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Abstract

Helium, produced by transmutations or injected, causes bubble formation in solids at elevated temperatures. For small bubbles, the gas pressure required to balance the surface tension reaches values which far exceed those obtainable in experiments to measure the equation of state for helium gas. Therefore, empirical gas laws cannot be considered applicable to the fluid-like densities existing in small bubbles. In order to remedy this situation, an equation of state for helium was developed from the theory of the liquid state. At very low densities, this theoretically derived equation of state agrees with experimental results. For high densities, however, gas pressures are predicted which are significantly higher than those derived from the ideal gas law, but also significantly lower than pressures obtained with the van der Waals law. When applied to equilibrium bubbles in solids, it is found that the high-density equation of state leads to less bubble swelling than the van der Waals law, but more than the ideal gas law. Furthermore, the number of helium atoms in equilibrium bubbles is nearly independent of temperature.

Introduction

The generation of helium atoms by nuclear transmutations in structural materials is of considerable concern to the design of fission reactor cores and future fusion reactors. For the purpose of studying the radiation damage of materials, helium is often injected in ion bombardment experiments. Since helium is rather insoluble in solids, it promotes the formation of voids, bubbles, and grain boundary cavities. In fact, helium is believed to be essential for the nucleation of voids at elevated temperatures.

The gas pressure in helium containing cavities may reach very large values. For example, in equilibrium bubbles of radius r , the gas pressure is given by

$$p = 2\gamma/r \quad (1)$$

where γ is the surface energy. For a typical value of $\gamma = 1 \text{ J/m}^2$, and a bubble radius of $r = 1 \text{ nm}$, the equilibrium gas pressure reaches the extraordinary value of 10^9 Pa or 10^4 times the atmospheric pressure. This pressure is an order of magnitude higher than what has been obtained in laboratory experiments carried out to measure the equation of state of gaseous helium [1]. Empirical equations of state, such as the van der Waals law, which have been fitted to the experimental data, cannot be extrapolated with any confidence to the high gas pressures existing in small bubbles. The more theoretically based virial equation of state, being a power series expansion in the density of gas atoms, is naturally restricted to low values of the densities. Again, its extrapolation to high pressures is not possible.

Accordingly, we have developed a high-density equation of state for gaseous helium which is applicable to densities as high as the liquid density of helium. In fact, the development of this equation of state is

based on the theory of the liquid state and the known interatomic potential for helium.

In contrast to the empirical equations of state, the high density equation of state can only be written in the form of implicit equations which must be solved numerically. However, one major purpose of the present paper is to provide auxiliary parameters in both graphical and analytical form which will greatly facilitate the remaining numerical evaluation of the high density equation of state. As a result, it can be easily applied in the analysis of void nucleation, bubble swelling, grain boundary cavity formation, blistering, etc. An application to equilibrium bubbles and bubble swelling is given in the present paper. The importance of the high density equation of state for predicting the onset of blistering has been demonstrated recently [2].

The Interatomic Potential of Helium

Based on a critical assessment of the interatomic potential of helium, Barker [3] concluded recently that the potential found by Beck [4] appears to provide one of the most satisfactory descriptions of the helium-helium interaction. In addition, it can also be presented in a relatively simple analytical form, namely

$$V(x)/k = A_0 \exp[-a_1 x - a_2 x^6] - \frac{D_0}{(x^2 + x_0^2)} \left[1 + \frac{x_2^2 + 3x_0^2}{x^2 + x_0^2} \right] \quad (2)$$

where

k = Boltzmann constant

$$A_0 = 4.6275 \cdot 10^6 \text{ K}$$

$$D_0 = 29.9950 \text{ K}$$

$$a_1 = 11.5764$$

$$a_2 = 0.12596$$

$$x_0 = 0.25597$$

$$x_2 = 0.62416$$

and

$$x = R/\sigma \quad . \quad (3)$$

Here, R is the interatomic distance and

$$\sigma = 0.2637 \text{ nm} \quad (4)$$

is the interatomic distance where the potential $V(R)$ is equal to zero. The minimum of the interatomic potential is at

$$R_m = 0.2969 \text{ nm} \quad (5)$$

and it has a depth of

$$\epsilon/k = V(R_m)/k = -10.37 \text{ K} \quad . \quad (6)$$

The form of the Beck potential is shown in Figure 1. As can be seen, the repulsive part of this potential is sufficiently soft, so that no definite diameter can be defined for the helium atom. It is nevertheless possible, as shown below, to define an effective diameter as a function of the gas temperature and density.

Equilibrium Thermodynamics of Liquids and Dense Gases

The thermodynamic properties of dense liquids and gases and of gases at temperatures far above the triple point are predominantly determined by the repulsive part of the interatomic potential. If this part could be approximated by a hard-sphere potential, then the thermodynamic properties could more easily be evaluated. This is based on the fact that both analytical and computer simulation results are available for this case. The most satisfactory equation of state for a hard-sphere system is the one given by Carnahan and Starling [5], which can be written in the form

$$z = \frac{p}{\rho kT} = \frac{1 + y + y^2 - y^3}{(1 - y)^3} \quad (7)$$

where

$$y = \frac{\pi}{6} \rho d_0^3 \quad (8)$$

is the packing fraction, ρ is the number density of gas atoms, d_0 the hard-sphere diameter, and T is the absolute temperature.

In order to take into account that the actual interatomic potential has a soft core as well as an attractive part, perturbation theories have been developed in the past [6,7,8] which have proven to be highly successful. In these theories, the interatomic potential $V(R)$ is first separated into a repulsive part $V_0(R)$ and a weak attractive part $w(R)$. The free energy of the system can then be written as a sum of contributions from

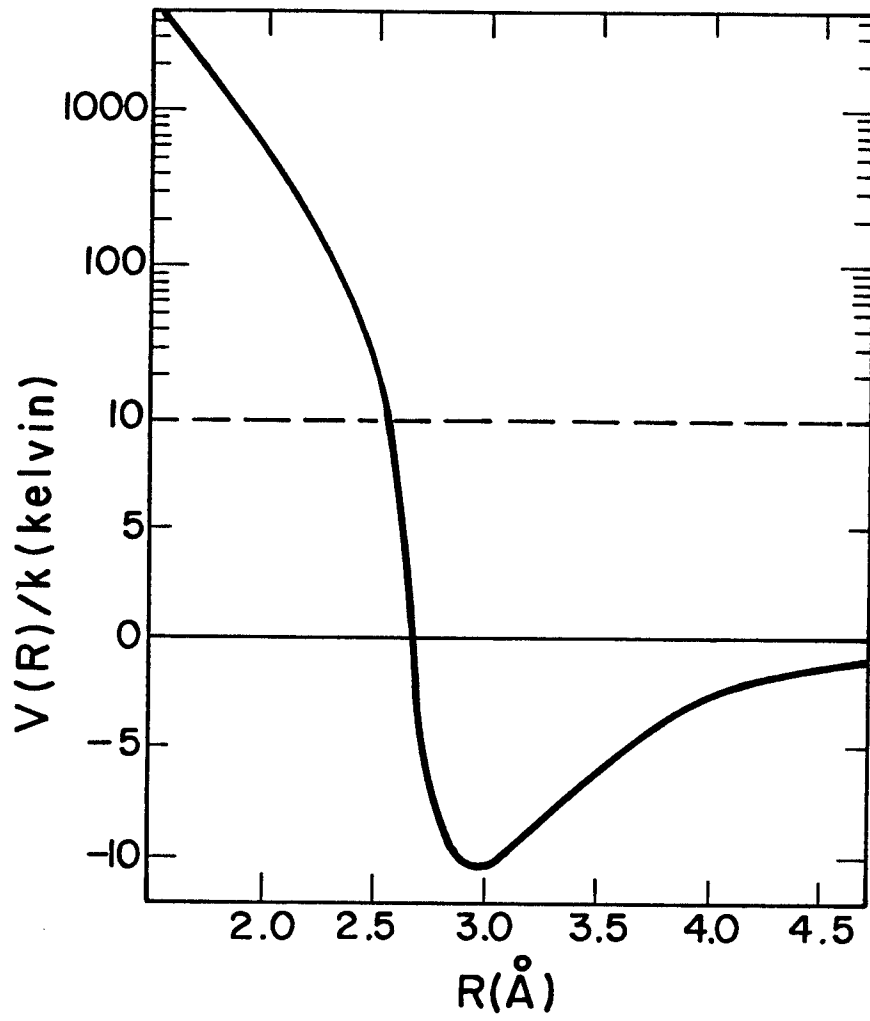


Fig. 1. Interatomic potential of helium

the repulsive and the attractive parts of the potential. The latter is on the order of ϵ/kT , and it can be neglected for a dense helium gas at elevated temperatures. For example, at a temperature of 500 K, $|\epsilon|/kT = 0.02$ which is small in comparison to $\frac{3}{2} kT$, approximately the average energy per atom.

The free energy contribution of the repulsive part of the potential is evaluated in the following manner. First, the repulsive part of the potential is replaced by

$$V_0[d + (R - d)/\alpha]$$

so that for $\alpha = 1$, the original potential is recovered, but for $\alpha = 0$, a hard-sphere potential is obtained with diameter d . With this parameter potential, the free energy is evaluated as a power series in α . The zero-order term, being independent of α , represents the free energy of a hard-sphere system. The first-order term, linear in α , is now made to vanish by a proper choice of the effective hard-sphere diameter d . Barker and Henderson [6] make the selection such that

$$d_B/\sigma = \int_0^{\infty} \{1 - \exp[-V_0(x)/kT]\} dx, \quad (9)$$

and they select the hard-sphere potential such that $V_0(x) \equiv V(x)$ for $x \leq 1$, and zero otherwise. In contrast, Weeks, Chandler, and Anderson [7] choose the repulsive part to be

$$V_0(x) = \begin{cases} V(x) + \epsilon & \text{for } x \leq R_m/\sigma \\ 0 & \text{for } x > R_m/\sigma \end{cases} \quad (10)$$

and also select a different criterion to determine the effective hard-sphere diameter. According to Verlet and Weiss [8], this diameter is determined by

$$d = d_B(1 + \psi\delta) \quad (11)$$

where d_B is given by Equation (9) with the potential $V_0(x)$ from Equation

(10). The factors in the correction term $\psi\delta$ are determined in the following manner:

$$(1 + \delta)d_B^2/\sigma^2 = \int_0^\infty \{1 - \exp[-V_0(x)/kT]\}xdx . \quad (12)$$

It can be computed by numerical integration after selecting the potential.

On the other hand, ψ is given by

$$\begin{aligned} 2\psi\{(2 + 7y)\sigma_0 - (1 - y)\sigma_1 - \frac{3}{2}y/(1 - y)^2\} \\ = (1 + 11y)\sigma_1 - (1 - y)\sigma_2 + 3yf/(1 - y)^3 \end{aligned} \quad (13)$$

where

$$f = -7.5 + y - 17.3595y^2 - 6.04y^3 \quad (14)$$

$$\sigma_0 = (1 - y/2)/(1 - y)^3 \quad (15)$$

$$\sigma_1 = (2 - 7.5y + 0.5y^2 - 5.7865y^3 - 1.51y^4)/(1 - y)^4 \quad (16)$$

$$\sigma_2 = (2 - 20y + 30y^2 + 0.17y^3 - 26.796y^4 + 11.2241y^5)/(1 - y)^5 \quad (17)$$

and

$$y = \frac{\pi}{6} \rho d^3 . \quad (18)$$

Since y and hence ψ depend on d , Equation (11) is an implicit equation for d . Once d and y are known, the gas pressure can be computed from the equation of state .

$$\frac{p}{\rho kT} = z = z_{HS}(y) - 4y\delta[\psi(\sigma_0 + \sigma_1) - \sigma_1 - \frac{1}{2}\sigma_2] \quad (19)$$

where $z_{HS}(y)$ is given by Equation (17).

Numerical Evaluation of the Equation of State

Using Equation (10) and the Beck potential, the integrals in Equations (9) and (12) were computed numerically. The quantity d_B/σ is shown in Figure 2, and δ is given in Figure 3.

Analytical approximations were also developed for these quantities. The equation

$$d_B/\sigma = B - C \log T - (a_2/a_1)(B - C \log T)^6 \quad (20)$$

with a_1 and a_2 given in conjunction with Equation (2), and

$$B = 1.23377, \quad C = 0.16296$$

reproduce the exact results with an error of less than or equal to 0.02% in the temperature range from 100 K to 2000 K.

It is evident from Figure 3 that $\log \delta$ can be approximated by a linear function of $\log T$ for temperatures $T \geq 200$ K. The relationship

$$\delta = 1.0767 \times 10^{-3} T^{0.384353}, \quad (21)$$

shown as the dashed line in Figure 3, fits the exact results to within 1.2% at $T = 200$ K. However, the error diminishes rapidly with increasing temperature.

To determine d , the following iteration procedure proves to be very effective. Initially, d is set equal to d_B , and ψ is computed with $y = \pi \rho d_B^3/6$. The correction term $\psi\delta$ is then used to compute an improved effective diameter according to Equation (11). Next, the correction is reevaluated with the improved d , and the procedure is repeated until a steady limit is reached for d . To achieve an accuracy of 0.1%, about one to four iterations are required, depending on the gas density ρ . The steady values of d and y are then inserted into the equation of state (19). The results are shown in Figure 4, plotted as a function of various density measures; the hard sphere packing fraction

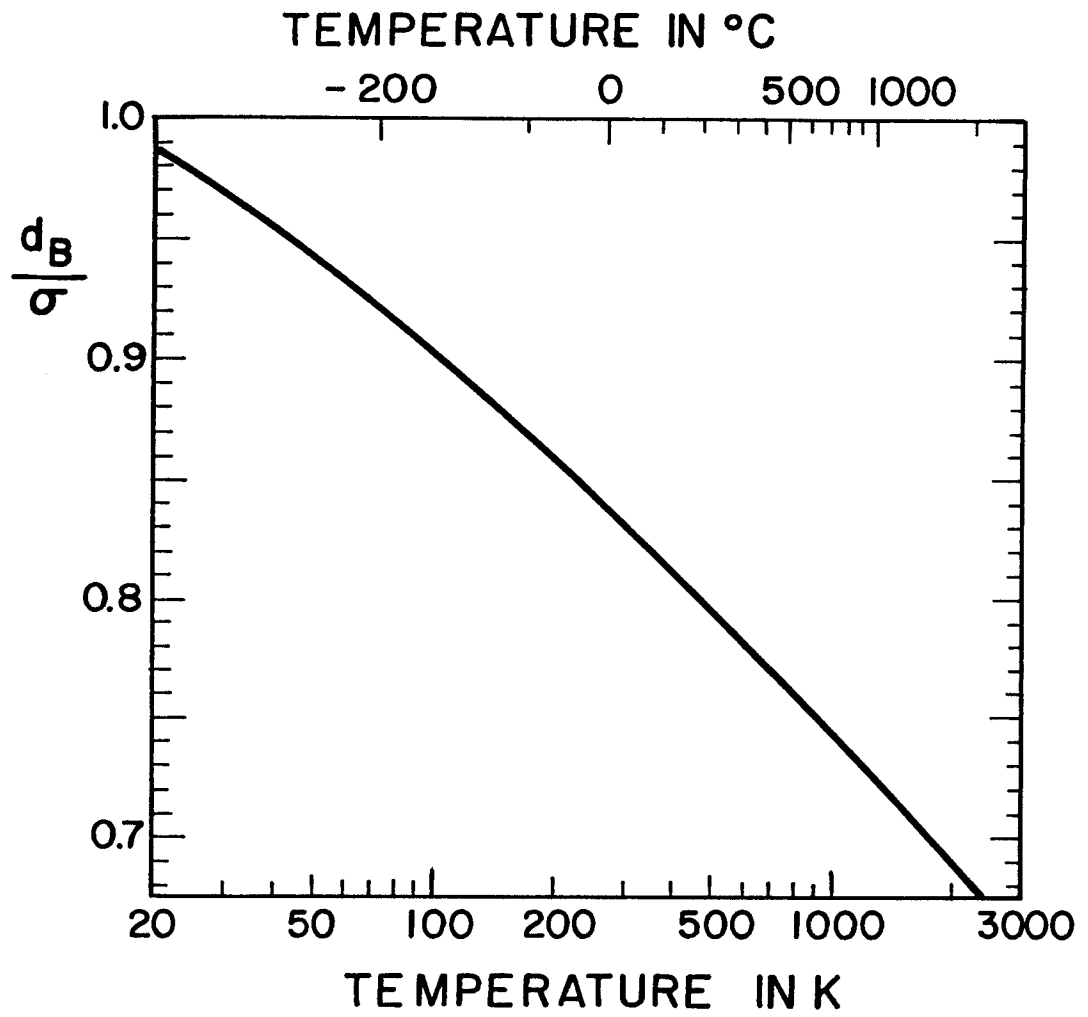


Fig. 2. Barker-Henderson diameter of helium

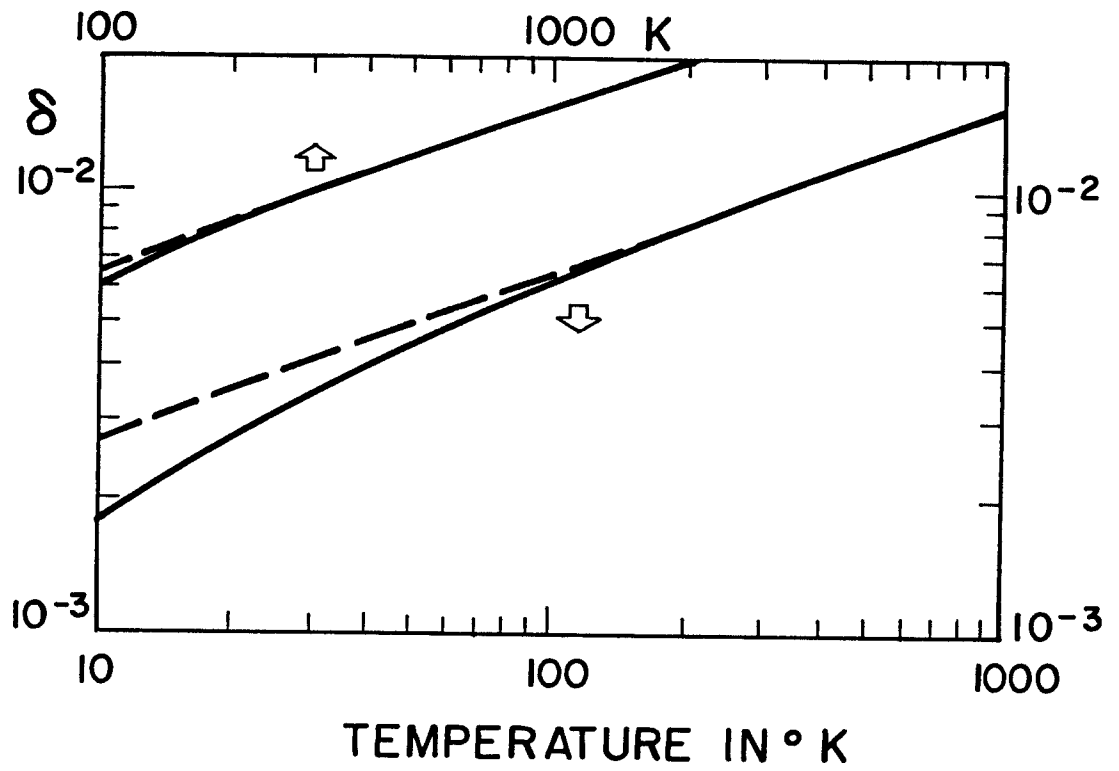


Fig. 3. Delta correction factor

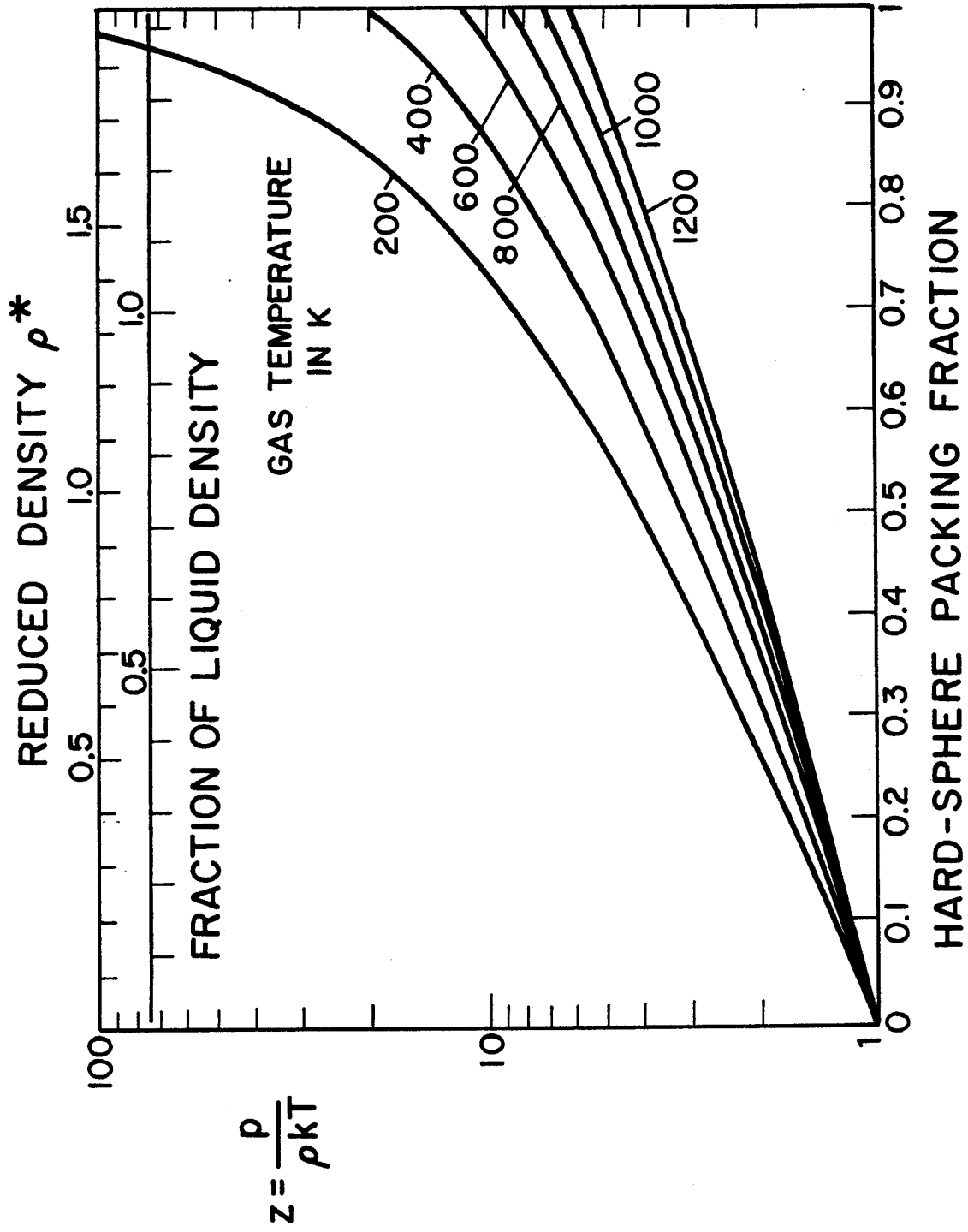


Fig. 4. High-density equation of state for helium

$$y_0 = \frac{\pi}{6} \rho \sigma^3; \quad (22)$$

the fraction of the liquid density

$$y_\ell = \frac{\pi}{6} \rho R_m^3;$$

and the reduced density

$$\rho^* = \rho \sigma^3 .$$

The experimental results are limited to densities $\rho_\ell \lesssim 0.2$ and values of $z \lesssim 1.4$ [1]. Within this region, however, our theoretical results are in good agreement with the experiments.

To facilitate the use of the high-density equation of state for helium, a tabulation is presented in Table 1.

Equilibrium Bubbles

As mentioned earlier, an equilibrium bubble satisfies the condition of Equation (1). Using the equation of state (19), the equilibrium bubble radius is given by

$$r = 2\gamma/[kT\rho z(\rho, T)] . \quad (23)$$

The helium density inside the bubbles may also be expressed in terms of macroscopic quantities, namely,

$$\rho = mN_b/S = C_{\text{He}}/S = f_{\text{He}}/S\Omega. \quad (24)$$

Here, m is the number of gas atoms per bubble, N_b is the number of bubbles per unit volume, and $S = \Delta V/V$ is the swelling due to bubbles. If we assume that all the helium is collected in bubbles, then mN_b is equal to the helium concentration per unit volume, C_{He} . The latter is related to the helium atom fraction, $f_{\text{He}} = \Omega C_{\text{He}}$, where Ω is the atomic volume. Using a value of $\Omega = 1.175 \times 10^{-29} \text{ m}^3$, and a surface energy of $\gamma = 1 \text{ J/m}^2$, the equilibrium bubble radius r can be computed from Equation (23) for a given ratio of

TABLE 1. EQUATION OF STATE, $p/(\rho kT)$, FOR GASEOUS HELIUM

		Hard-Sphere Packing Fraction y_0					
T(K)		0.1	0.2	0.3	0.4	0.5	0.6
200		1.284142	1.670906	2.205775	2.962480	4.069910	5.777579
400		1.230998	1.528855	1.917071	2.430522	3.123789	4.088414
600		1.203614	1.458731	1.781109	2.193093	2.727766	3.436904
800		1.185701	1.413978	1.696611	2.049820	2.496774	3.072177
1000		1.172625	1.381860	1.637067	1.950854	2.340776	2.832313
1200		1.162449	1.357186	1.591946	1.876970	2.226234	2.659540
1400		1.154188	1.337363	1.556091	1.818946	2.137441	2.527579
1600		1.147280	1.320927	1.526627	1.771722	2.065937	2.422575
1800		1.141372	1.306972	1.501802	1.732256	2.006708	2.336459
2000		1.136231	1.294906	1.480477	1.698592	1.956570	2.264174
2200		1.131696	1.284319	1.461876	1.669406	1.913388	2.202371

		Hard-Sphere Packing Fraction y_0					
T(K)		0.7	0.8	0.9	1.0	1.1	1.2
200		8.636251	14.32999	31.23658	20.55268	67.62907	70.41779
400		5.491900	7.674121	11.53730	11.63577	20.46828	23.69591
600		4.407288	5.796650	7.919768	8.627791	12.86362	15.10142
800		3.831113	4.867191	6.352102	7.114348	9.769965	11.49744
1000		3.464834	4.300098	5.448844	6.167564	8.108648	9.457442
1200		3.206269	3.912406	4.854368	5.515363	7.059941	8.185840
1400		3.012556	3.627679	4.429703	5.036213	6.316730	7.308920
1600		2.860555	3.408019	4.108008	4.667650	5.760923	6.126895
1800		2.737319	3.232363	3.856882	4.134366	4.981351	
2000		2.548012	2.966804	3.483076			

swelling to helium concentration, S/f_{He} . The results are shown in Figure 5 for three different temperatures. As a comparison, the results for the ideal gas law and for the van der Waals law are also shown. For the latter case, the hard-sphere diameter was assumed to be equal to σ .

We see that with the van der Waals law the swelling to helium ratio is overestimated, particularly for small bubble radii. Expressed differently, we find that the number of helium atoms which can be accommodated in small bubbles is substantially larger than the number predicted with the van der Waals gas law. The reason is, of course, the softness of the interatomic potential of helium.

This softness is also responsible for the decrease of the effective diameter of helium with increasing temperature. As a result, the product of pressure and volume, pV , or p/ρ , exhibits a much weaker temperature dependence than either the ideal gas law or the van der Waals law. A remarkable demonstration of this fact is displayed in Figure 6, which shows the relationship between the number of helium atoms in equilibrium bubbles of radius r . We see that the number of helium atoms contained in bubbles is almost independent of temperature within the temperature range where bubble formation occurs in stainless steels. This is particularly true for very small bubbles with radii equal to or smaller than 1 nm.

Conclusions

An equation of state for gaseous helium has been derived from its interatomic potential and from liquid state theories. This equation of state is valid for all gas densities up to the liquid state density, and it can be applied with confidence to very large gas pressures.

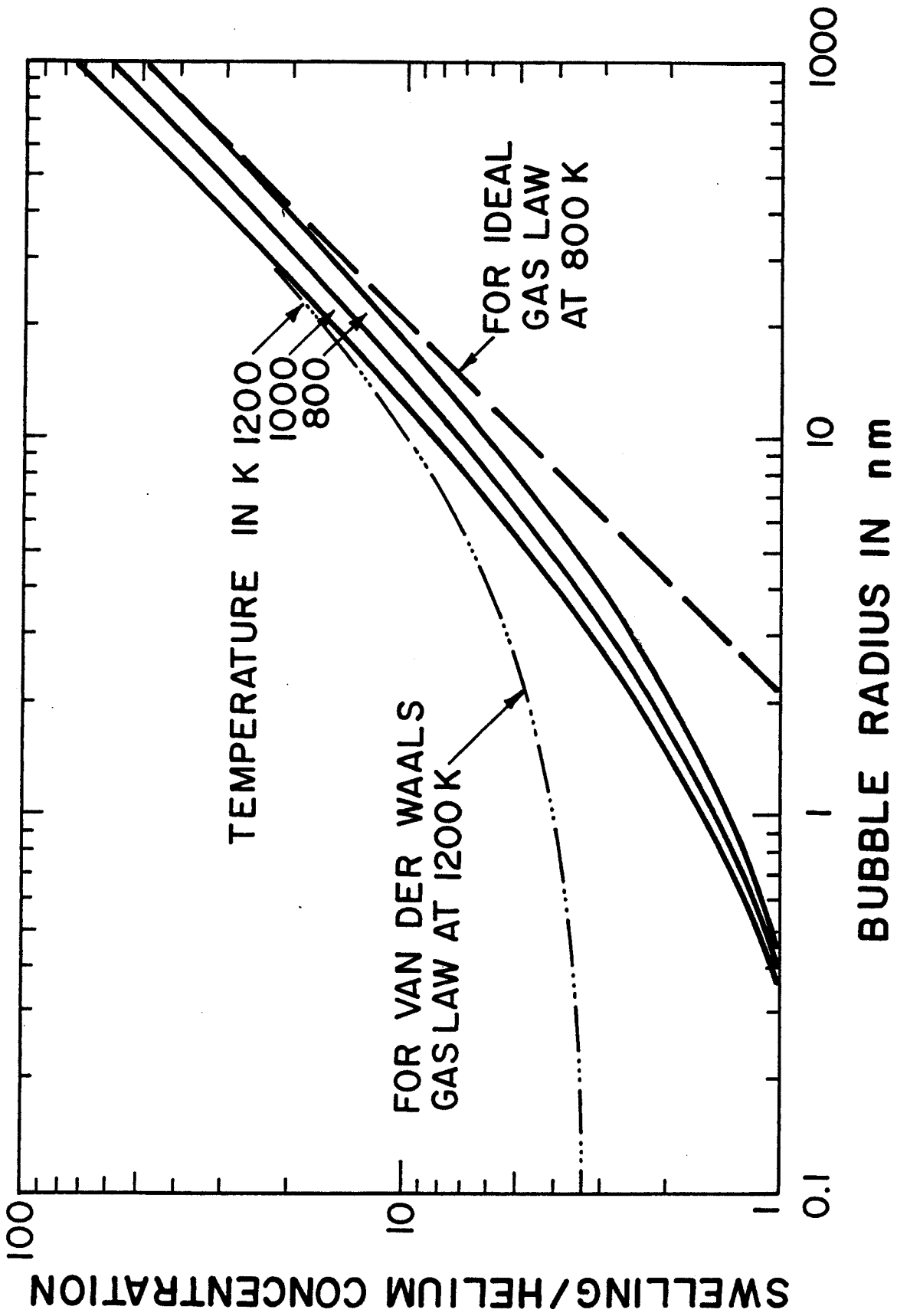
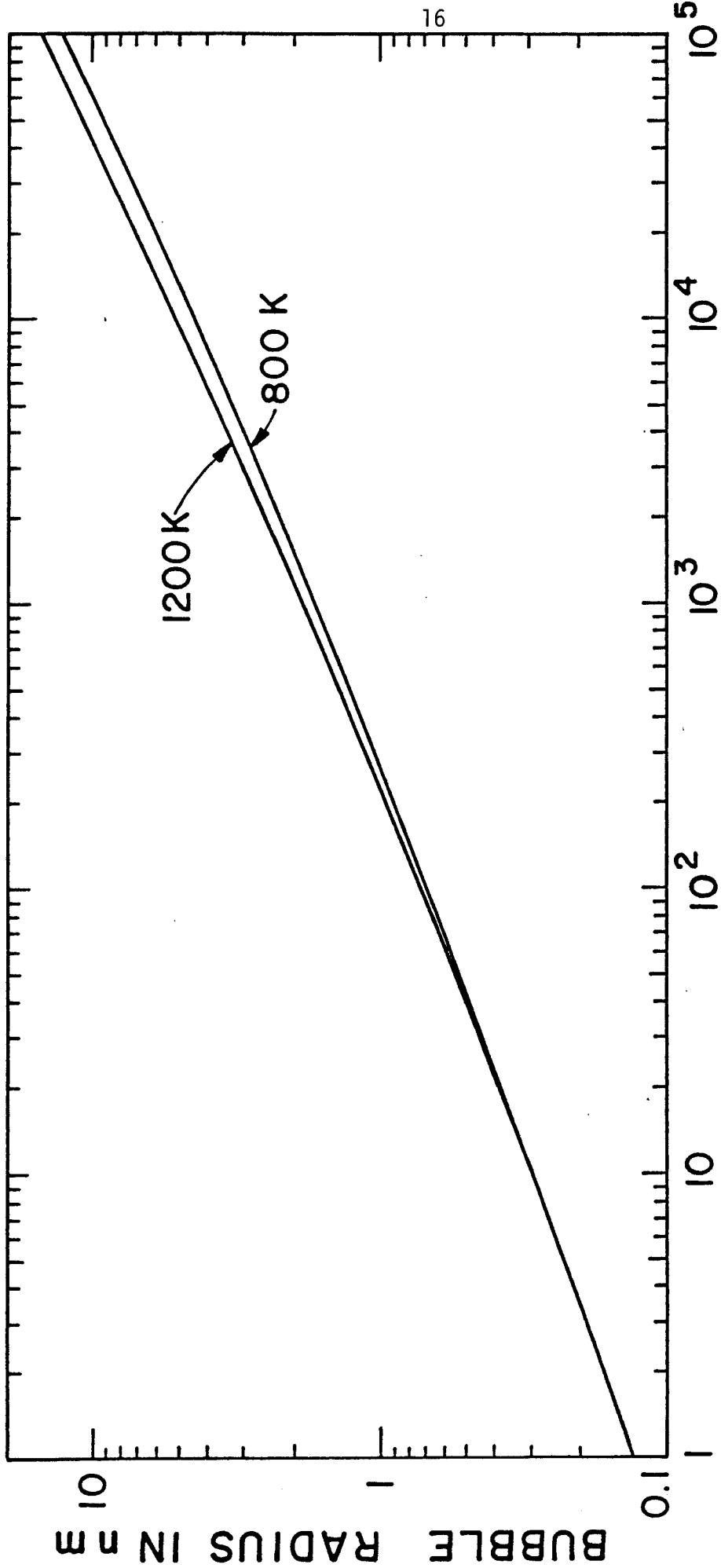


Fig. 5. Relationship between equilibrium bubble radius and the swelling to helium ratio



NUMBER OF HELIUM ATOMS

Fig. 6. Equilibrium bubble radius and number of helium atoms in the bubble

When applied to small gas bubbles in solids, it is found that the van der Waals gas law overpredicts the gas pressure. Furthermore, the present equation of state remedies the basic deficiency of the van der Waals gas law, namely, a fixed hard-sphere diameter or a minimum gas volume, assumed to be independent of temperature. Due to the fact that the effective helium diameter decreases with increasing temperature and pressure, the remarkable result is found that the number of helium atoms in a equilibrium bubble is very nearly independent of the temperature.

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