PHASE TRANSITIONS IN THE HARD-SQUARE LATTICE GAS

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We wish to present here some results for a two-dimensional lattice gas of hard-square molecules; these results suggest the existence of a first-order phase transition of the solid-fluid type for molecules with an exclusion range extending over first-, second-, and third-neighboring sites of a square lattice. See Fig. 1.

Let us first recall the situation for the hard-square molecules with first-neighbor exclusions only [Fig. 1(a)]: Approximate treatments of the Kikuchi type[1] lead to a second-order transition in the sense of Ehrenfest (finite jump in the compressibility); more recently Gaunt and Fisher[2] by means of low- and high-density expansions, and Runnels[3] applying the matrix method of Kramers-Wannier to lattices of infinite length and finite width, concluded that this system presumably displays a second-order transition of the logarithmic type.

Now molecular dynamics and Monte Carlo calculations have shown that a system of hard disks exhibits a phase transition which looks like first order. It may therefore be expected that a two-dimensional lattice gas of hard molecules will display a transition of the same kind provided the range of interaction includes a sufficiently large number of sites. We therefore carried out calculations similar to those of Runnels[3] for systems of hard molecules with exclusions extending up to second and third neighbors.

We considered a cylindrical lattice of infinite length and finite circumference N, and constructed for each case the appropriate Kramers-Wannier matrix M wherefrom the thermodynamic pressure is obtained as

$$p/kT = (1/N)\ln\lambda_{\max};$$

$\lambda_{\max}$ is the largest eigenvalue of M and was calculated by an iterative process on a IBM 7040 computer as a function of the chemical potential μ. The density ρ and the quantity $kT \times \partial\rho/\partial\mu$ (proportional to the compressibility) were subsequently obtained by differentiation.

For hard molecules with exclusions extending up to second neighbors [Fig. 1(b)] the even cases $2 \leqslant N \leqslant 12$ were handled; no anomaly was observed in the compressibility for $\rho < 0.23$ (maximum density is $\rho = 0.25$). The occurrence of a weak transition (e.g., third order) at higher density, though not completely ruled out, seems rather improbable because this particular system does not reach a well-defined structure at close packing.

The case of hard molecules with exclusions extending up to third neighbors [Fig. 1(c)] is somewhat more difficult because M must now take care of all possible configurations of <u>two</u> neighboring rings of N sites. In order to allow the system to reach the close-packing configuration of Fig. 1(c), N must be a multiple of 5. The values of $kT\partial\rho/\partial\mu$ as a function of μ/kT are plotted on Fig. 2 for $N = 5$ and 10 (ma-

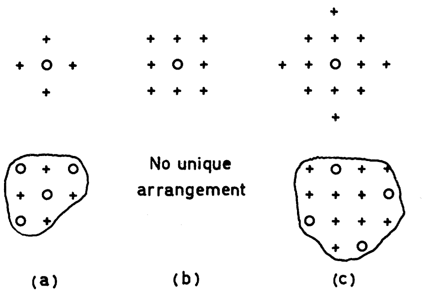

FIG. 1. Exclusion ranges and maximum-density packing for hard-square molecules with (a) first-neighbor, (b) first- and second-neighbor, (c) first-, second-, and third-neighbor exclusions.

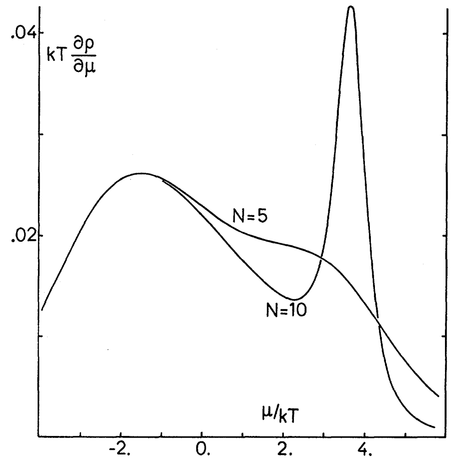

FIG. 2. Plot of $kT\partial\rho/\partial\mu$ vs μ/kT for $N = 5$ and 10; hard-square molecules of type (c) of Fig. 1.

trices 4×4 and 47×47, respectively, after due reduction for rotational symmetry around the cylinder). The small bump occurring around $\mu/kT\simeq3$ for $N=5$ is readily changed into a high narrow peak for $N=10$ at $\mu/kT\simeq3.6$ with the corresponding values $p/kT\simeq0.74$ and $\rho\simeq0.175$ (maximum density of this system is $\rho=0.20$). This clearly demonstrates that this system will (in the limit $N\rightarrow\infty$) display a phase transition. No definite conclusion about its exact nature can be drawn here. It appears, however, that the peak of Fig. 2 is much sharper than the corresponding one observed by Runnels[3] for first-neighbor exclusions only; therefore, the transition reported here could well be of the first-order type. This view is confirmed to some extent by approximate calculations for this same system based on the Rushbrooke-Scoins theorem[4] (which is nearly equivalent to the Kikuchi method): Including all configurations based on groups of five sites and less, we found a first-order phase transition with the following features:

$$\rho_{\text{fluid}}{}^*\simeq0.160,\ \rho_{\text{solid}}{}^*\simeq0.192,\ (p/kT)^*\simeq0.738,$$

$$(\mu/kT)^*\simeq3.64,\ S_{\text{fusion}}\simeq0.78k,$$

in good agreement with the position of the peak of Fig. 2.

A detailed account of this work will be published soon. We are much indebted to Professor I. Prigogine for his constant interest in this research.

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[3] L. K. Runnels, Phys. Rev. Letters 15, 581 (1965).

[4] See, for example, H. N. V. Temperley, Proc. Phys. Soc. (London) 80, 813 (1962).

MEASUREMENTS OF THE ULTRASONIC ATTENUATION IN LIQUID He^4 AT LOW TEMPERATURES*

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We wish to report some preliminary measurements of the attenuation of ultrasound, $\alpha(\omega, T)$, in liquid He^4 at low temperatures and at frequencies of 30, 90, and 150 Mc/sec, where ω is the angular frequency and T the absolute temperature. Interest in this work arose because of the disagreement among the various theoretical explanations advanced to explain the attenuation and because the reported experimental results failed to support any of the theories.

Landau and Khalatnikov[1] made a power series expansion of the dispersion relation, which for small momenta can be written $\epsilon(p)=cp(1-\gamma p^2)$, where c is the velocity of sound. They used the available experimental results to evaluate the constants and pointed out that γ was positive; consequently, energy and momentum could not be conserved in a three-phonon process. They concluded, therefore, that the lowest order process that could contribute to the attenuation was a four-phonon process. For this latter mechanism, Khalatnikov[2] showed that α varied as ωT^6. Others[3-5] assumed the three-phonon process and found that α varies as ωT^4. Kawasaki[6] justified this assumption by pointing out that if the energy uncertainty ($\delta\epsilon$) arising from the finite lifetime (τ) of the thermal phonons satisfied the inequality $\delta\epsilon=\hbar/\tau\geqslant3\gamma\bar{p}^2\hbar\omega$, then the three-phonon process could take place. The average thermal phonon momentum $\bar{p}$ is $3kT/c$. Recently Kwok, Martin, and Miller[7] and Pethick and ter Haar[8] recalculated the attenuation arising from a three-phonon mechanism by taking into account the finite phonon lifetime and found[8]

$$\alpha=\frac{\pi^3}{60}\frac{(u+1)^2}{\rho}\frac{\omega(kT)^4}{\hbar^3c^6}\times[\arctan\omega\tau-\arctan(\tfrac{3}{2}\gamma\bar{p}\omega\tau)],\qquad(1)$$

where ρ is the density and $u=(\rho/c)\partial c/\partial\rho$. At temperatures below 500 mdeg, $\omega\tau\gg1$ for the frequencies used in our experiments and one can then replace $\arctan\omega\tau$ by $\pi/2$. In the one limit where $\frac{3}{2}\gamma\bar{p}\omega\tau<1$, one recovers the previously mentioned expression for the three-phonon process, $\alpha\propto\omega T^4$; in the other limit where $\frac{3}{2}\gamma\bar{p}^2\omega\tau>1$, one obtains an expression