

Nuclear Paramagnetism of Helium-3–Helium-4 Solutions above 0.9°K*

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The temperature dependence of the nuclear susceptibility of pure He³ and He³–He⁴ mixtures of He³ concentrations 0.81, 0.70, 0.38, and 0.14 has been determined with an accuracy of $\pm 1\%$ for $0.92 < T < 2.9^\circ\text{K}$. This work is an extension of that of Fairbank, Ard, and Walters, and shows that within experimental error the temperature dependence for the solutions is the same as that of the pure liquid. The maximum deviation of the susceptibilities from an inverse temperature dependence is approximately 5%. These results indicate that the susceptibility is insensitive to the average separation of the He³ atoms, contrary to the behavior that might be expected from a Fermi system in which exchange is important. A perturbation calculation, however, suggests that such behavior can be understood as a near cancellation of terms arising from the exclusion principle and the exchange interaction.

I. INTRODUCTION

THE first measurements of the nuclear paramagnetism of liquid He³ by Fairbank, Ard, and Walters¹ showed that some of the properties of a Fermi gas are reflected in its behavior. Above 1°K, the susceptibility is approximately proportional to T^{-1} , as in a nondegenerate system of fermions. As the temperature is lowered below 1°K, the susceptibility departs from this Curie-law behavior and approaches a value independent of temperature, characteristic of a degenerate system of fermions. These measurements have recently been repeated and extended. Workers at Illinois² and Duke³ have made accurate investigations of the temperature and pressure dependence of the susceptibility in the degenerate region below 1°K. This paper gives results of susceptibility measurements accurate to $\pm 1\%$ on the pure liquid and on some He³–He⁴ solutions in the nondegenerate region above 1°K.

For liquid helium-3 near the absolute zero of temperature the measured susceptibility is too large to be consistent with a simple independent-particle model. In such a model the susceptibility χ_F and heat capacity C_v of a system of degenerate fermions satisfy the relation⁴

$$\frac{\chi_F/\chi_c}{C_v/\frac{3}{2}Nk} = \frac{9}{2\pi^2},$$

where $\chi_c = C/T$ and $\frac{3}{2}Nk$ are the classical susceptibility and heat capacity, respectively. For He³ this ratio is significantly greater than $9/2\pi^2$. The enhanced susceptibility is interpreted as the result of the exchange interaction; in fact, the exchange interaction is so strong that He³ is nearly ferromagnetic.⁵

The strong exchange interaction evident in the low-temperature susceptibility of He³ must also have an important influence on the susceptibility at higher temperatures where the system is nondegenerate. A crude idea of the effect of exchange can be obtained from a "local-field" calculation. We assume, following Stoner,⁶ that each spin sees a field $H' = H + \alpha M$, where α is the "local-field" constant determined by the exchange interaction. In this case the susceptibility becomes

$$\chi/\chi_c = \frac{\chi_F/\chi_c}{1 - \alpha\chi_F}.$$

For α positive and independent of temperature, χ/χ_c exhibits a maximum greater than unity and approaches the classical limit from above.⁷ As illustrated in Fig. 1, this maximum is pronounced for large values of α but

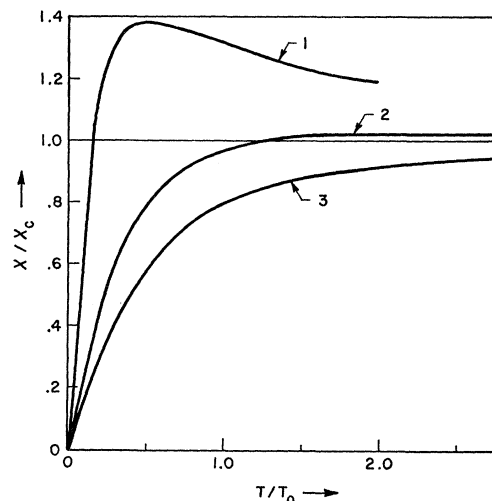


FIG. 1. The susceptibility of a Fermi system including exchange plotted as χ/χ_c versus T/T_0 . $\chi_c = C/T$ is the Curie susceptibility and T_0 is the Fermi degeneracy temperature. The value of the exchange parameter α in curves (1), (2), and (3) is $T_0/2C$, $2T_0/9C$, and 0, respectively.

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¹ W. M. Fairbank, W. B. Ard, and G. K. Walters, Phys. Rev. **95**, 566 (1954).

² A. C. Anderson, W. Reese, and J. C. Wheatley, Phys. Rev. **127**, 671 (1962).

³ A. Low Thomson, Horst Meyer, and E. Dwight Adams, Phys. Rev. **128**, 509 (1962).

⁴ N. F. Mott, Proc. Phys. Soc. (London) **47**, 571 (1935).

⁵ M. J. Buckingham, Nuovo Cimento Suppl. **9**, 306 (1958).

⁶ E. C. Stoner, Proc. Roy. Soc. (London) **A154**, 656 (1936).

⁷ A similar behavior is exhibited by the hard-sphere Fermi-gas model. See K. Huang, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1963), p. 282.

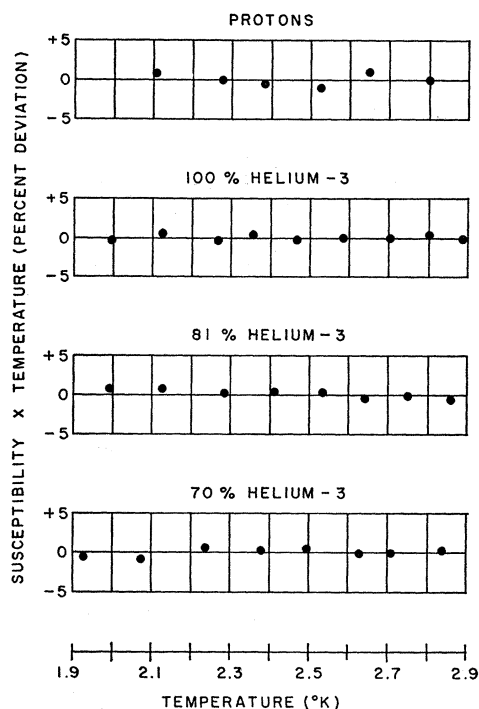


FIG. 2. Plot of susceptibility data at temperatures above 2°K. The proton measurements serve as a check on spectrometer linearity.

disappears in the limit $\alpha=0$. If the exchange parameter appropriate to the observed low-temperature susceptibility is assumed independent of temperature, then χ/χ_c for He^3 would be described by curve 1. However, it should be noted that both the degeneracy temperature T_0 of the Fermi system and the exchange parameter α depend on the average separation of the fermions, which is a function of the temperature, pressure, and He^3 - He^4 concentration.

The early measurements of the susceptibility of pure He^3 at high temperature¹ indicate that no pronounced maximum in χ/χ_c occurs. A detailed study of the susceptibility as a function of temperature and density in the region above the degeneracy temperature, however, was not reported. Some preliminary results⁸ indicated that accurate measurements of the susceptibility of He^3 - He^4 solutions in the nondegenerate region might prove interesting,⁹ since changes of concentration might affect the temperature at which spin degeneracy occurs. Measurements¹⁰ on the melting curve of He^3 - He^4 mixtures also suggested that the onset of spin ordering in the mixtures might occur at a higher temperature than for pure He^3 . We have made susceptibility measure-

ments on pure He^3 and He^3 - He^4 mixtures of He^3 concentrations 0.81, 0.70, 0.38, and 0.14. The mixtures enable us to extend measurements to average separations of the He^3 atoms larger than those accessible with the pure liquid alone. Except for the lowest concentration samples, measurements are accurate to $\pm 1\%$ and extend from 0.92 to 2.9°K.

II. EXPERIMENTAL DETAILS

A. Measurement of Magnetization

We have employed the technique of adiabatic fast passage¹¹ to measure the nuclear magnetization. The conditions for adiabatic fast passage impose the following inequalities on the sweep rate dH_0/dt and the strength of the rf field H_1 :

$$H_1/T_2 \ll |dH_0/dt| \ll |\gamma| H_1^2.$$

The magnetic field is swept through resonance fast enough that relaxation effects are not important, yet slow enough that passage is adiabatic. This method has the advantage that the signal amplitude is proportional to the magnetization and is independent of field inhomogeneities and small variations in the rf level and sweep rate. In addition, there are no saturation corrections or line-shape effects to take into account.

The scheme for detection of the nuclear-resonance signal has been described elsewhere.¹² The detected signal is recorded on a Sanborn model 370 dual channel dc amplifier-recorder. The detector output is amplified on one channel operating at maximum gain and then fed into a precision potential divider. The signal is then recorded on the second channel. The potential divider is set prior to each measurement so that the recorded signal amplitude will be nearly constant. This procedure eliminates the problem of nonlinearity in the recorder.

Prior to passage through resonance, the magnetization is permitted to grow to its equilibrium value. If the sample is initially unmagnetized, a steady-state magnetization will be approached according to the expression

$$M(t)/M_0 \rightarrow [1 - (T_1/T_2)/\delta^2][1 - \exp(-t/T_1)], \quad \delta \gg 1,$$

where $\delta = (H_0 - \omega/|\gamma|)/H_1$, and ω is the frequency of the rf field. After waiting a time $6T_1$ with $\delta \approx 100$, the magnetization has grown to within 0.25% of its equilibrium value. After equilibrium is established, H_0 is swept through resonance subject to the conditions of adiabatic fast passage. The values of the relevant parameters for the least favorable case in our experiments were $\gamma \approx 2 \times 10^4 \text{ G}^{-1} \text{ sec}^{-1}$, $T_2 \approx 3 \text{ sec}$, $dH_0/dt \approx 25 \text{ G sec}^{-1}$, and $H_1 \approx \frac{1}{3} \text{ G}$. The adiabatic-fast-passage conditions are satisfied here by two orders of magnitude.

¹¹ F. Bloch, Phys. Rev. **70**, 460 (1949).

¹² F. J. Low and H. E. Rorschach, Jr., Phys. Rev. **120**, 1111 (1960).

⁸ H. A. Schwettman and H. E. Rorschach, Jr., in *Proceedings of the Seventh International Conference in Low Temperature Physics* (University of Toronto Press, Toronto, 1961), p. 604.

⁹ W. M. Fairbank, in *Proceedings of the Seventh International Conference in Low Temperature Physics* (University of Toronto Press, Toronto, 1961), p. 583.

¹⁰ H. Weinstock, F. P. Lipschultz, C. F. Kellers, P. M. Tedrow, and D. M. Lee, Phys. Rev. Letters **9**, 193 (1962).

The linearity of detection and the temperature independence of our spectrometer sensitivity have been established by measuring the strength of the proton signal from the nylon sample chamber as a function of temperature (see Figs. 2 and 3). The proton signal amplitude obeys Curie's law to within $\pm 1\%$ over the temperature range $1.2 < T < 2.8^\circ\text{K}$.

B. Temperature Measurement

Above 2°K , the temperature was inferred from the vapor pressure of the helium bath. Here temperature measurement is complicated by the presence of thermal gradients in the bath. To minimize such gradients, the temperature was monotonically lowered during the course of an experiment. Cooling of the liquid below the surface thus proceeds first by evaporation and then by convection. Conduction may be neglected. Large temperature gradients are reduced by evaporation. The pressure at any level h below the surface is $P = P_{\text{top}} + \rho gh$. Thus evaporation can be an effective means of heat transfer if the gradient dT/dh satisfies the condition:

$$dT/dh > \rho g (dT/dP)_{\text{v.p.}}, \quad (1)$$

where $(dT/dP)_{\text{v.p.}}$ is the slope of the vapor-pressure curve. The gradient could be larger if superheating were important. Convection remains an effective means of heat transfer so long as $d\rho/dh < 0$, and can further reduce the temperature gradient. The change of density with depth h is

$$\begin{aligned} \frac{d\rho}{dh} &= \left(\frac{\partial\rho}{\partial P}\right)_T \frac{dP}{dh} + \left(\frac{\partial\rho}{\partial T}\right)_P \frac{dT}{dh} \\ &= \rho^2 K g - \rho\beta(dT/dh), \end{aligned}$$

yielding the condition

$$dT/dh > \rho g K / \beta, \quad (2)$$

where K is the isothermal compressibility and β is the coefficient of thermal expansion. The actual temperature gradient in a particular experiment depends on the heat input but normally is bounded by the values given in Eqs. (1) and (2). Above the λ point the gradient given by Eq. (1) is greater than that given by Eq. (2). We have assumed the full value $\Delta T = \rho gh(dT/dP)_{\text{v.p.}}$ in correcting our temperature measurements. The correction is less than 1% .

Below 2°K , He³ vapor-pressure thermometry¹³ was employed. This method was necessary because of the problem of film reflux,¹⁴ and the small vapor pressure of He⁴. The He³ vapor-pressure thermometer is a closed system consisting of a vapor-pressure bulb, a pressure-sensing tube, and a manometer. The dimensions of the system and the quantity of gas are fixed such that liquefaction of the He³ begins at 2.0°K and the bulb is eight-tenths full at 0.9°K . The diameter of the pressure-sensing tube is 0.030 in., and thus above

¹³ S. G. Sydoriak and T. R. Roberts, Phys. Rev. **106**, 175 (1957).

¹⁴ S. G. Sydoriak and T. R. Roberts, Phys. Rev. **118**, 901 (1960).

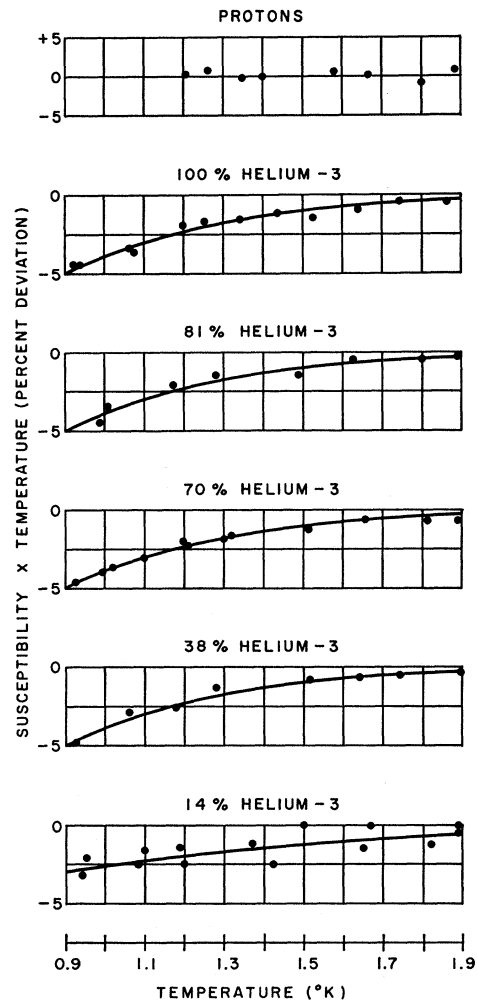


FIG. 3. Plot of susceptibility data at temperatures below 2°K . The proton measurements serve as a check on spectrometer linearity.

0.90°K the temperature correction arising from thermomolecular pressure difference is a small fraction of 1% .

C. The Determination of Sample Concentrations and Molar Volumes

To the extent that He⁴ represents an inert matrix by which He³ can be diluted, the magnetic measurements can be extended toward the classical limit through the use of He³-He⁴ mixtures. Since the susceptibility measurements are relative, it is unnecessary to know the concentration of these mixtures with great accuracy. The temperature variation of the molar volume is a strong function of concentration only in the region of high temperature and low He⁴ content. Concentrations were therefore inferred within 1% from vapor-pressure measurements.¹⁴ In the mixtures of low He⁴ content the concentrations were checked with a mass spectrometer.¹⁵

¹⁵ The authors are indebted to Dr. G. K. Walters and Texas Instruments Incorporated for the analysis of our samples.

Prior to condensation in the sample chamber, each sample was passed through a liquid-He⁴ cooled trap. Precautions, outlined by Sydoriak and Roberts,¹⁴ were taken to ensure that the concentration of the sample remained constant during the course of the experiment. The temperature was lowered monotonically and the capillary leading to the sample chamber was jacketed. The vapor pressure of the sample was monitored throughout the measurement.

Molar-volume data for pure He³ have been taken from the work of Sherman and Edeskuty.¹⁶ Data for mixtures have been taken from the work of Kerr.¹⁷

III. RESULTS

Our measurements of the susceptibility of pure He³ and several He³-He⁴ mixtures are presented in Figs. 2 and 3. The data are plotted in the form χT versus T ; the ordinate is percent deviation. The proton measurements used to check our spectrometer are also plotted here.

The deviation of the susceptibility of the pure liquid from an inverse temperature dependence is very small above 1.2°K. At 1.2°K the data suggest a possible 2% deviation. Below this temperature χT falls more rapidly. With the possible exception of the 14% mixture, the temperature dependence for the mixtures is the same as the pure liquid, within experimental error.

There is certainly no evidence of a maximum in χT such as that suggested by the local-field calculation presented in the Introduction. In fact, our results are reasonably consistent with the supposition that the susceptibility of He³ follows the Curie law down to temperatures approaching 1°K.

No measurements have been made to normalize the data for the various samples relative to one another. In the case of the pure He³ and the 81 and 70% mixtures, the large density variation in each sample as a function of temperature and the considerable density overlap between samples suggest that the susceptibility is independent of density over this region. This conclusion is consistent with previous measurements of the susceptibility of the pure liquid as a function of pressure at 1.2°K¹⁸; no density dependence is observed from the vapor-pressure curve to the melting curve.

Some of our previous measurements⁸ on a 90% solution showed a more rapid decrease of χT than the measurements reported here. It is possible that the capillary may have been blocked during the early ex-

periments, in which case we would have to assume that our previous measurements were actually made on a constant number of atoms. Since the measurements were made at constant pressure, we did not have a continuous check on this point. The magnitude of the discrepancy agrees with this assumption.

Despite the absence of normalization the susceptibility measurements in the nondegenerate region present an interesting problem. Formally we can write the susceptibility as $\chi = \chi_c [1 + f(\rho, T)]$ where $f(\rho, T)$ represents the correction to the Curie law. This correction arises from the Fermi statistics and the direct and exchange interactions. The experimental results then suggest that $f(\rho, T)$ is nearly constant for large variations of density and temperature. This must be true in a region where one expects large deviations from the Curie susceptibility on the basis of a non-interacting Fermi-gas model.

We have calculated the magnetization of a weakly interacting system of He³ atoms in the low-density limit to study the departure from Curie's law as the density is increased. The details of this calculation are given in the Appendix. In the approximation of the calculation, the function $f(\rho, T)$ is given by the sum of two terms

$$f(\rho, T) = f_1 + f_2.$$

f_1 is a correction due to the exclusion principle and is given to lowest order by

$$f_1 = \frac{-h^3}{16(\pi m k)^{3/2}} \frac{N/V}{T^{3/2}} = \frac{4A}{k} \frac{N/V}{T}.$$

f_2 is a correction due to exchange and is given to lowest order by

$$f_2 = \frac{4G}{k} \frac{N/V}{T},$$

where G depends on the temperature and the cutoff radius a . For purposes of comparison, G has been evaluated as a function of temperature assuming $a = 2.175$ Å. This value of the cut-off radius was used by Goldstein¹⁹ to reproduce the ground-state energy of liquid He³. In Table I are listed the values of A (statistical parameter) and G (exchange parameter) for temperatures from

TABLE I. The statistical parameter A and the exchange parameter G as functions of the temperature.

$T^\circ\text{K}$	A	G
1	-0.62×10^{-38}	0.33×10^{-38}
2	-0.44	0.42
3	-0.36	0.38
4	-0.31	0.31
6	-0.25	0.18
9	-0.21	0.08

¹⁶ R. H. Sherman and F. J. Edeskuty, *Ann. Phys. (N. Y.)* **9**, 522 (1960).

¹⁷ E. C. Kerr, in *Proceedings of the Fifth International Conference on Low Temperature Physics and Chemistry* (University of Wisconsin Press, Madison, Wisconsin, 1958), p. 158, and private communication. We are indebted to Dr. Kerr for providing us with molar-volume data at intermediate concentrations; the data agree to within 0.5% with the values reported by T. P. Ptukha, *Zh. Eksperim. i Teor. Fiz.* **34**, 33 (1958) [English transl.: *Soviet Phys. JETP* **7**, 22 (1958)].

¹⁸ W. M. Fairbank and G. K. Walters, *Nuovo Cimento Suppl.* **9**, 297 (1958).

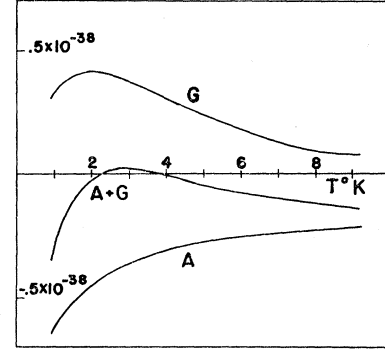
¹⁹ L. Goldstein, *J. Chem. Phys.* **18**, 538 (1950).

1 to 9°K; Fig. 4 shows the temperature dependence of the two terms and their sum. It is interesting to note that the statistical and exchange corrections very nearly cancel between 2 and 4°K. Since both f_1 and f_2 depend linearly on density, the cancellation will occur independent of density. This is consistent with recent measurements on the gas where it is reported that the susceptibility is independent of density.²⁰ Above 4°K the exchange correction is decreasing exponentially with increasing temperature and thus the statistical term dominates. The magnetic properties approach those of an ideal Fermi gas, however, only for temperatures well above 9°K. The ideal-Fermi-gas behavior cannot be obtained by variations of density at lower temperature. Below 2°K the exchange term decreases, leading to a rapid decrease in f . Although the correction terms given above are valid only in the low-density limit (or, stated another way, for temperatures well above the degeneracy temperature), the calculation does suggest that the approximate Curie-law behavior exhibited in our measurements on He³-He⁴ mixtures can be understood as a near cancellation of terms arising from the exclusion principle and the exchange interaction.

IV. CONCLUSIONS

Accurate measurements of the nuclear susceptibility of some He³-He⁴ solutions above 0.9°K show that the temperature dependence of the susceptibility per atom is nearly independent of concentration. A perturbation calculation, valid for a Fermi system in the limit of

FIG. 4. The exchange parameter G , the statistical parameter A , and their sum, as functions of the temperature for a cutoff radius $a=2.175$ Å.



weak degeneracy, shows that these results can be interpreted as a near cancellation of two terms. One term results from the increase of antiparallel spin alignment with increased density and lowered temperature due to the Pauli principle. The other arises from an increase of parallel spin alignment with increased density and lowered temperature due to exchange. These measurements suggest that it is not possible to explain the observed increase of the temperature of the minimum in the melting curves of He³-He⁴ solutions¹⁰ with respect to that of pure He³ by an increase of the temperature at which spin ordering sets in for the solutions.

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APPENDIX

We consider a weakly interacting system of fermions near the classical limit. The free energy of the noninteracting system is extended to include interactions between particles in the plane-wave states \mathbf{k} and \mathbf{k}' . Imposing the condition that the total number of particles is N the variational function becomes²¹

$$\sum_{\mathbf{k}} n_{\mathbf{k}}^+ \{ \epsilon_{\mathbf{k}} + \frac{1}{2} \sum'_{\mathbf{k}'} [n_{\mathbf{k}'}^+ (V_0 + J(\mathbf{k}, \mathbf{k}')) + n_{\mathbf{k}'}^- V_0] - \mu H - \lambda \} + kT \sum_{\mathbf{k}} [n_{\mathbf{k}}^+ \ln n_{\mathbf{k}}^+ + (1 - n_{\mathbf{k}}^+) \ln(1 - n_{\mathbf{k}}^+)] \\ + \sum_{\mathbf{k}} n_{\mathbf{k}}^- \{ \epsilon_{\mathbf{k}} + \frac{1}{2} \sum'_{\mathbf{k}'} [n_{\mathbf{k}'}^- (V_0 + J(\mathbf{k}, \mathbf{k}')) + n_{\mathbf{k}'}^+ V_0] + \mu H - \lambda \} + kT \sum_{\mathbf{k}} [n_{\mathbf{k}}^- \ln n_{\mathbf{k}}^- + (1 - n_{\mathbf{k}}^-) \ln(1 - n_{\mathbf{k}}^-)], \quad (\text{A1})$$

where the primed summation means omission of the term $\mathbf{k} = \mathbf{k}'$, and

$n_{\mathbf{k}}^+$ = occupation number for state \mathbf{k} and spin up,

$n_{\mathbf{k}}^-$ = occupation number for state \mathbf{k} and spin down,

$$\epsilon_{\mathbf{k}} = \hbar^2 k^2 / 2m,$$

$$V_0 = \frac{4\pi}{V} \int_a^\infty V(r) r^2 dr,$$

$$J(\mathbf{k}, \mathbf{k}') = -\frac{4\pi}{V} \int_a^\infty \frac{\sin |\mathbf{k} - \mathbf{k}'| r}{|\mathbf{k} - \mathbf{k}'| r} V(r) r^2 dr,$$

λ = chemical potential.

²⁰ J. E. Opfer, K. Luszczynski, and R. E. Norberg, Phys. Rev. **140**, A100 (1965).

²¹ N. Bernardes and D. F. Brewer, Rev. Mod. Phys. **34**, 190 (1962).

Here plane waves have been assumed in writing the potential and exchange energies and a cutoff radius a has been introduced.

The variation of Eq. (A1) with respect to $n_{\mathbf{k}}^+$ and $n_{\mathbf{k}}^-$ gives a set of coupled equations for the occupation numbers:

$$kT \ln\left(\frac{n_{\mathbf{k}}^{\pm}}{1-n_{\mathbf{k}}^{\pm}}\right) + \epsilon_{\mathbf{k}} \mp \mu H - \lambda = -\sum'_{\mathbf{k}'} n_{\mathbf{k}'}^{\pm} J(\mathbf{k}, \mathbf{k}').$$

In this approximation the potential energy V_0 results only in a redefinition of the chemical potential. In the absence of interactions the occupation numbers near the classical limit are

$$n_{\mathbf{k}}^{\pm} \simeq \exp\left(\frac{\lambda - \epsilon_{\mathbf{k}}}{kT}\right) \left\{ 1 \pm \frac{\mu H}{kT} \left[1 - 2 \exp\left(\frac{\lambda - \epsilon_{\mathbf{k}}}{kT}\right) \right] - \exp\left(\frac{\lambda - \epsilon_{\mathbf{k}}}{kT}\right) \right\}.$$

In the presence of interactions the occupation numbers can be obtained by iteration. To calculate the first-order correction to the magnetization, terms must be retained to first order in $n_{\mathbf{k}}^+ + n_{\mathbf{k}}^-$ and to second order in $n_{\mathbf{k}}^+ - n_{\mathbf{k}}^-$. The result is

$$n_{\mathbf{k}}^{\pm} \simeq \exp\left(\frac{\lambda - \epsilon_{\mathbf{k}}}{kT}\right) \left\{ 1 - \exp\left(\frac{\lambda - \epsilon_{\mathbf{k}}}{kT}\right) - \frac{1}{kT} \sum'_{\mathbf{k}'} \exp\left(\frac{\lambda - \epsilon_{\mathbf{k}'}}{kT}\right) J(\mathbf{k}, \mathbf{k}') \right. \\ \left. \pm \frac{\mu H}{kT} \left[1 - 2 \exp\left(\frac{\lambda - \epsilon_{\mathbf{k}}}{kT}\right) - \frac{2}{kT} \sum'_{\mathbf{k}'} \exp\left(\frac{\lambda - \epsilon_{\mathbf{k}'}}{kT}\right) J(\mathbf{k}, \mathbf{k}') \right] \right\}.$$

Now the chemical potential λ is determined by the relation

$$N = \sum_{\mathbf{k}} (n_{\mathbf{k}}^+ + n_{\mathbf{k}}^-) = 2 \sum_{\mathbf{k}} \exp\left(\frac{\lambda - \epsilon_{\mathbf{k}}}{kT}\right) - \frac{4E_x}{kT} - 2 \sum_{\mathbf{k}} \exp\left[\frac{2}{kT}(\lambda - \epsilon_{\mathbf{k}})\right], \quad (\text{A2})$$

where the exchange energy E_x is

$$E_x = \frac{1}{2} \sum_{\mathbf{k}} \exp\left(\frac{\lambda - \epsilon_{\mathbf{k}}}{kT}\right) \sum'_{\mathbf{k}'} \exp\left(\frac{\lambda - \epsilon_{\mathbf{k}'}}{kT}\right) J(\mathbf{k}, \mathbf{k}').$$

The magnetization is

$$M = \mu \sum_{\mathbf{k}} (n_{\mathbf{k}}^+ - n_{\mathbf{k}}^-) = \frac{\mu^2 H}{kT} \left\{ 2 \sum_{\mathbf{k}} \exp\left(\frac{\lambda - \epsilon_{\mathbf{k}}}{kT}\right) - \frac{8E_x}{kT} - 4 \sum_{\mathbf{k}} \exp\left[\frac{2}{kT}(\lambda - \epsilon_{\mathbf{k}})\right] \right\},$$

and using Eq. (A2) we have to first order

$$M = \frac{N\mu^2 H}{kT} \left\{ 1 - \frac{4E_x}{NkT} - \frac{2}{N} \sum_{\mathbf{k}} \exp\left[\frac{2}{kT}(\lambda - \epsilon_{\mathbf{k}})\right] \right\}.$$

We recognize $N\mu^2 H/kT$ as the Curie magnetization, $-4E_x/NkT$ as the exchange correction, and $-(2/N) \sum_{\mathbf{k}} \exp[(2/kT)(\lambda - \epsilon_{\mathbf{k}})]$ as the statistical correction.

The first-order statistical and exchange corrections to the magnetization now can be calculated, if we use the free-particle density of states. The statistical correction is identical to that for the noninteracting system:

$$\frac{-h^3}{16(\pi mk)^{3/2}} \frac{N/V}{T^{3/2}}.$$

To calculate the exchange correction we must evaluate the total exchange energy E_x :

$$E_x = \frac{-\pi N^2 \hbar^6}{2V(2\pi mkT)^3} \int d\mathbf{k} \exp[-(\rho k)^2] \int d\mathbf{k}' \exp[-(\rho k')^2] \int_a^{\infty} \frac{\sin|\mathbf{k} - \mathbf{k}'|r}{|\mathbf{k} - \mathbf{k}'|r} V(r) r^2 dr,$$

where $p^2 = \hbar^2/2mkT$. The variables \mathbf{k} and \mathbf{k}' can be separated by use of the Gegenbauer addition theorem²²:

$$\frac{\sin|\mathbf{k}-\mathbf{k}'|r}{|\mathbf{k}-\mathbf{k}'|r} = - \sum_{m=0}^{\infty} (m+\frac{1}{2}) \frac{J_{m+1/2}(kr)}{k^{1/2}} \frac{J_{m+1/2}(k'r)}{k'^{1/2}} P_m(\cos\theta),$$

where θ is the angle between \mathbf{k} and \mathbf{k}' . If we choose a coordinate system with \mathbf{k} along the z axis, the angular integration in \mathbf{k}' gives $4\pi\delta_{m0}$. Then the angular integration in \mathbf{k} gives 4π and we obtain

$$E_x = \frac{-N^2\hbar^6}{V(mkT)^3} \int_a^{\infty} r^2 dr V(r) \left[\int_0^{\infty} J_{1/2}(kr) \exp(-p^2 k^2) k^{3/2} dk \right]^2.$$

The integral over k is²³

$$\frac{r^{1/2}}{(\hbar^2/mkT)^{3/2}} \exp\left(\frac{-r^2}{4p^2}\right),$$

and we have for the exchange energy

$$E_x = - \frac{N^2}{V} \int_a^{\infty} r^2 dr V(r) \exp(-mkTr^2/\hbar^2).$$

The exchange correction to the magnetization is

$$\left(\frac{4N/V}{kT}\right)G = \left(\frac{4N/V}{kT}\right) \int_a^{\infty} r^2 dr V(r) \exp(-mkTr^2/\hbar^2).$$

The magnitude of the integral G can be estimated for He³. We use the Slater-Kirkwood potential²⁴

$$V(r) = Ae^{-\alpha r} - Br^{-6},$$

where

$$\begin{aligned} A &= 77 \times 10^{-11} \text{ erg}, \\ B &= 0.149 \times 10^{59} \text{ erg cm}^6, \\ \alpha &= 4.60 \times 10^8 \text{ cm}^{-1}. \end{aligned}$$

The integral is thus

$$\begin{aligned} G &= A \int_a^{\infty} r^2 e^{-\alpha r} \exp(-r^2/2p^2) dr - B \int_a^{\infty} r^{-4} \exp(-r^2/2p^2) dr \\ &= G_1 + G_2, \end{aligned}$$

where

$$G_1 = A(2p^2)^{3/2} e^{\alpha^2 p^2/2} \int_{y_0}^{\infty} (y^2 - \sqrt{2}\alpha p y + \alpha^2 p^2/2) e^{-y^2} dy,$$

and

$$G_2 = - [B/(2p^2)^{3/2}] \int_{z_0}^{\infty} z^{-4} e^{-z^2} dz,$$

with

$$y_0 = (a/\sqrt{2}p) + (\alpha p/\sqrt{2}), \quad z_0 = a/\sqrt{2}p.$$

The values of G_1 and G_2 depend on the relative magnitudes of the dimensionless parameters $a/\sqrt{2}p$, $\alpha p/\sqrt{2}$, $a/\sqrt{2}p + \alpha p/\sqrt{2}$. Anticipating the numerical results, we have approximately

$$\begin{aligned} a &\simeq 2 \times 10^{-8} \text{ cm}, \\ \alpha &\simeq 4.6 \times 10^8 \text{ cm}^{-1}, \\ p &= \hbar/(2mkT)^{1/2} \simeq 2 \times 10^{-8} \text{ cm} \quad \text{for } m = m(\text{He}^3) = 5 \times 10^{-24} \text{ g} \quad \text{and } T = 2^\circ\text{K}. \end{aligned}$$

²² G. N. Watson, *Theory of Bessel Functions* (Cambridge University Press, London, 1922), p. 366.

²³ Reference 22, p. 393.

²⁴ J. C. Slater and J. G. Kirkwood, *Phys. Rev.* **37**, 682 (1931).

Thus $z_0 \approx 0.7$, $\alpha p/\sqrt{2} \approx 6.5$, and we evaluate G_1 in the limit $y_0 \gg 1$, $\alpha p/\sqrt{2} \gg z_0$. The result is

$$G_1 = A(2p^3)^{3/2} e^{-\alpha a} e^{-z_0^2} \left\{ \frac{1}{4y_0} \left(\frac{1}{y_0^2} \right) + z_0 \left(\frac{1}{2y_0^2} - \frac{3}{4y_0^4} + \dots \right) + \frac{z_0^2}{2y_0^2} \left(1 - \frac{1}{2y_0^2} + \frac{3}{4y_0^4} - \dots \right) \right\}.$$

G_2 is given by

$$G_2 = -\frac{B}{3a^3} \{ (1 - 2z_0^2) e^{-z_0^2} + 2(\pi)^{1/2} z_0^3 (1 - \text{erf} z_0) \}.$$

It should be noticed that the expression for G_1 and G_2 involve the term $\exp(-z_0^2) \propto \exp(-\gamma T)$, which cannot be obtained from an expansion in powers of $(1/kT)$. The tabulation of $G = G_1 + G_2$ as a function of temperature for $a = 2.175 \text{ \AA}$ is given in Table I and Fig. 4.

Intermolecular Three-Body Forces and Third Virial Coefficients*

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Nonadditivity corrections to the third virial coefficients $C(T)$ of the noble gases have been calculated for the three-body exchange interactions in the first and second orders of perturbation theory using approximate formulas of Jansen based on the Gaussian model. Denoting these corrections by ΔC_1 and ΔC_2 , respectively, and the correction for the triple dipole interaction by ΔC_3 , it is found that $\Delta C_1 < 0$, $\Delta C_2 > 0$, $\Delta C_3 > 0$, $\Delta C_1 + \Delta C_2 < 0$, and the total nonadditivity correction ($\Delta C_1 + \Delta C_2 + \Delta C_3$) is small because of cancellations. The values of ΔC_1 and ΔC_2 are somewhat inaccurate, principally because of uncertainty in the Gaussian-density width parameter. Qualitatively, the results provide support for the additivity hypothesis, and do not help to explain existing discrepancies with experiment.

INTRODUCTION

SIGNIFICANT discrepancies occur at low temperatures between the measured third virial coefficients of the noble gases and the values calculated from the Lennard-Jones (12, 6) potential as well as other pairwise-additive empirically determined potential functions.^{1,2} These discrepancies are larger than the experimental errors and polynomial-fitting uncertainties.³ The object of this investigation, as stated previously,⁴ is to

determine to what extent the discrepancies can be traced to the neglect of three-body interactions, i.e., to the nonadditivity of intermolecular forces.

The three-body interactions can be classified into three types: (1) the first-order triple-overlap exchange interaction⁵ which corresponds to the nonadditivity of the valence forces, (2) the second-order single-overlap exchange contribution,⁶ and (3) the third-order triple-dipole potential.⁷ The effect of the triple-dipole interaction on the third virial coefficient $C(T)$ has been investigated by several authors.^{4,8,9} These calculations all show that the nonadditivity effects are appreciable and tend to remove a good part of the discrepancy. Whereas the triple-dipole potential is represented by a

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‡ Operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

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