slab, with nine layers of substrate sandwiched between one adsorbed layer on each surface.

We then (conceptually) removed the two adsorbed layers and calculated the heat capacity C_v^{sub} for a nine-layer slab of the substrate material with free surfaces. (The same 45 $\bar{q}$ values were used.) Finally, we calculated the heat capacity per adsorbed atom C^a by taking the difference

$$C^a = (C_v - C_v^{sub})/2\bar{N}. \tag{2.7}$$

Here $\bar{N}$ is the total weight of the sample points in the surface Brillouin zone which are represented by those in the irreducible one-eighth. (In the present case, for the 17×17 mesh that gives 45 points in the irreducible one-eighth, $\bar{N}= 256$.) One can think of $\bar{N}$ as being the number of adsorbed atoms on each of the two surfaces, since the number of $\bar{q}$ values in the Brillouin zone is equal to the number of planar lattice points, which in the present case is equal to the number of adsorbed atoms on one surface.

Our values for the ϵ and σ of adsorbate and substrate atoms were taken from the articles of Horton[10] (for Ne, Ar, Kr, and Xe) and de Boer[11] (for He). We took the spacing between atoms in

the substrate to be that appropriate for the given substrate material at 0 °K: With $\sqrt{2}a$ the nearest-neighbor distance, $\sigma/a = 1.284$ for Ar, 1.289 for Kr, and 1.292 for Xe.

We mention that the thickness of our slab should be adequate for calculations of the adsorbate heat capacity, since the effect of the adsorbate does not penetrate very deeply. Also, our (17×17) mesh of $\bar{q}$ values should be adequate at those temperatures where the adsorbate heat capacity has an appreciable value ($T > 1$ °K).

III. RESULTS

In Figs. 1 and 2, the calculated values of the adsorbate heat capacity are shown for seven systems: ^{4}He on Xe; Ne on Ar, Kr, and Xe; Ar on Kr and Xe; and Kr on Xe.

In attempting to treat ^{3}He and ^{4}He on Ne, Ar, and Kr, and ^{3}He on Xe, we found that the quasiharmonic approximation does not even exist for these systems, just as it does not exist for bulk He,[12] because of the very large zero-point vibrations of the He atoms. For example, in our calculations for He on Ar, U decreases monotonically as d increases from 0.76a to 0.97a. (The static energy is minimized at $d = 0.76a$.) For $d > 0.97a$, some of the quasiharmonic frequencies ω become imaginary. There is thus no value of d for which U is minimized and the frequencies are all real, so a consistent quasiharmonic calculation is impossible. For ^{4}He on Xe, however, the binding is strong enough (and the mass large enough) to bring d down into the range where a calculation
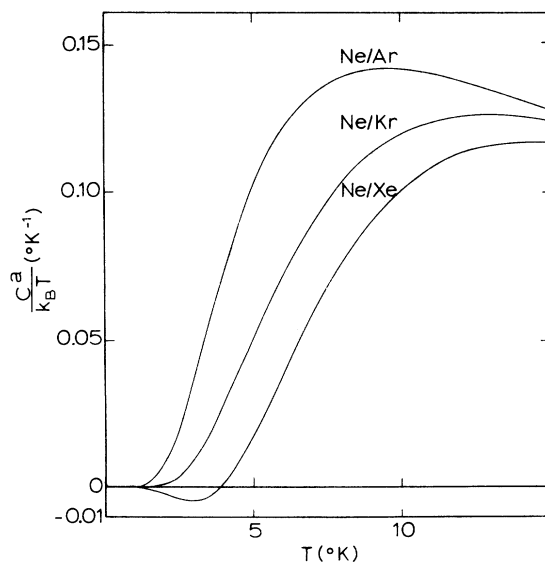
TABLE I. Interplanar spacings.

System	d/a
He on Xe	0.804
Ne on Ar	0.887
Ne on Kr	0.823
Ne on Xe	0.745
Ar on Kr	0.973
Ar on Xe	0.897
Kr on Xe	0.951

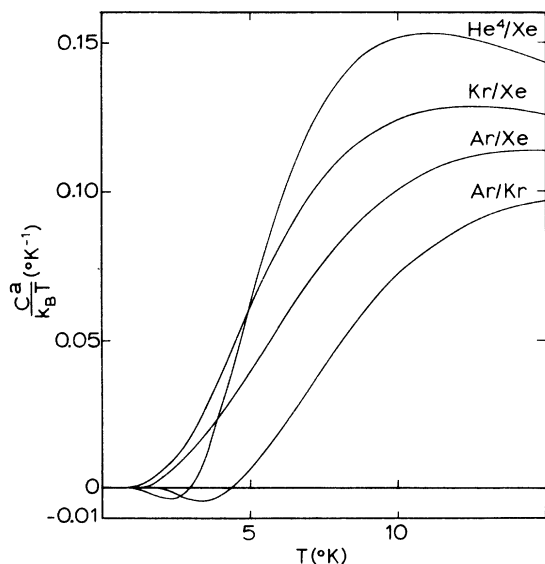FIG. 1. Heat capacity per adsorbed atom C^a as a function of the temperature T for Ne on Ar, Kr, and Xe.

FIG. 2. C^a vs T for ^{4}He on Xe, for Ar on Kr and Xe, and for Kr on Xe.

is possible.

We mention that the calculated values of C^a for Ne adsorbates have been raised considerably above the values that we obtained previously in the harmonic approximation.[13] This is not unexpected, of course, because the large zero-point vibrations of the Ne atoms result in large values of d, so that the force constants and frequencies are very much reduced for vibrations normal to the surface, and as a consequence C_v increases according to (2.4).

In Figs. 1 and 2, C^a falls rapidly at low temperatures, in qualitative agreement with the experimental results for He in registry with a graphite substrate[2] and the results of Antoniou et al.[4,7] for He and Ne on graphite. For Ne on Xe, Ar on Kr, and ^{4}He on Xe, the calculated C^a becomes slightly negative at low temperatures.

To our knowledge, the calculations of this paper are the first for real adsorbate-substrate systems (as opposed to mass-defect models[14,15]). Experimental studies of any of the systems that we have treated would be of interest.

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