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HELIUM EQUATION OF STATE FOR SMALL CAVITIES: RECENT DEVELOPMENTS*

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The pressure of helium in small bubbles can reach values up to 10^{11} Pa. In the temperature range from 200 K to 1200 K no high pressure-volume data are available. Theoretical work performed recently on equations of state for both gaseous and solid helium are reviewed and the obtained equations are presented. Curvature corrections applicable to very small bubbles are also given.

1. INTRODUCTION

Helium produced by (n,α) reactions or injected in metals is essentially insoluble. Therefore, it has the natural tendency to precipitate and to form bubbles. The pressure in small bubbles can be extremely large, and a realistic equation of state (EOS) is required to evaluate it. Unfortunately, the experimentally determined EOS for helium does not completely cover the range of temperatures and pressures of interest. This is illustrated in Fig. 1 where the various regions are shown in which experimental data have been obtained. It is seen that only the recent measurements by Mills et al.² cover the range of pressures equal to $2\gamma/r$, where γ is the surface energy and r the radius of the bubble. A typical value for γ is 2 J/m^2 . However, measurements at elevated temperatures are still lacking. Accordingly, theoretical EOS have been developed recently for gaseous and solid helium, and a summary of the obtained results is presented in the following.

2. THE GASEOUS EOS ACCORDING TO PERTURBATION THEORY^{3,4}

The fluid is modeled as a system of hard

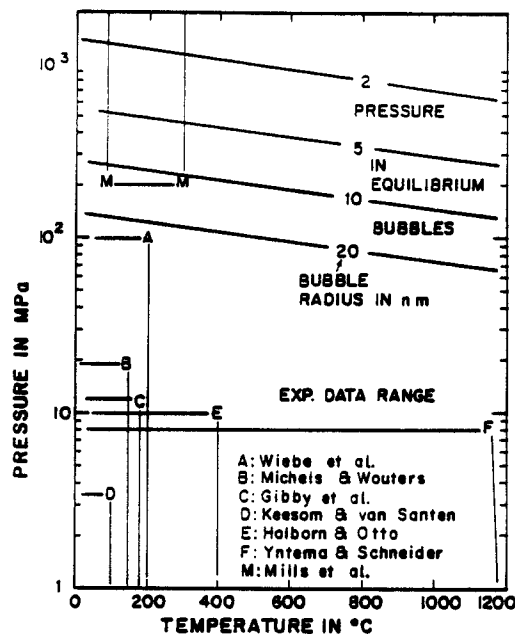


FIGURE 1

Ranges of temperature and pressure where experimental data exist for the EOS of helium. References to data can be found in Ref. 1.

spheres. However, in order to account for the "softness" of the repulsive part of the actual interatomic potential, the diameter d of the particles is made to depend on temperature and

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density according to

$$d = d_B(T)[1 + \delta(T) \psi(y)] \quad (1)$$

where $y = (\pi/6)d^3N/V$ is the "soft-sphere" packing fraction and N is the number of particles in the volume V . If the interatomic potential $U(x)$ is expressed in terms of the dimensionless distance $x = r/\sigma$, where σ is the distance r where U becomes repulsive, then

$$d_B(T)/\sigma = \int_0^{x_m} \{1 - \exp[-(U + \epsilon)/kT]\} dx \quad (2)$$

$$\begin{aligned} \{1 + \delta(T)\}(d_B/\sigma)^2 = \\ 2 \int_0^{x_m} \{1 - \exp[-(U + \epsilon)/kT]\} x dx . \end{aligned} \quad (3)$$

x_m denotes the location of the minimum of $U(x)$, i.e. $U(x_m) = -\epsilon$. The function^{5,6} $\psi(y)$ makes Eq. (1) an implicit relationship for d , and numerical solution is required. Once d or y are known, the compressibility factor $z = pV/NkT$ is given by⁷

$$z_{HS} = (1 + y + y^2 - y^3)/(1 - y)^3 \quad (4)$$

within the hard-sphere approximation. Several corrections to this equation are, however, required to account for quantum effects and for the attractive part of the interatomic potential.

2.1. The Quantum Correction

For a fluid comprised of light atoms, quantum corrections are important.³ These corrections give rise to an additional term to the compressibility factor which can be written in the form

$$z_Q = \frac{h^2}{m(kT)^2 \sigma^2} y \frac{\sigma}{d} \frac{\partial}{\partial y} [y\beta(y)] \quad (5)$$

where

$$\begin{aligned} \beta(y) = g(1,y) \left(-\frac{dU}{dx}\right)_{x=d/\sigma} \\ + \left(\frac{\sigma}{d}\right)^2 \int_{d/\sigma}^{2d/\sigma} \left(-\frac{dU}{dx}\right) \frac{\partial g}{\partial x} x^2 dx . \end{aligned} \quad (6)$$

Here, $g(x,y)$ is the radial distribution function.

2.2. The Contribution from the Potential Well

The treatment of a fluid as an effective hard-sphere system neglects the attractive part of the interatomic interaction. If the potential well is approximated by a square well of depth ϵ and width $(d_w - d)$, then Reijnhard⁸ has shown that the following term must be added to the compressibility factor:

$$z_A = -4y(d_w/d)^3 g(d_w/d_1 y) \{1 - \exp(-\epsilon/kT)\} \quad (7)$$

2.3. Evaluation of the Gaseous EOS

The total compressibility factor is therefore

$$z = z_{HS} + z_Q + z_A . \quad (8)$$

In evaluating z , the interatomic potentials $U(x)$ of both Beck⁹ and Young et al.¹⁰ were utilized. For the radial distribution function, the simple approximation

$$g(x,y) = \quad (9)$$

$$\begin{cases} 0 & \text{for } x < \frac{d}{\sigma} \\ \exp\left\{\frac{1}{2} y \left(x \frac{\sigma}{d} - 2\right)^2 \left(x \frac{\sigma}{d} + 4\right)\right\} & \text{for } \frac{d}{\sigma} < x < 2 \frac{d}{\sigma} \\ 1 & \text{for } x > 2 \frac{d}{\sigma} \end{cases}$$

developed by Shinomoto¹¹ was employed. The extent of the potential well was assumed to be given by $d_w = 0.35 \text{ nm}$.

Figure 2 shows the predicted results for the Beck potential. The EOS for the gaseous state is represented by the curve below the break points, whereas the solid EOS, discussed in the following section, is shown by the curves above the break points. The empirical EOS of Mills et al.,² valid for temperatures at or below 300 K, is also shown for compari-

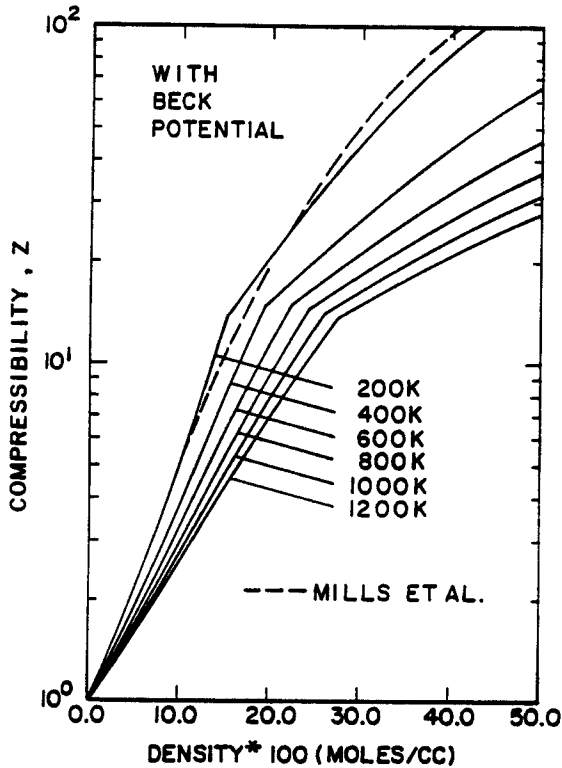


FIGURE 2
Theoretical EOS after Wolfer using the Beck potential for the fluid EOS.

son for 200 K.

2.4. Gaseous EOS Based on the Virial Expansion

According to the virial expansion of the EOS, the compressibility factor may be written in terms of a power series in $(1/V)$. Using a four term expansion, Trinkaus¹² empirically adjusted the expansion coefficients such that they agree at low densities with the conventional virial coefficients, but reproduce the compressibility factor at freezing,

$$z_2 = 0.1225 v_2 T^{-0.555} \quad (10)$$

where

$$v_2 = 56 T^{-1/4} \exp[-0.145 T^{1/4}] \quad (\text{in } \text{Å}^3) \quad (11)$$

is the volume per atom upon freezing. Trinkaus obtains then

$$z = (1 - \rho)(1 + \rho - 2\rho^2) + (1 - \rho)^2 \rho B(T)/v_2 + (3 - 2\rho)\rho^2 z_2 - 50(1 - \rho)\rho^2 \quad (12)$$

$$\text{where } \rho = v_2/v < 1 \quad (13)$$

$$\text{and } B(T) = 170 T^{-1/3} - 1750/T \quad (\text{in } \text{Å}^3) \quad (14)$$

Figure 3 gives the comparison between the above EOS by Trinkaus and the empirical results of Mills et al.

3. THE SOLID EOS FOR HELIUM

In the quasi-harmonic approximation of the solid, the free energy is the sum of the potential energy A_0 of an ideal lattice with all atoms located at their equilibrium positions plus a vibrational free energy A_h . As a result of this division, the pressure may also be written as a sum of two contributions,

$$p_0 + p_h, \text{ where } p_0 = -\partial A_0/\partial V \text{ and } p_h = -\partial A_h/\partial V.$$

The evaluation of p_0 or A_0 for solid helium requires extensive quantum-mechanical computations for the following reasons. First, the interatomic interaction in a non-ionic solid is determined by the electronic structure of the valence and conduction bands at high densities. Second, in the case of solid helium, the ground-state vibrations (at 0°K) are no longer negligible, and the nucleus must be described by a wave-function rather than by a point charge fixed at the ideal lattice point. The latter aspect is particularly important at low densities of the solid when the average interatomic distance is larger than the atomic diameter σ , i.e. when the packing fraction

$$y_0 = \frac{\pi}{6} \sigma^3 N/V \quad (15)$$

is less than one.

Ground-state pressures for this case have been obtained by Hansen and Pollock,¹³ and their results are shown in Fig. 4. For higher

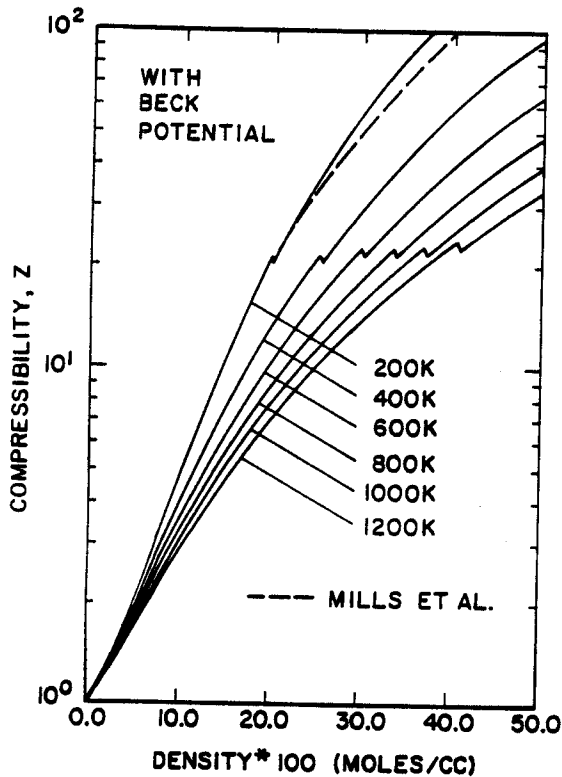


FIGURE 3
EOS for the fluid and solid state of helium after Trinkaus.

densities, both Young et al.¹⁰ and Zeller¹⁴ have carried out electron band structure calculations, and their results are also indicated in Fig. 4. Finally, Trinkaus¹² evaluated the static lattice energy for an fcc He crystal assuming that the pair-interaction is given by Beck's potential. The derived ground-state pressure is remarkably close to the electron band structure results of Young et al. and to the results of Hansen and Pollock for medium densities. Deviations at very high densities are as expected, since the Young potential is softer than the Beck potential.

Both the low-density results of Hansen and Pollock¹³ and the high-density results of Young et al.¹⁰ can be fitted to an equation of the form

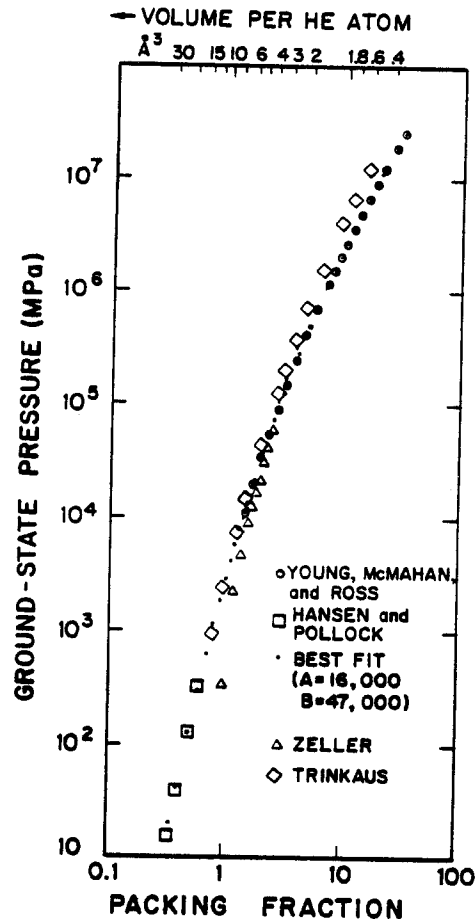


FIGURE 4
The ground-state pressure of solid helium at 0°K as a function of the packing function.

$$p_0(\text{MPa}) = [a + b]^6 \quad (16)$$

$$\text{where } a = \left[\frac{1}{2} B^{1/2} + Q^{1/2} \right]^{1/3} \quad (17)$$

$$b = \left[\frac{1}{2} B^{1/2} - Q^{1/2} \right]^{1/3} \quad (18)$$

$$\text{and } Q = \frac{1}{27} (B^3/A)^{1/2} + \frac{1}{4} B y_0^2 \quad (19)$$

A and B are two constants with the values indicated in Fig. 4.

The ground state pressure obtained by Trinkaus is given by

$$p_0 = 4.3 \times 10^8 [1 - (v/16)^3] \times \exp(-4.52 v^{1/3})/v \quad (20)$$

where v is the volume per atom in \AA^3 .

It must be noted that Eq. (16) is not entirely consistent as the results by Young et al. contain no contributions of the ground-state vibrations to p_0 . However, for high packing fractions, vibrations contribute relatively little to the total pressure.

In order to estimate the pressure contribution of lattice vibrations at finite temperatures two approaches have been developed. In one case, the Debye theory is employed together with a volume dependent Debye temperature given by

$$\theta_D(V, T) = \theta_{Dm}(T)(v_m/V)^Y \quad (21)$$

where θ_{Dm} is the Debye temperature at melting and given by the Lindemann law

$$\theta_{Dm} = 16.15931 T^{1/2} y_{om}^{1/3} \quad (22)$$

The packing fraction at melting, y_{om} , is based on the theoretical results of Young et al.¹⁰ which can be expressed by the equation

$$y_{om}^{1/3} = 0.15542 T^{0.359} + 1.1292 \times 10^{-6} T^{1.903} \quad (23)$$

and the Grüneisen constant can be obtained by taking the derivative $(-d \ln \theta_{Dm}/d \ln V)$ of Eq. (22). The pressure contribution by thermal vibrations is then obtained from

$$p_h = 9\gamma kT(N/V)(T/\theta_D)^3 \int_0^{\theta_D/T} dx x^3/(e^x - 1), \quad (24)$$

where the term due to ground-state vibrations has been omitted as it is already included in p_0 for low packing fractions.

The compressibility factor for the above EOS for solid helium is shown in the upper

parts of Fig. 2.

A second approach to the solid EOS is to treat the lattice vibration with the Einstein approximation and to evaluate the root mean square of the phonon density of state. This has been carried out by Trinkaus¹² using the Beck potential as the interaction potential and evaluating anharmonic corrections. The effective Einstein temperature can be expressed by the relationship

$$\theta_E^* = 11800 v^{-1/2} \exp[-0.8 v^{1/2}] \quad (25)$$

where v is the volume per atom in \AA^3 , and the vibrational energy is given approximately by the high-temperature formula

$$E_h^* = 3NkT \left[1 + \frac{1}{12} \left(\frac{\theta_E^*}{T} \right)^2 \right]. \quad (26)$$

The pressure produced by the lattice vibration is then given by

$$p_h = \gamma E_h^*/V \quad (27)$$

where $\gamma = -d \ln \theta_E^*/d \ln v$.

Adding to this pressure p_h the ground-state pressure as obtained by Trinkaus, the results shown in Fig. 3 are obtained.

4. CURVATURE CORRECTIONS

The application of the EOS of helium to bubbles is certainly justified if the bubble radius R is significantly larger than the helium atom radius, and if the number of helium atoms in contact with the metal is less than the number of helium atoms in contact with each other. Both conditions become increasingly violated as the bubble approaches atomistic dimensions. As a result, curvature corrections have been derived for the gaseous and the solid helium. With respect to the gas, curvature effects arise when the gas atoms will predominantly impinge on the metal surface at normal angles. Indeed, when the gas atoms are confined within a small cavity

of radius not much larger than the atomic radius, glancing collisions occur with low probability. This effect has recently been investigated by Wehner and Wolfer¹⁵ by evaluating the particle distribution function for a hard sphere gas near a solid curved wall.

The enhancement of pressure above the value on a flat surface is shown in Fig. 5 for various ratios of bubble radius R to atom radius, and as a function of the packing fraction y_0 . It is seen that the pressure in small bubbles of atomic dimensions can be substantially larger than the value obtained with a macroscopic gas law.

For helium at high densities contained in a small bubble, surface corrections to the lattice energy have been obtained by Trinkaus.¹² It can be shown that the pressure of helium on a cavity wall of radius R is enhanced by the factor

$$P(R)/P(\infty) \cong 1 + 0.6 \Omega_{\text{He}}^{1/3}/R \quad (28)$$

where Ω_{He} is the atomic volume of helium.

REFERENCES

1. N.V. Tsederberg, V.N. Popov, and N.A. Morozova, "Thermodynamic and Thermophysical Properties of Helium," Atomizdat, Moscow 1968; Israel Program for Scientific Translations, Jerusalem 1971.
2. R.L. Mills, D.H. Liebenberg, and J.C. Bronson, Phys. Rev. B 21 (1980) 5137.
3. J.A. Barker and D. Henderson, Rev. Mod. Phys. 48 (1976) 587.
4. H.C. Anderson, D. Chandler and J.D. Weeks, Adv. Chem. Phys. 34 (1976) 105.
5. L. Verlet and J.J. Weiss, Phys. Rev. A5 (1972) 432; and Mol. Phys. 24 (1972) 1013.

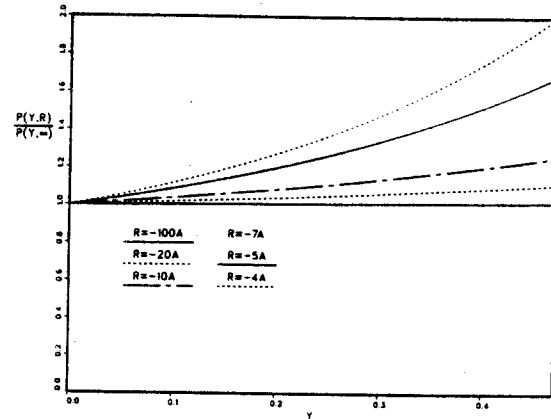


FIGURE 5
Ratio of pressures exerted by a fluid on a bubble surface with curvature radius R and on a flat surface for different ratios of bubble radius, R , to atomic radius, A .

6. W.G. Wolfer, in "Effects of Radiation on Materials," Eds. H.R. Brager and J.S. Perrin, ASTM-STP-725 (1981) 201.
7. N.F. Carnahan and K.E. Starling, J. Chem. Phys. 51 (1969) 635.
8. R. Reijnhart, Physica 83A (1976) 533.
9. D.E. Beck, Mol. Phys. 14 (1968) 311.
10. D.A. Young, A.K. McMahon, and M. Ross, Phys. Rev. B24 (1981) 5119.
11. S. Shinomoto, Phys. Letters 89A (1982) 19.
12. H. Trinkaus, Rad. Effects, in print.
13. J.P. Hansen and E.L. Pollock, Phys. Rev. A5 (1972) 2651.
14. R. Zeller, private communication.
15. M.F. Wehner and W.G. Wolfer, DAFS report DOE/ER-0046/13, Vol. 1, May 1983, p. 148.