## Comments and Addenda

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# Second virial coefficients of two-dimensional helium: The Beck potential*

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The second virial coefficients of two-dimensional systems of $He^3$ and $He^4$ have been calculated assuming that the atoms interact via the Beck potential. The virial coefficient and its contribution to the specific heat are almost the same as calculated previously with a Lennard-Jones potential. Therefore small discrepancies between experimental data and our previous calculation are ascribed to effects of the substrate.

In a recent paper,[1] the specific heat of low-density helium monolayers was calculated assuming that (i) the system behaves as if it were two dimensional at the temperatures of interest; (ii) the specific heat is adequately represented by the first two terms of its virial expansion; (iii) the helium interaction can be modeled by the standard Lennard-Jones 6-12 potential; and (iv) any effects of the substrate upon the specific heat can be ignored. That these assumptions were rather well justified was indicated by the good agreement between experimental data and calculated results. The comparison between theory and experiment is shown in Figs. 1 and 2 where the quantity

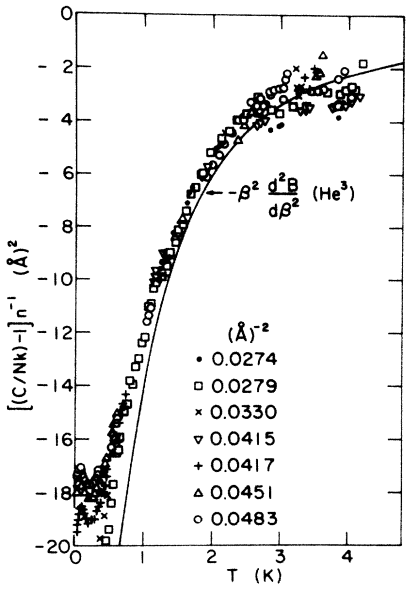


FIG. 1. Comparison of the deviation of the specific heat from unity per unit density, $(C/Nk-1)m^{-1}$, for adsorbed $He^3$ as determined experimentally and calculated assuming a Lennard-Jones 6-12 potential.

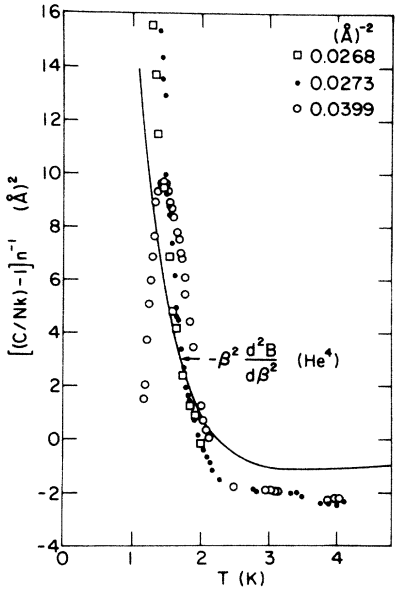


FIG. 2. Comparison of the deviation of the specific heat from unity per unit density, $(C/Nk-1)m^{-1}$, for adsorbed $He^4$ as determined experimentally and calculated assuming a Lennard-Jones 6-12 potential.

$(C/Nk-1)n^{-1}$ is shown versus temperature. Here $C/Nk$ is the specific heat in units of Boltzmann's constant and $n$ is the areal particle density in $\text{Å}^{-2}$. We note that the agreement with the $He^4$ data, while good, is inferior to the excellent agreement with the $He^3$ data. It is unlikely that this difference can be attributed to a failure of assumption (i), as it has been calculated[2] that the first excited state corresponding to motion perpendicular to the substrate has an excitation energy some 70 K greater than at the bottom of the lowest band. That assumption (ii) is adequate is indicated by the fact that the experimental data taken at different densities fall on a universal function of temperature when plotted as in Figs. 1 and 2. This is expected if the first two terms of a virial expansion are adequate, for then

$$C/Nk = 1-n\beta^2 \frac{d^2B(\beta)}{d\beta^2},$$

where $\beta = 1/kT$ and $B$ is the second virial coefficient, so that

$$(C/Nk-1)n^{-1} = -\beta^2 \frac{d^2B(\beta)}{d\beta^2},$$

which is a function of temperature only. It is the purpose of this note to report the result of an investigation of the adequacy of assumption (iii).

We have calculated the second virial coefficients $B$, $\beta dB/d\beta$ which occurs in the virial expansion of the entropy, and $\beta^2 d^2B/d\beta^2$, assuming that the atoms interact via the Beck[3] potential

$$V(r) = Ae^{-\alpha r-\gamma r^6} - \frac{B}{(r^2+a^2)^3}\left(1+\frac{2.709+3a^2}{r^2+a^2}\right),$$

where $A = 4.638\times 10^6$ K, $B = 1.00685\times 10^4$ K Å$^6$, $a = 0.675$ Å, $\alpha = 4.390$ Å$^{-1}$, and $\gamma = 3.746\times 10^{-4}$ Å$^{-6}$.

This potential has the correct theoretical dependence on distance for large particle separation and a short-range repulsive part fitted to theoretical values. In addition it reproduces the experimentally determined second virial coefficient of the bulk gas. The Beck potential differs from the Lennard-Jones potential primarily in that the repulsion is somewhat "softer" and the minimum

TABLE I. Second virial coefficient and related quantities for two-dimensional $He^3$ using the Beck potential.

| $T$ | $B$ | $\beta\frac{dB}{d\beta}$ | $\beta^2\frac{d^2B}{d\beta^2}$ | $T$ | $B$ | $\beta\frac{dB}{d\beta}$ | $\beta^2\frac{d^2B}{d\beta^2}$ |
|---|---|---|---|---|---|---|---|
| 0.100 00 | 24.158 74 | 76.045 54 | 13.834 99 | 3.100 00 | −1.482 17 | −8.253 68 | 3.358 71 |
| 0.200 00 | −10.332 79 | 27.957 11 | 23.654 06 | 3.200 00 | −1.222 59 | −8.098 44 | 3.215 20 |
| 0.300 00 | −17.870 06 | 10.264 92 | 25.856 90 | 3.300 00 | −0.975 70 | −7.948 42 | 3.082 46 |
| 0.400 00 | −19.465 10 | 1.288 91 | 25.136 84 | 3.400 00 | −0.740 58 | −7.803 48 | 2.959 38 |
| 0.500 00 | −19.153 21 | −3.828 10 | 23.366 36 | 3.500 00 | −0.516 41 | −7.663 42 | 2.844 98 |
| 0.600 00 | −18.159 63 | −6.915 11 | 21.322 50 | 3.600 00 | −0.302 43 | −7.528 08 | 2.738 38 |
| 0.700 00 | −16.938 43 | −8.828 37 | 19.311 99 | 3.700 00 | −0.097 96 | −7.397 26 | 2.638 82 |
| 0.800 00 | −15.675 42 | −10.020 61 | 17.449 75 | 3.800 00 | 0.097 62 | −7.270 80 | 2.545 62 |
| 0.900 00 | −14.449 36 | −10.751 05 | 15.770 61 | 3.900 00 | 0.284 89 | −7.148 51 | 2.458 19 |
| 1.000 00 | −13.292 42 | −11.176 77 | 14.275 80 | 4.000 00 | 0.464 38 | −7.030 22 | 2.375 98 |
| 1.100 00 | −12.215 49 | −11.397 13 | 12.953 01 | 4.100 00 | 0.636 56 | −6.915 74 | 2.298 52 |
| 1.200 00 | −11.219 55 | −11.477 12 | 11.785 26 | 4.200 00 | 0.801 87 | −6.804 93 | 2.225 39 |
| 1.300 00 | −10.301 02 | −11.460 36 | 10.754 83 | 4.300 00 | 0.960 73 | −6.697 62 | 2.156 21 |
| 1.400 00 | −9.454 43 | −11.376 80 | 9.844 93 | 4.400 00 | 1.113 51 | −6.593 65 | 2.090 65 |
| 1.500 00 | −8.673 71 | −11.247 31 | 9.040 37 | 4.500 00 | 1.260 56 | −6.492 89 | 2.028 40 |
| 1.600 00 | −7.952 82 | −11.086 66 | 8.327 64 | 4.600 00 | 1.402 19 | −6.395 19 | 1.969 19 |
| 1.700 00 | −7.286 05 | −10.905 39 | 7.694 96 | 4.700 00 | 1.538 70 | −6.300 41 | 1.912 79 |
| 1.800 00 | −6.668 17 | −10.711 09 | 7.132 05 | 4.800 00 | 1.670 38 | −6.208 44 | 1.858 96 |
| 1.900 00 | −6.094 43 | −10.509 26 | 6.630 04 | 4.900 00 | 1.797 47 | −6.119 14 | 1.807 52 |
| 2.000 00 | −5.560 59 | −10.303 88 | 6.181 22 | 5.000 00 | 1.920 22 | −6.032 41 | 1.758 28 |
| 2.100 00 | −5.062 85 | −10.097 81 | 5.778 94 | 6.000 00 | 2.950 93 | −5.284 71 | 1.358 44 |
| 2.200 00 | −4.597 83 | −9.893 14 | 5.417 45 | 7.000 00 | 3.720 09 | −4.702 17 | 1.069 02 |
| 2.300 00 | −4.162 53 | −9.691 34 | 5.091 75 | 8.000 00 | 4.316 32 | −4.233 48 | 0.844 91 |
| 2.400 00 | −3.754 27 | −9.493 46 | 4.797 53 | 9.000 00 | 4.791 93 | −3.846 58 | 0.663 91 |
| 2.500 00 | −3.370 66 | −9.300 20 | 4.531 05 | 10.000 00 | 5.179 87 | −3.520 58 | 0.513 55 |
| 2.600 00 | −3.009 58 | −9.112 05 | 4.289 04 | 11.000 00 | 5.501 99 | −3.241 27 | 0.386 07 |
| 2.700 00 | −2.669 14 | −8.929 27 | 4.068 67 | 12.000 00 | 5.773 38 | −2.998 65 | 0.276 25 |
| 2.800 00 | −2.347 62 | −8.752 03 | 3.867 48 | 13.000 00 | 6.004 81 | −2.785 47 | 0.180 34 |
| 2.900 00 | −2.043 51 | −8.580 38 | 3.683 30 | 14.000 00 | 6.204 17 | −2.596 30 | 0.095 41 |
| 3.000 00 | −1.755 44 | −8.414 29 | 3.514 26 | 15.000 00 | 6.377 42 | −2.426 98 | 0.019 01 |

TABLE II. Second virial coefficient and related quantities for two-dimensional $He^4$ using the Beck potential.

| $T$ | $B$ | $\beta\frac{dB}{d\beta}$ | $\beta^2\frac{d^2B}{d\beta^2}$ | $T$ | $B$ | $\beta\frac{dB}{d\beta}$ | $\beta^2\frac{d^2B}{d\beta^2}$ |
|---|---|---|---|---|---|---|---|
| 0.100 00 | −1184.902 99 | −1862.794 40 | −1089.534 90 | 3.100 00 | −8.920 01 | −16.947 97 | 1.213 41 |
| 0.200 00 | −415.034 46 | −608.629 08 | −303.522 98 | 3.200 00 | −8.389 78 | −16.456 49 | 1.239 22 |
| 0.300 00 | −231.015 33 | −328.933 90 | −156.007 50 | 3.300 00 | −7.890 52 | −15.995 46 | 1.255 58 |
| 0.400 00 | −154.067 28 | −214.409 46 | −99.312 43 | 3.400 00 | −7.419 51 | −15.561 92 | 1.264 18 |
| 0.500 00 | −113.292 04 | −154.438 53 | −69.628 02 | 3.500 00 | −6.974 36 | −15.153 32 | 1.266 39 |
| 0.600 00 | −88.560 74 | −118.522 49 | −51.278 90 | 3.600 00 | −6.552 94 | −14.767 41 | 1.263 36 |
| 0.700 00 | −72.167 35 | −95.100 98 | −38.807 13 | 3.700 00 | −6.153 35 | −14.402 24 | 1.256 07 |
| 0.800 00 | −60.588 33 | −78.891 25 | −29.836 11 | 3.800 00 | −5.773 90 | −14.056 05 | 1.245 29 |
| 0.900 00 | −52.008 43 | −67.162 29 | −23.150 52 | 3.900 00 | −5.413 08 | −13.727 31 | 1.231 68 |
| 1.000 00 | −45.408 09 | −58.373 38 | −18.050 74 | 4.000 00 | −5.069 51 | −13.414 64 | 1.215 81 |
| 1.100 00 | −40.175 60 | −51.596 91 | −14.097 65 | 4.100 00 | −4.741 96 | −13.116 83 | 1.198 11 |
| 1.200 00 | −35.924 25 | −46.245 55 | −10.997 80 | 4.200 00 | −4.429 31 | −12.832 75 | 1.178 98 |
| 1.300 00 | −32.398 88 | −41.932 17 | −8.546 07 | 4.300 00 | −4.130 55 | −12.561 44 | 1.158 73 |
| 1.400 00 | −29.425 03 | −38.393 05 | −6.594 21 | 4.400 00 | −3.844 76 | −12.302 00 | 1.137 63 |
| 1.500 00 | −26.879 73 | −35.443 46 | −5.032 45 | 4.500 00 | −3.571 10 | −12.053 61 | 1.115 88 |
| 1.600 00 | −24.674 00 | −32.950 95 | −3.777 94 | 4.600 00 | −3.308 80 | −11.815 54 | 1.093 68 |
| 1.700 00 | −22.741 96 | −30.818 58 | −2.767 28 | 4.700 00 | −3.057 16 | −11.587 14 | 1.071 17 |
| 1.800 00 | −21.033 86 | −28.974 08 | −1.951 33 | 4.800 00 | −2.815 52 | −11.367 78 | 1.048 48 |
| 1.900 00 | −19.511 43 | −27.362 73 | −1.291 70 | 4.900 00 | −2.583 31 | −11.156 91 | 1.025 71 |
| 2.000 00 | −18.144 76 | −25.942 46 | −0.758 11 | 5.000 00 | −2.359 97 | −10.954 03 | 1.002 95 |
| 2.100 00 | −16.910 14 | −24.680 53 | −0.326 55 | 6.000 00 | −0.519 74 | −9.276 89 | 0.786 16 |
| 2.200 00 | −15.788 54 | −23.551 14 | 0.022 15 | 7.000 00 | 0.813 68 | −8.050 14 | 0.600 02 |
| 2.300 00 | −14.764 48 | −22.533 70 | 0.303 36 | 8.000 00 | 1.824 61 | −7.108 76 | 0.443 67 |
| 2.400 00 | −13.825 25 | −21.611 68 | 0.529 45 | 9.000 00 | 2.617 13 | −6.360 62 | 0.311 47 |
| 2.500 00 | −12.960 31 | −20.771 60 | 0.710 44 | 10.000 00 | 3.254 66 | −5.749 88 | 0.198 15 |
| 2.600 00 | −12.160 83 | −20.002 43 | 0.854 45 | 11.000 00 | 3.778 10 | −5.240 57 | 0.099 12 |
| 2.700 00 | −11.419 38 | −19.295 03 | 0.968 09 | 12.000 00 | 4.215 06 | −4.808 34 | 0.010 01 |
| 2.800 00 | −10.729 62 | −18.641 80 | 1.056 77 | 13.000 00 | 4.584 88 | −4.435 98 | −0.073 84 |
| 2.900 00 | −10.086 15 | −18.036 35 | 1.124 91 | 14.000 00 | 4.901 46 | −4.110 87 | −0.157 58 |
| 3.000 00 | −9.484 29 | −17.473 27 | 1.176 13 | 15.000 00 | 5.175 09 | −3.823 38 | −0.246 77 |

occurs at a separation which is 0.1 Å larger.

The calculation of the second virial coefficient for the two-dimensional systems was carried out in a manner essentially identical to that described in Ref. 1. The sole difference is that quantities were calculated only for temperatures less than 15 K so that, to obtain the same estimated accuracy as in Ref. 1, phase shifts needed to be calculated only for momenta $K$ up to a value of $10/\sigma$, where $\sigma$ is the Lennard-Jones range parameter. Our results for $B$, $\beta\, dB/d\beta$, and $\beta^2 d^2B/d\beta^2$ are given in Tables I and II. In Fig. 3 are shown the differences $B_{LJ}-B_{Beck}$, $\beta^2 d^2(B_{LJ}-B_{Beck})/d\beta^2$ for $He^3$ and $He^4$, which are seen to be extremely small in the temperature range of interest. A comparison of Figs. 2 and 3 indicates that the difference in the calculated specific heats arising from the use of the Beck potential rather than the Lennard-Jones is much smaller than the discrepancy between the measured $He^4$ specific heats and that calculated in Ref. 1 with the Lennard-Jones interaction. Thus the discrepancy cannot be attributed to the use of that potential, but is rather al-

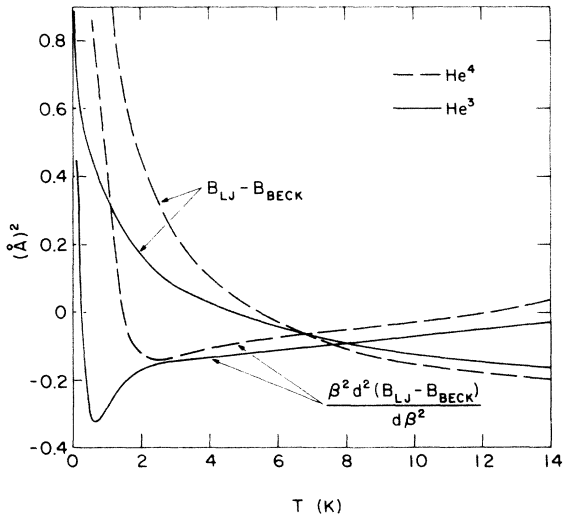


FIG. 3. Shown here are the differences between the calculated second virial coefficients using the Lennard-Jones and Beck potentials for adsorbed $He^3$ and $He^4$. Also shown is the second derivative of this difference with respect to inverse temperature.

most certainly due to the presence of the substrate.

There are many ways in which the presence of the substrate is made manifest in a calculation of the specific heat. First, there are effects which are simply due to the presence of the periodic substrate potential. This potential causes the first density-independent terms in the virial expansion of the specific heat to differ from unity by an amount which decreases at high temperatures; that is,

$$C/Nk = 1 + f(T) - n\beta^2 \frac{d^2B}{d\beta^2} + \cdots ,$$

with $f(T)$ approaching zero as $T$ increases without limit. Such a correction is evidently not large, however, for if it were, the experimental data plotted as $(C/Nk-1)n^{-1}$ would not fall on a universal curve. The presence of the periodic potential also causes a change in the second virial coefficient by destroying the translational invariance assumed in Ref. 1. However, the fact that the substrate potential has such a small effect on the single-particle spectrum[2] indicates that this effect is also likely to be small. It is our belief that the more important substrate effects are those which alter the interaction of two adsorbed atoms from that which exists between them in free space. This belief is strengthened by the fact that the discrepancy between the calculations of Ref. 1 and the experimental data is greater for the $He^4$, which is somewhat more tightly bound to the substrate, than for the $He^3$. The interaction between adsorbed atoms can be altered, *inter alia*, by the polarization of the atoms due to the substrate[4] and by exchange of virtual substrate phonons.[5] It is hoped that an investigation of the small discrepancy which now exists between the measured and calculated specific heat of adsorbed monolayers can be used to elucidate the effective interaction between adsorbed atoms and the mechanisms by which this interaction is produced.

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