J. Phys. C: Solid St. Phys., 1970, Vol. 3. Printed in Great Britain

The compressibilities of solid ^{3}He and ^{4}He at high pressures

G. G. CHELL
Department of Physics, Rutgers University, New Brunswick, New Jersey 08903, USA

MS. received 2nd February 1970

Abstract. The compressibilities of solid ^{3}He and ^{4}He were calculated in the molar volume range 12–18 cm^3 using first-order self-consistent phonon theory. Good agreement is obtained with experiment, but it is shown that beyond a molar volume of 14 cm^3 the omission of short-range correlations introduces increasing uncertainties. It is shown that in the calculations the complete expression for the self-consistent bulk modulus must be used.

1. Introduction

There has recently been a renewed interest in self-consistent phonon theory (SCP) originally proposed by Born (1951) and later rederived in various forms by others (Hooton 1955 a, b, Koehler 1966 a, b, Choquard 1967, Horner 1967, for example). The scheme resums the anharmonic terms appearing in first-order perturbation theory into a renormalized harmonic approximation and is equivalent to a first-order variational principle calculation of the free energy. There have been several theoretical calculations on the properties of quantum solids using the SCP approximation. In particular it has been stressed (Hooton 1955 c) that when SCP is applied to solid helium real frequencies are obtained, in contrast to earlier quasiharmonic calculations. ^{3}He and ^{4}He offer a strong challenge to the theory not only because of the large displacements of the atoms from their equilibrium sites, and thus their exceptionally large anharmonicity, but also, as we shall see at low densities, there is the formidable problem of short-range correlations (src).

Earlier theoretical investigations of solid helium including src and using a variational principle were performed by Nosanow and his co-workers (Nosanow 1964, 1966, Nosanow and Mullin 1965, Hetherington *et al.* 1967). They used an *ad hoc* function, the so-called Jastrow factor, to simulate these correlations. A cluster expansion technique and an uncorrelated Gaussian wave function were used. Horner (1967) calculated certain properties, in particular elastic constants, of solid ^{3}He with Nosanow's Jastrow factor but using a correlated Gaussian wave function. His method involved summing an infinite class of diagrams of the usual anharmonic expansion. The working expression used by Horner in his paper (equation (58)) is incomplete and his calculated elastic constants should be treated with reserve. Calculations have been made by Koehler (1967, 1968) and Gillis *et al.* (1968) using the variational principle. Attempts at including src by employing different methods to those above have been made by Guyer (1969) who used a generalization of the cluster expansion involving a sequence of Hamiltonians, and Horner (1970) who used the Bethe–Goldstone equation and summed ladder diagrams to all orders to produce src. In this paper we shall be primarily interested in the results obtained by Horner (1970) and will give further details on these later.

Whereas src play an important rôle in theoretical calculations of solid helium at low pressures (low densities) it is not obvious that they are important at elevated pressures. At high pressures the displacements of the atoms from their equilibrium sites are reduced, thus reducing the halfwidth of the Gaussian wave function. There is likely to be less penetration of the wave function into the hard-core repulsive part of the potential, and therefore a corresponding reduction in src effects. However, this can be compensated by the fact that two atoms are now closer together, and the halfwidth of the Gaussian has to be correspondingly smaller to produce an equivalent penetration of the hard core. Whichever of these two effects dominates will determine whether or not src are important. Since calculations on helium involving src are usually rather tedious and the existing theory is still rather controversial, it would be interesting to know whether there are circumstances when they can reasonably be neglected.

Morley and Kliewer (1969, to be referred to as MK) have performed a series of calculations on the vibrational properties of hexagonal close-packed ^{3}He and ^{4}He in the molar volume range 10–16 cm^3. They advanced arguments suggesting that at these compressed volumes src effects could be neglected. In their paper they gave expressions, obtained from Begbie (1947), for the elastic constants where they had replaced the normal force constants by the smeared, self-consistent force constants of SCP. The work of Choquard (1967) and Götze and Michel (1968) has shown that their expression alone is not consistent with SCP and thus their work is not a complete SCP elastic constants theory. Chell *et al.* (1970) indicate that the order of magnitude of the correction is large for helium.

Subsequently Horner (1970) also found that compressibilities deduced from the work of MK differed substantially from experiment. Horner's SCP compressibilities of ^{3}He and ^{4}He in the same density range as MK and including src gave relatively good agreement with experiment. The marked difference between the two calculations Horner attributed to the effects of src. We take the view that in the volume range considered in this paper (12–18 cm^3) the major difference between the two results are to be traced to the need for the complete SCP theory of elastic constants.

In this paper we calculate the bulk modulus, hence the compressibility, of solid ^{3}He and ^{4}He without src in the molar volume range 12–18 cm^3. We used a nearest-neighbour interaction, face-centred cubic model, and believe that the salient features of our calculation are model independent and will carry over to a hexagonal close-packed model. The bulk modulus is an isotropic property, and we have good reason to assert that for isotropic properties and short-range forces the differences due to structure will be small (the ground state energies of the two structures differ by only 0·01% (Barron and Domb 1955) and the Debye θ's differ by only a few per cent (Feldman 1965)). Our particular approximations must be kept in mind when assessing our numerical results. Our expression for the bulk modulus is a correction of the expression used by MK and represents (Choquard 1967, Götze and Michel 1968, Klein *et al.* 1970) the true SCP bulk modulus. The results of Klein *et al.* (1970) for Ne at 0 K indicated that our correction is important for helium. In this paper, therefore, we also study the difference between results based on the expressions of Klein *et al.* and those of MK.

2. Theory

The set of self-consistent equations used for iteration to obtain the renormalized frequencies in SCP theory are given in Klein *et al.* (1970). We do not repeat them here but use the same notation and definitions as that paper wherever possible.

The bulk modulus B_{SC} is given by

$$B_{\mathrm{SC}} = V\left(\frac{\partial^2 F_{\mathrm{SC}}}{\partial V^2}\right)_T = -V\left(\frac{\partial P_{\mathrm{SC}}}{\partial V}\right)_T = X_{\mathrm{SC}}^{-1} \tag{2.1}$$

where P_{SC}, the self-consistent pressure, is

$$P_{\mathrm{SC}} = \frac{-N}{6V}\sum_k X_\alpha^k \langle \phi_\alpha^k \rangle_{\mathrm{SC}} \tag{2.2}$$

and X_{SC} is the compressibility. Performing the volume differentiation we obtain

$$B_{\mathrm{SC}} = B_{\mathrm{SC}}(L) + B_{\mathrm{SC}}(T) \tag{2.3}$$

where

$$B_{\mathrm{SC}}(L) = \frac{N}{18V}\sum_k (X^k_\alpha X^k_\beta \langle \phi^k_{\alpha\beta}\rangle_{\mathrm{SC}} - 2X^k_\alpha \langle \phi^k_\alpha\rangle_{\mathrm{SC}})$$

$$B_{\mathrm{SC}}(T) = \frac{1}{3MV}\sum_k \sum_{qs} S^k(q)\, X^k_\mu \langle \phi^k_{\alpha\beta\mu}\rangle_{\mathrm{SC}}\, e^{qs}_\alpha e^{qs}_\beta \,\frac{(U_{qs} + TC_{qs})}{\omega^2_{qs}}\,\gamma^{\mathrm{SC}}_{qs}$$

where $\gamma^{\mathrm{SC}}_{qs}$ is the self-consistent Grüneisen parameter discussed in Klein *et al.* (1970). $B_{\mathrm{SC}}(L)$ is recognizable as the smeared lattice contribution to B_{SC}. MK in their expression for the elastic constants gave the equivalent to this term only. $B_{\mathrm{SC}}(T)$ is the temperature-dependent part of B_{SC}. It involves an integral equation through its dependence on $\gamma^{\mathrm{SC}}_{qs}$, for if we write $\gamma^{\mathrm{SC}}_{qs}$ out fully we have

$$\gamma^{\mathrm{SC}}_{qs} = -\frac{e^{qs}_\alpha e^{qs}_\beta}{3M\omega^2_{qs}}\sum_k S^k(q)\, X^k_\mu \langle \phi^{\,k}_{\alpha\beta\mu}\rangle_{\mathrm{SC}} - \frac{2e^{qs}_\alpha e^{qs}_\beta}{NM^2\omega^2_{qs}}\sum_{p\lambda}\sum_k S^k(p)\, S^k(q)\left(\frac{U_{p\lambda} + TC_{p\lambda}}{\omega^2_{p\lambda}}\right)$$
$$\times\, e^{p\lambda}_\mu e^{p\lambda}_\nu \langle \phi^k_{\mu\nu\alpha\beta}\rangle_{\mathrm{SC}}\, \gamma^{\mathrm{SC}}_{p\lambda}. \qquad (2.4)$$

This equation has been given and discussed in Klein *et al.* (1970). The integral equation arises out of the volume dependence of the correlation function Λ_k (see Klein *et al.*) occurring in the wave-function when the expectation values are taken.

3. Application and discussion

We have calculated the compressibility of solid ^{3}He and ^{4}He at 0 K in the molar volume range 12–18 cm^3. We used a Lennard-Jones (12–6) potential function ϕ.

$$\phi(r) = 4\varepsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\}$$

where $\varepsilon = 10{\cdot}22$ K and $\sigma = 2{\cdot}556$ Å. The parameters are the same as those used by MK and Horner (1970). The bulk modulus was calculated in two ways to give a check on numerical accuracy—firstly by numerical differentiation of the pressure using equation (2.2) and secondly using equation (2.3). The integral equation involved in the second calculation can be solved either by iteration or from frequencies calculated *ab initio* for different volumes. We used the latter method. Our results were further checked against an independent calculation made by V. V. Goldman (private communication). The compressibilities for ^{3}He and ^{4}He are displayed in figures 1 and 2 respectively together with the results of Horner (1970), MK and experiment.

Beyond 14 cm^3 molar volume our results are indicated by a dotted curve, because we found that for larger volumes there was appreciable penetration of the Gaussian wave function into the hard core of the potential. This resulted in the numerical integrations, needed to evaluate the expectation values, becoming sensitive to the cutoff in the repulsive part of the potential (see also MK). Thus at 12 cm^3 molar volume the free energy and bulk modulus changed by approximately 0·3% when the cutoff was varied over a distance of 0·3σ inside the core. At 14 cm^3 the change was approximately 0·5% over a region of cutoff variation of 0·2σ. At 16 and 18 cm^3 molar volume the variation with cutoff is more pronounced and the actual values taken for the integrals become more uncertain. For this reason the results beyond 14 ccs are indicated by a dotted curve. Even with the uncertainty in these values it can be seen that our calculations, which included the explicit temperature dependent part of the bulk modulus $B_{\mathrm{SC}}(T)$, remove the major part of the difference between MK's compressibilities and experiment. At high pressures, where our results are more certain, they agree better with experiment than Horner's. The difference between Horner's and the values calculated here can be taken as a measure of the effect of numerical approximations, src, structure etc.

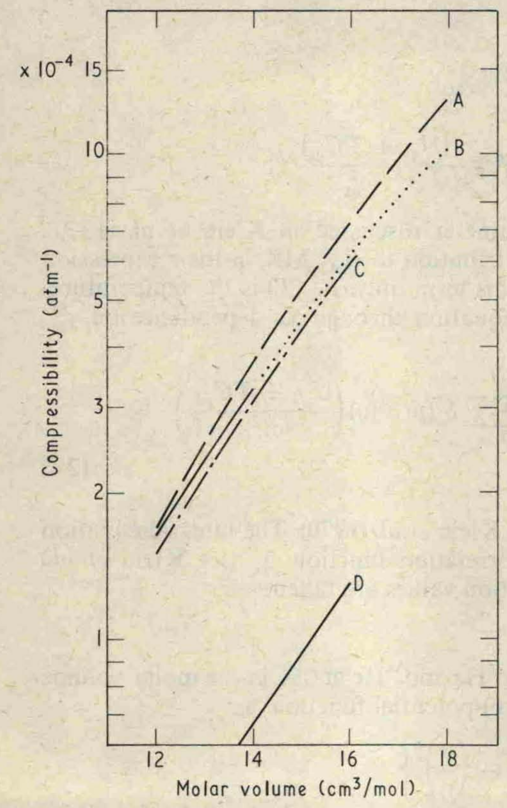

Figure 1. Compressibility of ^{3}He against molar volume. A, Horner (1970); B, present paper; C, experiment (Dugdale and Franck 1964); D, Morley and Kliewer (1969).

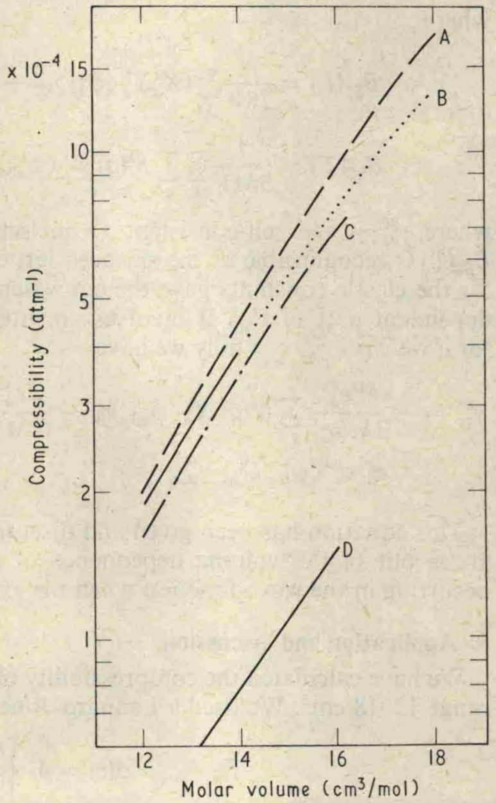

Figure 2. Compressibility of ^{4}He against molar volume. A, B, C, D, same references as in figure 1.

We summarize the results as follows. The present calculations illustrate three things: (i) the desirability of using the complete expression, equation (2.3), for calculating the bulk modulus and compressibility of helium; (ii) up to a molar volume of approximately 14 cm^3, compressibilities that are independent of cutoff are obtained without the use of src; (iii) the major difference between MK's compressibilities and experiment is due to the former's incomplete expressions for the SCP elastic constants and not their neglect of src.

Acknowledgments

The author would like to thank Professor G. K. Horton, Dr M. L. Klein and Mr V. V. Goldman for many helpful discussions. Thanks are also due to the US Air Force Office of Scientific Research for their support under grant No. AFOSR 68-1372 and the Rutgers Research Council for support under grant No. Quantum Crystals 07-2180.

References

Barron, T. H. K., and Domb, C., 1955, *Proc. R. Soc.* A, **227**, 447–65.
Begbie, G. H., 1947, *Proc. R. Soc.* A**188**, 189–208.
Born, M., 1951, *Fest. Akad. D. Wiss. Göttingen, Math. phys. Klasse* (Berlin: Springer-Verlag).
Chell, G. G., Goldman, V. V., Klein, M. L., and Horton, G. K., 1970, *Phys. Rev.*, to be published.
Choquard, P. F., 1967, *The Anharmonic Crystal* (New York: Benjamin).
Dugdale, J. S., and Franck, J. P., 1964, *Phil. Trans. R. Soc.*, **257**, 1–29.

Feldman, C., 1965, *Proc. Phys. Soc.*, **86**, 865–71.

Gillis, N. S., Koehler, T. R., and Werthamer, N. R., 1968, *Phys. Rev.*, **175**, 1110–15.

Götze, W., 1967, *Phys. Rev.*, **156**, 951–62.

Götze, W., and Michel, K. H., 1968, *Z. Phys.*, **217**, 170–87.

Guyer, R. A., 1969, *Solid St. Commun.*, **7**, 315–18.

Hetherington, J. H., Mullin, W. I., and Nosanow, L. M., 1967, *Phys. Rev.*, **154**, 175–88.

Hooton, D. J., 1955 a, *Phil. Mag.*, **46**, 422–42.

—— 1955 b, *Z. Phys.*, **142**, 42–57.

—— 1955 c, *Phil. Mag.*, **46**, 485–98.

Horner, H., 1967, *Z. Phys.*, **205**, 72–90.

—— 1970, *Phys. Rev.* **1**, A, 1722–9.

Klein, M. L., Chell, G. G., Goldman, V. V., and Horton, G. K., 1970, *J. Phys.* C: *Solid St. Phys.*, **3**, 806–9.

Koehler, T. R., 1966 a, *Phys. Rev. Lett.*, **17**, 89–91,

—— 1966 b, *Phys. Rev.*, **144**, 789–98.

—— 1967, *Phys. Rev. Lett.*, **18**, 654–6.

—— 1968, *Phys. Rev.*, **165**, 942–50.

Morley, G. L., and Kliewer, K. L., 1969, *Phys. Rev.*, **180**, 245–59.

—— 1966, *Phys. Rev.*, **146**, 120–33.

Nosanow, L. H., 1964, *Phys. Rev. Lett.*, **13**, 270–2.

Nosanow, L. H., and Mullin, W. I., 1965, *Phys. Rev. Lett.*, **14**, 133–6.