values over the entire range. Some of the calculated points lie as much as 5% below the experimental values, but since this is about the statistical uncertainty of the calculated points not much weight can be attached to this apparent disagreement. The Monte Carlo results show considerably more scatter, indicating that not all the chains generated were sufficiently long to obtain good equilibrium averages. Here also, the agreement with the experimental values is well within the statistical uncertainty of the calculations.

In Fig. 7(b) the calculated and experimental values for the "reduced molar internal energy" $U_i/N_0\epsilon$ are compared.

$$U_i/N_0\epsilon=(U-3RT/2)/N_0\epsilon. \qquad (6)$$

Here N_0 is Avogadro's number and U is the total energy per mole. The disagreement between the calculated and experimental energies is definitely greater than the expected statistical errors in the calculated values. The molecular dynamics calculations all yield values for the internal energy which are systematically more than 3% too low, while the maximum statistical error in the calculated values is expected to be less then 2%. This result can be explained by the assumption that the Lennard-Jones potential with the values used for the parameters is not quite appropriate for argon. The fact that the calculated energy is too low does not necessarily mean that the attractive part of the intermolecular potential used in these calculations is too deep. It may also be that this potential well is too wide, that is, that the attractive part of the potential does not approach zero rapidly enough with increasing distance. This latter interpretation is supported by the work of Mikolaj and Pings,[18] who have managed to invert x-ray scattering data in argon at low densities to obtain a representation of the actual intermolecular potential for argon.

Recently another theoretical method for treatment of the fluid state has emerged. In this approach the behavior of a real fluid is represented as a perturbation expansion about the behavior of a similar system of hard spheres, the perturbation being generated by the differences between the actual intermolecular potential and the hard sphere potential. The behavior of the hard sphere system can be calculated from analytical theories to a reasonable degree of accuracy even at high densities, due to the particular simplicity of the hard sphere interaction.

Calculations by Barker and Henderson[14] with such a theory, using the Lennard-Jones potential with the same parameters as used in the computer calculations discussed above, show that the low-order perturbation terms are sufficient to give fairly good agreement with experiment. The results of their calculations are included in Fig. 7 for comparison. It can be seen that these calculations yield somewhat poorer agreement with the experimental data than is obtained from the molecular dynamics calculations, although the agreement is much better than has been obtained with any other *analytical* approach for which calculations have been carried out.

CONCLUSION

An experimental method has been developed and utilized to provide accurate P–V–T data for the dense fluid phase and for the solid–fluid phase transition in argon over a wide temperature and pressure range. A standard thermodynamic analysis has been applied to derive the entropy and energy from the experimental P–V–T data. The best calculations for the equilibrium thermodynamic behavior of the fluid phase were found to be in relatively good agreement with the experimental and derived thermodynamic data. However, indications were found that the Lennard-Jones potential used in the calculations does not quite represent the correct potential for argon. The Lindemann equation for melting was tested using the experimentally determined molar volumes of the solid at melting, and it was found that the Lindemann "constant" varied by about 12% over the range covered by the data. Extension of the method to higher pressures and temperatures and to gases other than argon is planned.

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[18] P. G. Mikolaj and C. J. Pings, Phys. Rev. Letters **16**, 4 (1966).