Critical temperatures of two-dimensional condensation in the first adlayer of noble gases on the cleavage face of graphite

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A set of adsorption isotherms of Ar on the basal face of graphite gives for the critical temperature of twodimensional condensation in the first adlayer a value of 59 ± 1 K, significantly different from that previously accepted. This value, together with those obtained for Kr and Xe, agrees well with the prediction of a virial expansion truncated after the fourth coefficient, suggesting that the liquid phases of the first monolayers of noble gases adsorbed on graphite are not significantly perturbed by the surface structure.

I. INTRODUCTION

In a recent article Estevez, Gould, and Cole¹ compare experimental and theoretical estimates of critical temperatures of noble gases for threedimensional (3D) as well as two-dimensional (2D) systems, the latter being the first layers of these gases adsorbed on the basal face of graphite. Their discussion of the 2D problem is somewhat marred by two defects: (i) the experimental values they take for the critical temperatures of 2D condensation of Ar and Ne on graphite are incorrect; (ii) the theoretical estimates of the 2D critical temperatures are based on virial expansions limited to the third term. Both these shortcomings can now be partly overcome. Indeed, we shall present here a new determination of the 2D critical temperature for the first layer of Ar on graphite, showing that the previously accepted value was somewhat high. More important for our discussion is the fact that the fourth virial coefficient for assemblies of Lennard-Jones (LJ) disks has been recently calculated,² resulting in a much more precise estimate of the 2D critical temperature. At last we think that the comparison between theory and experiment can be improved now by using for the LJ potential the parameters derived by McDonald and Singer³ from liquid-state properties rather than the classical one based on the value of the second virial coefficient of the gaseous phase.

II. EXPERIMENTAL RESULTS

In Fig. 1 a set of adsorption isotherms of Ar on graphite in the monolayer domain and at temperatures close to the critical value are shown. By a procedure we have described earlier,^{4,5} we estimate that $T_{20}(Ar) = 59 \pm 1$ K, a value in good agreement with that of 58 ± 1 K recently proposed by Millot.⁶ Our value should be somewhat more accurate, since it was estimated from a larger number of isotherms in the vicinity of the critical temperature. Both are significantly lower than a value of 67 K previously proposed by Steele and Karl⁷ from heat-capacity measurements. But in these already old measurements the calorimetric signal attributed to the critical behavior was rather low compared to the background. Thomy and Duval⁸ also give a rather high value of 65 K, but do not show the isotherms from which it is estimated. On the other hand the adsorption isoterms of Jura and Criddle⁹ clearly indicate that $T_{22}(Ar) < 63.8$ K, strongly supporting the result of Millot⁶ and ourselves.

For Kr and Xe on graphite the results of Thomy and Duval⁸ seem very reliable: $T_{\infty}(\text{Kr}) = 87$ K and $T_{\infty}(\text{Xe}) = 117$ K. However, for Kr we shall retain the result of Larher¹⁰ $T_{\infty}(\text{Kr}) = 85.3$ K, quite close to that of Thomy and Duval, but probably more accurate since it is estimated from a larger number of adsorption isotherms close to the critical point. In Table I the best estimates of T_{∞} for Ar, Kr, and Xe are given.

III. DISCUSSION

Potential barriers to translation for Ar, Kr, and Xe parallel to the basal plane of graphite have been estimated¹¹ as being equal to 37, 41, and 37 K, respectively. They are lower than the 2D thermal-motion energies of these atoms at their critical temperatures of 2D condensation on graphite so that a very high mobility of the atoms in the corresponding critical states is expected. This is a very strong argument for using continuum rather than lattice models for the analysis of the experimental results.

A method, simple in its principle, for estimating critical constants, is from truncated virial expansions. This has been done by Barker, Leonard, and Pompe¹² for 3D particles interacting through a 6-12 Lennard-Jones potential. They found that the critical temperatures $T_{3e}^* = kT_{3e}/\epsilon$

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FIG. 1. Adsorption isotherms of Ar on the basal face of graphite in the domain of formation of the monolayer and in the vicinity of the critical temperature.

were 1.449, 1.300, and 1.291, respectively, when the virial expansion was truncated after the third, fourth, and fifth coefficients. It appears that only a very rough estimate of a critical temperature can be expected when the fourth virial coefficient is not taken into account as was the case in the Estevez *et al.*¹ treatment of the 2D case. On the other hand, the small change in T_{3c} , 0.7%, when the fifth term is added to the virial series, leads us to conjecture that the estimate of T_{2c} from a series truncated after the fourth term is of sufficient accuracy for comparison with experimental data. We give now a semiempirical justification of this surmise.

How good an approximate theory is can generally be assessed by choosing a model potential for the molecular interactions and comparing the theoretical results with those obtained in computer experiments. Unfortunately this procedure works badly in the vicinity of critical points because the periodic boundary condition used in the computer simulations fails to account for the long-range fluctuations which play an outstanding part in the vicinity of critical points.¹³ As a consequence we have to compare theoretical results with real experimental ones.

The difficulty which arises in such a procedure is that real atoms interact through pair potentials much more complicated than the Lennard-Jones function and that three-body forces are not at all negligible.¹⁴ However it has been shown that a 6-12 Lennard-Jones potential constitutes a good effective expression to account for the equation of state of argon.¹⁵ Consequently a reasonable comparison of theoretical and experimental results can be expected on condition that a coherent

TABLE I. Critical temperature of 2D condensation of Ar, Kr, and Xe in the first adlayer adsorbed on the basal face of graphite.

Gas	<i>T_{2c}/</i> K	<i>Т_{3с}/</i> К	T ₂ , Experimental value	c/T _{3c} Estimate from virial series truncated after the fourth term	
Ar Kr Xe	$59 \pm 1^{a} \\ 85.3 \pm 1^{10} \\ 117 \pm 1^{8}$	150.8 ^b 209.4 ^b 287.733 ^b	0.391 0.407 0.404	0,381	

^aThis work.

^bReference 16.

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	• •	T_c^*	ρ_c^*	p_c^*	$p_c^*/\rho_c^* T_c^*$
Experimental	Ar	1.287	0.664	0.249	0.291
values ^a	Kr	1.284	0.664	0.245	0.287
	Xe	1.281	0.659	0.241	0.286
Estimate from virial series ^b truncated	fifth term	1.291	0.547	0.249	0.352
after the)	fourth term	1.300	0.561	0.257	0.352

TABLE II. Reduced critical constants of Ar, Kr, and Xe and theoretical estimates from virial series.

^aReference 16.

^bReference 12.

set of values of ϵ and σ is used for the effective pair potential of the adsorbates. Such a set has been derived by McDonald and Singer³ from the comparison of Monte Carlo results with experimental data: density and internal energy of the liquid at zero pressure over a large temperature range, but of course well below the critical point.

Using their value for ϵ and σ (line b of Table 5 in Ref. 3) and the critical data of Ref. 16, we have estimated the reduced critical constant of Ar, Kr, and Xe (Table II). The fact that these constants are almost the same for three noble gases as predicted by the classical law of corresponding states is a test of the coherence of the set of ϵ and σ values.

As far as the critical temperature is concerned the agreement with theory should be considered as good even when the virial series is truncated after the fourth term. Improvement of the theory by addition of further terms to the virial series might well result in worse agreement. What we conjecture is that the success achieved in three dimensions by the joint use of an effective potential and an approximate statistical theory is not significantly changed when going to two dimensions. This means that we accept for the ratio of the critical temperatures in two and three dimensions the ratio of the values obtained from the virial series truncated after the fourth term,^{2,12} i.e., $T_{xc}/T_{xc} = 0.492/1.291 = 0.381$.

A first interesting point concerning the experimental results (Table I) is that the ratio T_{xc}/T_{xc} is the same for Ar, Kr, and Xe, within experimental error. This is in contrast with the results observed in first adlayers of rare gases on lamellar halides for which important variations of the ratio T_{xc}/T_{xc} , in the range 0.40–0.55, strikingly related to the dimensional incompatibility between the adsorbate and the substrate, were observed.^{4,17,18} At the cleavage face of lamellar halides, potential barriers to translation are much higher than on graphite,¹⁹ so that these results were explained in term of the formation of a registered crystalline monolayer. In comparison, the lack of variation of the ratio T_{∞}/T_{∞} for Ar, Kr, and Xe on graphite supports the hypothesis that the measured critical temperatures correspond to a 2D gas-liquid transition, the law of corresponding states predicting in such a case that T_{∞}/T_{∞} is constant.²⁰

The theoretical results suggest a decreasing trend of the calculated ratio T_{x}/T_{x} as the number of terms of the virial expansion increases. As the theoretical estimate is already lower than the experimental one, by 5% on an average, the disagreement between theory and experiment might worsen as the statistical theory is improved by addition of new terms to the virial expansion. In the present conjoncture, the agreement between theory and experiment should be considered as satisfying, in particular since we are using an effective potential for the interaction between adatoms. Clearly from the calculations of Estevez *et al.*¹ quantum effects have a negligible influence on the value of T_{2c}/T_{3c} for Ar, Kr, and Xe. For neon of course we expect a lower value of kT_{e}/ϵ than for the heavier noble gases.²¹ According to Estevez et al.¹ the converse would be observed for Ne on graphite. However the experimental value they quote for T_{2c} (Ref. 22) concerns a 2D condensation in the second layer, where the potential barriers to translation are much higher than those encountered by the heavier rare gases at the surface of graphite. This temperature compares well with those obtained in second layers of Ar on lamellar halides for instance.¹⁸ A continuum model is obviously inadequate to account for the behavior of such systems.

Thomy and Duval⁸ have proposed a value of 75 K for the critical temperature of 2D condensation of CH₄ on graphite. Since these authors did not measure adsorption isotherms below 77.3 K, which is already 2.3 K above the proposed value of T_{xx} , the precision on this datum appears to us

difficult to assess, so that we have not included it in Table I. But of course the value $T_{20} = 75$ K yields a ratio $T_{\infty}/T_{\infty} = 75/190.55 = 0.394$ very close to those observed for Ar, Kr, and Xe and consequently supports the argument of this paper. It is of interest to point out an observation made by Sanders, Bretz, and Cole²³ that for the first adlayer on graphite kT_{∞}/ϵ increases from Xe to Ar and again from Ar to CH_4 . The first part of the statement is no longer true when a correct value of T_{∞} is taken for Ar. The second part contradicts our point of view and is puzzling since these authors also take for CH_4 the value of T_{20} proposed by Thomy and Duval.⁸ Of course the apparent conflict lies in the fact that Sanders *et al.*²³ have not taken a coherent set of ϵ leading to constant T_{∞}/ϵ as predicted by the classical law of corresponding states. When the parameters of McDonald and Singer³ which obey this law, are used kT_{2c}/ϵ for CH₄ takes the same value as for Ar, Kr, and Xe.

Among the critical constants only the tempera-

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ture has been discussed for two reasons: (i) the theory is much less effective in predicting the other two, density and pressure, as Table II shows for 3D systems; (ii) no really precise estimation of such 2D parameters is at present available.

We have compared the experimental results with a single theoretical estimate, although other theoretical predictions are known. Among these a Percus-Yevick (compressibility) estimate gives $T_{\infty}^* = 0.50$ (Ref. 24) very close to the value based on the virial expansion truncated after the fourth term $T_{\infty}^* = 0.492$. On the other hand, estimates by perturbation theories of Steele²⁵ and Henderson²⁶ yield higher values $T_{2c}^{*} = 0.60$ and 0.56, respectively. However, as noted by Henderson, such theories are not expected to give good estimates of a critical temperature since they would predict a positive critical temperature for a one-dimensional system. Neither are the estimates from computer simulations,^{27,28} as explained earlier.

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