

1976

# Compression of Gases at Moderate and High Densities

J. S. Yu

Follow this and additional works at: <https://docs.lib.purdue.edu/icec>

---

Yu, J. S., "Compression of Gases at Moderate and High Densities" (1976). *International Compressor Engineering Conference*. Paper 231.  
<https://docs.lib.purdue.edu/icec/231>

This document has been made available through Purdue e-Pubs, a service of the Purdue University Libraries. Please contact [epubs@purdue.edu](mailto:epubs@purdue.edu) for additional information.

Complete proceedings may be acquired in print and on CD-ROM directly from the Ray W. Herrick Laboratories at <https://engineering.purdue.edu/Herrick/Events/orderlit.html>

## COMPRESSION OF GASES AT MODERATE AND HIGH DENSITIES

J. S. Yu, Professor of Mechanical Engineering  
School of Engineering and Physical Sciences  
West Virginia Institute of Technology  
Montgomery, West Virginia 25136

### ABSTRACT

The cell method developed by Lennard-Jones and Devonshire is applied by using a two-potential model for the configurational energy to the determination of the equation of state of argon, nitrogen, and methane up to nearly half the liquid densities in the temperature range from 0 to 150°C. The Lennard-Jones 6-12 potential and the Kihara hard core model with parameters determined from the second virial coefficients at low densities are used, respectively, for the calculation of the energy of the geometrically symmetric lattice and the excess potential energy arising from molecular motions. Calculated results compare favorably well with existing experimental data.

### INTRODUCTION

The classical theories for imperfect gases are powerful in sustaining mathematical rigor in describing the dynamics of molecules to all orders of direct and indirect interactions. On applying the theory of cluster expansions[1,2] to real fluids, however, only a few low order virial coefficients can be evaluated exactly due to the fact that intolerable and ever-increasing mathematical complexities are encountered as one attempts to handle a cluster of a larger number of molecules simultaneously interacting with one another. Thus only dilute systems can be adequately treated. On the other hand, the hierarchy of an infinite number of integral equations[3,4] must be appropriately truncated in order to determine the radial distribution function which is ultimately essential for the evaluation of the thermodynamic properties. Approximation methods, such as the Yvon-Born-Green equation[4], the hyper-netted-chain equation[3], and the Percus-Yevick equation[5], have been applied to argon with the use of the Lennard-Jones 6-12 potential; yet agreement with experiments is still qualitative in nature in spite of the large amount of numerical calculations that must be performed for the multiple integrals involved. A refinement of the hyper-netted-chain and the Percus-Yevick equation to include explicitly the triple potentials has been given by Rushbrooke and Silbert[6] and by Rowlinson [7]; no numerical results have yet been made available.

The cell method, developed by Lennard-Jones and Devonshire[8] for imperfect gases, is simple in procedure and easy to use. Although it has the drawback due to the approximate manner in evaluating the classical partition function of being not valid for dilute gases, and although presently existing calculations using the Lennard-Jones potential indicated that it appeared to describe the state of solids or "expanded solids" rather than fluids, it, nevertheless, has been proved valuable in interpreting the thermodynamic properties of dense fluids and fluid mixtures. A critical and detailed examination of the cell method has been given by Barker[9]. This paper shows that the cell method can be modified to yield compressibility factors for nonpolar and nearly spherical molecules comparable with experimental measurements for a limited range in density. The results for argon, nitrogen and methane are in reasonable agreement with experimental data.

### BRIEF DESCRIPTION OF THE CELL METHOD

The formulation of the cell method[8,9,10,11] is briefly reviewed here for the purpose of clarity. The classical canonical partition function for a system of  $N$  identical molecules is

$$Z = \frac{1}{N! h^{3N}} \int \dots \int e^{-H(\vec{q}; \vec{p})/kT} d\vec{q} d\vec{p}, \quad (1)$$

where  $(\vec{q}; \vec{p}) = (q_1, q_2, \dots, q_N; p_1, p_2, \dots, p_N)$  are the coordinates and momenta of the  $N$  molecules,  $d\vec{q} d\vec{p}$  is the volume element in the neighborhood of  $(\vec{q}; \vec{p})$ ,  $T$  is the absolute temperature,  $k$  the Boltzmann constant and  $h$  the Planck constant. The Hamiltonian of the system is assumed to have the form

$$H(\vec{q}; \vec{p}) = \sum_{i=1}^N \frac{p_i^2}{2m} + V(\vec{q}), \quad (2)$$

in which  $m$  is the mass of a molecule,  $V$  the total potential energy of the system which is assumed to depend only upon the coordinates of the molecules. Integrating over the momenta in equation (1) yields

$$Z = \frac{1}{N!} \left( \frac{2\pi mkT}{h^2} \right)^{3N/2} \int \dots \int e^{-V(\vec{q})/kT} d\vec{q}. \quad (3)$$

In the cell method approximation, the coordinate space of the system is divided in an appropriate symmetric manner into  $N$  equal cells, one for each molecule; and, in the limit of high densities, the motion of a molecule is confined to within its own cell in the field of force due to all the other molecules in the neighboring cells. Let the energy per molecule be  $w$  when every molecule is at the center of its cell. The potential energy in excess of  $w$  of a molecule at a distance  $r$  from the center of its own cell is the sum of the contributions, averaged over the spherical surface of radius  $r$  about the cell center, from all the other molecules when they are fixed at the centers of their respective cells, and the contributions arising from the correlations of molecular motions in different cells[9]. Let this excessive potential energy be denoted by  $u(r)$ . The partition function is then

$$Z = \left( \frac{2\pi mkT}{h^2} \right)^{3N/2} e^{-Nw/kT} \left[ 4\pi \int_0^\delta e^{u(r)/kT} r^2 dr \right]^N, \quad (4)$$

and the equation of state is given by the usual thermodynamic relation

$$\frac{pv}{kT} = \frac{v}{N} \left( \frac{\partial \ln Z}{\partial v} \right)_T, \quad (5)$$

in which  $p$  is the pressure and  $\delta$  is the radius of a sphere having a volume equal to the cell volume per molecule  $v$ .

#### PHENOMENOLOGICAL TOTAL POTENTIAL ENERGY

It is assumed, as in most practically useful theories of fluids, that the contributions to the configurational energy arising from direct many-body interactions are included in an effective pair potential in terms of which the total potential energy of a fluid is pairwise additive. Thus

$$V = \sum_{i \neq j}^N \phi(r_{ij}), \quad (6)$$

where  $\phi(r_{ij})$  is the effective pair potential between molecules  $i$  and  $j$  separated at a distance  $r_{ij}$  from each other. Denote by the subscripts  $i_0$  and  $j_0$  the cell centers of the two molecules. Then one has the identity

$$\begin{aligned} \phi(r_{ij}) &= \phi(r_{i_0j_0}) + [\phi(r_{ij_0}) - \phi(r_{i_0j_0})] + [\phi(r_{j_0i_0}) \\ &\quad - \phi(r_{i_0j_0})] + \{[\phi(r_{ij}) - \phi(r_{ij_0})] \\ &\quad - [\phi(r_{j_0i_0}) - \phi(r_{i_0j_0})]\}, \end{aligned} \quad (7)$$

where the brace represents the contribution arising from the correlations of molecular motions. The potential energy of the system can thus be written in the form

$$\begin{aligned} V &= Nw + \sum_{i \neq j}^N \{[\phi(r_{ij_0}) - \phi(r_{i_0j_0})] + \frac{1}{2}[\phi(r_{ij}) \\ &\quad - \phi(r_{ij_0})] - \frac{1}{2}[\phi(r_{j_0i_0}) - \phi(r_{i_0j_0})]\} \\ &= Nw + \frac{1}{2} \sum_{i \neq j}^N \{[\phi(r_{ij_0}) + \phi(r_{ij})] \end{aligned}$$

$$- [\phi(r_{i_0j_0}) + \phi(r_{j_0i_0})]\}, \quad (8)$$

where

$$w = \frac{1}{2N} \sum_{i \neq j}^N \phi(r_{i_0j_0}) \quad (9)$$

is the "lattice energy" per molecule when all molecules are at their centers.

In order to make further practical progress within the realm of the cell method, it is necessary to calculate, or estimate, the correlation correction due to the motions of the molecules as expressed in equation (8). The direct complete evaluation of this correction is extremely difficult, if not impossible, due to mathematical difficulties[9] and the lack of an adequate effective pair potential which would effectively account for the many-body interactions for all molecular configurations. It appears plausible, although arbitrary from the point of view of mathematical rigor, to "smear" the cells of the  $j$  molecules, referring to a certain  $i$  molecule, with certain probability distribution for the evaluation of the correlation correction term. Thus it becomes possible to write

$$V = Nw + \sum_{i \neq j}^N \sum_{i \neq j}^N [\psi_{ij}(\vec{r}_i) - \psi_{ij}(0)], \quad (10)$$

where  $\psi_{ij}(\vec{r}_i)$ , which is defined as the potential  $\frac{1}{2}[\phi(r_{ij_0}) + \phi(r_{ij})]$  after smearing over the  $j$ -cells, represents the statistical average change in the potential energy when a molecule  $i$  moves from its cell center to the position  $\vec{r}_i$ . The smearing scheme outlined above suggests to inquire into the question whether it is possible to find an "equivalent" effective pair potential in terms of the distance between  $\vec{r}$  and the cell center of another molecule in concern such that the cell method can be used to yield results comparable to experimental measurements. In this sense of approximation, therefore, it seems conceivable to adopt a two-potential model: one for the "lattice" energy of the hypothetical solid when all molecules are at their cell centers, and another for the energy augmentation given by the brackets in equation (10). The present work shows the comparison between the experimental compressibility factors for argon, nitrogen and methane and those calculated by using this approximation.

#### LENNARD-JONES AND KIHARA PAIR POTENTIALS

The effective pair potential by no means can be made to represent the true potential energy of a many body system because there exists many-body forces which are not pairwise additive. From the assumption of pairwise additivity, however, statistical mechanical calculations do yield results which agree, quantitatively at low densities and at least qualitatively at moderate and high densities, with experimental observations. The use of an effective pair potential, wherever possible, is obviously for the purpose of avoiding mathematical complications arising from many-body interactions. Although many

fluids and fluid mixtures have been investigated with the use of the Lennard-Jones potential, it is now known that this potential fails in predicting the temperature-dependence of thermodynamic properties of fluids at low and moderate densities[12,13], indicating that this potential is not effective in correlating molecular motions. For crystalline molecular solids of inert gases, however, Rossi and Danon[11] have shown that the Lennard-Jones potential can be used as an effective pair potential to yield reasonable results for the cohesive energy. The Lennard-Jones potential has the form

$$\phi_{LJ}(s) = 4\epsilon_{LJ} \left[ \left( \frac{\sigma_{LJ}}{s} \right)^{12} - \left( \frac{\sigma_{LJ}}{s} \right)^6 \right], \quad (11)$$

where  $s$  is the distance between two molecules, and  $\epsilon_{LJ}$  and  $\sigma_{LJ}$  are constant parameters.

For a molecule moving in the field of other molecules, as in the case of a gas, Kihara[14] has developed from the consideration of the geometry of convex molecules a hard core model for the effective pair potential which has been applied with reasonable success for the evaluation of both the second virial and the Joule-Thomson coefficients of gases within a rather wide range in temperature[15, 16]. The Kihara potential has the form

$$\psi_K(s) = 4\epsilon_K \left[ \left( \frac{1 - \gamma}{s/\sigma_K - \gamma} \right)^{12} - \left( \frac{1 - \gamma}{s/\sigma_K - \gamma} \right)^6 \right], \quad (12)$$

where  $\gamma$  is the measure of the size of the hard core,  $s$  the distance between the centers of two molecules,  $\epsilon_K$  the depth of the potential and  $\sigma_K$  the value of  $s$  for which  $\psi_K(s) = 0$ . Unlike the Lennard-Jones potential which has two constants, the Kihara potential is a function characterized by three empirical parameters, thus making it more flexible in correlating thermodynamic properties. The core size for homopolar gases at low densities is in general regarded as a constant characterized by the interatomic distance of the molecules, but its magnitude is expected to decrease as the density of the gas is increased(see Concluding Remarks).

From scattering experiments on pairs of molecules and quantum mechanical calculations for the dipole-dipole interactions between pairs of molecules, it is now learned that[13], comparing to the Lennard-Jones potential with parameters determined from experimental physical properties, the correct effective pair potential is less steep on the repulsive side at short intermolecular separations, the minimum of the potential is deeper(probably by as much as one-third), and the potential is much shallower at large intermolecular separations(probably by as much as one-half). The Lennard-Jones and the Kihara potentials for nitrogen are plotted in Figure 1 for comparison. It is seen that the latter, except for the slope of the repulsive portion at small intermolecular separations, is expected to be a better pair potential than the former because it has a deeper minimum and is shallower at large intermolecular separations. The intermolecular potentials

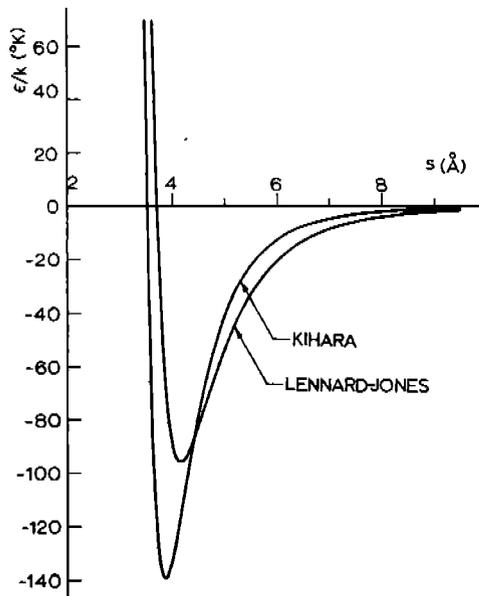


Fig. 1. The Lennard-Jones and the Kihara potential for nitrogen

for argon and methane have similar characteristics in comparison.

#### EVALUATION OF POTENTIAL ENERGIES $w$ AND $u$

Following Lennard-Jones, the coordinate space of the system is divided in such a manner that the centers of the cells form a face-centered cubic lattice. Let  $a$  denote the distance between nearest neighbors. Then the cell volume is given by

$$a^3 = \sqrt{2} v, \quad (13)$$

and the radius of the spherical volume available for a molecule to move about is

$$\delta = \frac{1}{\sqrt{2}} \left( \frac{3}{2\pi} \right)^{1/3} a. \quad (14)$$

To a molecule at the center of its cell, there are 12 neighbors arranged on a sphere of radius  $a$ , 6 on a sphere of radius  $\sqrt{2}a$  and 24 on a sphere of radius  $\sqrt{3}a$ . In the evaluation of the potential energy of a molecule, only neighbors on the three nearest shells will be considered. The contributions to the potential energy due to other distant neighbors are small enough to be neglected in practically all cases.

The smearing scheme mentioned above is equivalent to finding a potential effective for the cell method in terms of the distance between the position of a molecule and the average, weighted by the intermolecular energy, positions of its neighbors. Since the Kihara hard core model has the features comparable to those of a correct effective pair potential and has been used to predict reasonably well the temperature-dependence of the thermodynamic properties of gases, it is believed that this model,

if used for the evaluation of the excessive potential  $u(r)$ , should prove to give better results than the Lennard-Jones potential. The present approximation assumes that the neighbor molecules on the average occupy the origins of their respective centers.

Consider a molecule at a position  $\vec{r}$  from its cell center and one of its neighbors on the  $n$ th shell ( $n = 1, 2, 3$ ). The distance between the two molecules is

$$y_n = a(n + \zeta^2 - 2\sqrt{n}\zeta\cos\theta)^{1/2}, \quad (15)$$

where

$$\zeta = r/a, \quad (16)$$

and  $\theta$  is the angle between the position vector  $\vec{r}$  and the line joining the centers of the two cells, and the Kihara pair potential is

$$\psi_{Kn}(\vec{r}) = 4\epsilon_K \left[ \left( \frac{1 - \gamma}{y_n/\sigma_K - \gamma} \right)^{12} - \left( \frac{1 - \gamma}{y_n/\sigma_K - \gamma} \right)^6 \right]. \quad (17)$$

Introduce the notations

$$\rho = 2^{1/6}(1 - \gamma)\sigma_K, \quad (18)$$

$$v_K = v/\rho^3, \quad (19)$$

$$\beta = \gamma(2v_K)^{-1/3}/(1 - \gamma), \quad (20)$$

where  $v$  again is the cell volume, and  $\rho$  is the distance between the surface of the hard core and the point at which  $\psi_K = \epsilon_K$ . Equation (17) can be written as

$$\begin{aligned} \psi_{Kn}(\vec{r}) = & \frac{\epsilon_K}{4v_K^4} [(n + \zeta^2 - 2\sqrt{n}\zeta\cos\theta)^{1/2} - \beta]^{-12} \\ & - \frac{\epsilon_K}{v_K^2} [(n + \zeta^2 - 2\sqrt{n}\zeta\cos\theta)^{1/2} - \beta]^{-6}. \end{aligned} \quad (21)$$

The contribution to the average potential energy of a molecule at a distance  $\zeta a$  from the center of its own cell due to a molecule on the  $n$ th shell can be obtained by averaging  $\psi_{Kn}(\vec{r})$  over the spherical surface of radius  $\zeta$  to have the form

$$\begin{aligned} \bar{\psi}_{Kn}(\zeta) = & \frac{\epsilon_K}{880v_K^4} \left\{ \frac{1}{\sqrt{n}\zeta} [(\zeta_1 - \beta)^{-11}(11\zeta_1 - \beta) \right. \\ & \left. - (\zeta_2 - \beta)^{-11}(11\zeta_2 - \beta)] \right\} \\ & - \frac{\epsilon_K}{40v_K^2} \left\{ \frac{1}{\sqrt{n}\zeta} [(\zeta_1 - \beta)^{-5}(5\zeta_1 - \beta) \right. \\ & \left. - (\zeta_2 - \beta)^{-5}(5\zeta_2 - \beta)] \right\}, \end{aligned} \quad (22)$$

where

$$\zeta_1 = \sqrt{n} - \zeta, \quad (23)$$

$$\zeta_2 = \sqrt{n} + \zeta. \quad (24)$$

Let  $N_n$  be the number of molecules on the  $n$ th shell, i.e.,  $N_1 = 12$ ,  $N_2 = 6$ , and  $N_3 = 24$ . The total potential energy in excess of  $w$  is then

$$u(\zeta) = \sum_{n=1}^3 N_n [\bar{\psi}_{Kn}(\zeta) - \bar{\psi}_{Kn}(0)], \quad (25)$$

where

$$\bar{\psi}_{Kn}(0) = \frac{\epsilon_K}{4v_K^4} (\sqrt{n} - \beta)^{-12} - \frac{\epsilon_K}{v_K^2} (\sqrt{n} - \beta)^{-6}. \quad (26)$$

The potential energy of interaction per molecule when all molecules are at the centers of their cells, as implied by the mechanical procedures in the development of the cell model, should be approximated by the cohesive energy of a crystal at the corresponding lattice spacing. Since the Lennard-Jones potential yields reasonable cohesive energies for molecular crystals of inert gases, it appears appropriate, a priori from evidences available in the literature, that this potential may be used for the determination of  $w$ . Summing over the pair potentials given by equation (11) between a molecule and its neighbors on the three nearest shells yields, upon dividing by a factor of 2 for the purpose of averaging, the result

$$w = \frac{6\epsilon_{LJ}}{v_{LJ}^2} \left( \frac{1.011}{v_{LJ}^2} - 2.273 \right), \quad (27)$$

where

$$v_{LJ} = \frac{1}{\sqrt{2}} \left( \frac{a}{\sigma_{LJ}} \right)^3. \quad (28)$$

#### EQUATION OF STATE

We define a dimensionless temperature and a dimensionless volume

$$\theta = kT/\epsilon_K, \quad (29)$$

$$v = 4\pi\sqrt{2}v_K \int_0^{0.5527} e^{-u(\zeta)/\epsilon_K\theta} \zeta^2 d\zeta. \quad (30)$$

The partition function given by equation (4) is then

$$Z = \left( \frac{2\pi mkT}{h^2} \right)^{3N/2} v_K^{3N} e^{-Nw/\epsilon_K\theta} \quad (31)$$

and the compressibility factor is given by

$$\frac{pv}{kT} = v_K \left[ \frac{1}{v} \left( \frac{\partial v}{\partial v_K} \right)_{\theta} - \frac{1}{\epsilon_K\theta} \frac{dw}{dv_K} \right]. \quad (32)$$

In equation (32),  $v$  is defined in equation (30) and

$$\frac{dw}{dv_K} = 12\epsilon_{LJ} \left(\frac{\sigma_{LJ}}{\rho}\right)^6 \frac{1}{v_K^3} \left[-\frac{2.021}{v_K^2} \left(\frac{\sigma_{LJ}}{\rho}\right)^6 + 2.273\right], \quad (33)$$

$$\left(\frac{\partial v}{\partial v_K}\right)_\theta = \frac{v}{v_K} - 4\pi\sqrt{2} \frac{v_K}{\epsilon_K \theta} \times \int_0^\infty \frac{0.5527}{dv_K} \frac{du(\zeta)}{dv_K} e^{-u(\zeta)/\epsilon_K \theta} \zeta^2 d\zeta, \quad (34)$$

where

$$\frac{du(\zeta)}{dv_K} = \sum_{n=1}^3 N_n \left[ \frac{d\bar{\psi}_{Kn}(\zeta)}{dv_K} - \frac{d\bar{\psi}_{Kn}(0)}{dv_K} \right], \quad (35)$$

and the derivatives of  $\bar{\psi}_{Kn}$  with respect to  $v_K$  can be obtained from equations (22) and (26) to have the explicit expressions

$$\begin{aligned} \frac{d\bar{\psi}_{Kn}(\zeta)}{dv_K} &= \frac{\epsilon_K}{220v_K^5} \left\{ \frac{1}{\sqrt{n}\zeta} [(\zeta_1 - \beta)^{-11}(11\zeta_1 - \beta) \right. \\ &\quad \left. - (\zeta_2 - \beta)^{-11}(11\zeta_2 - \beta)] \right\} \\ &\quad - \frac{\beta\epsilon_K}{264v_K^5} \left\{ \frac{1}{\sqrt{n}\zeta} [(\zeta_1 - \beta)^{-12}(12\zeta_1 - \beta) \right. \\ &\quad \left. - (\zeta_2 - \beta)^{-12}(12\zeta_2 - \beta)] \right\} \\ &\quad + \frac{\epsilon_K}{20v_K^3} \left\{ \frac{1}{\sqrt{n}\zeta} [(\zeta_1 - \beta)^{-5}(5\zeta_1 - \beta) \right. \\ &\quad \left. - (\zeta_2 - \beta)^{-5}(5\zeta_2 - \beta)] \right\} \\ &\quad - \frac{\beta\epsilon_K}{30v_K^3} \left\{ \frac{1}{\sqrt{n}\zeta} [(\zeta_1 - \beta)^{-6}(6\zeta_1 - \beta) \right. \\ &\quad \left. - (\zeta_2 - \beta)^{-6}(6\zeta_2 - \beta)] \right\}, \quad (36) \end{aligned}$$

and

$$\frac{d\bar{\psi}_{Kn}(0)}{dv_K} = \frac{\epsilon_K \sqrt{n} [-1 + 2v_K^2 (\sqrt{n} - \beta)^6]}{v_K^5 (\sqrt{n} - \beta)^{13}}, \quad (37)$$

where the notations given by equations (20), (23), and (24) have been used.

#### CALCULATED RESULTS AND COMPARISON WITH EXPERIMENTS

The compressibility factors  $pv/KT$  for argon, nitrogen and methane are calculated by using equations (32) through (37). The potential parameters employed

in the present calculations are given in Table 1. The parameters of the Kihara potential are reported by Sherwood and Prausnitz[15], and those of the Len-

Table 1. The Lennard-Jones and the Kihara potential parameters

Gas	$\epsilon_{LJ}/k(^{\circ}K)$	$\sigma_{LJ}(\text{\AA})$	$\epsilon_K/k(^{\circ}K)$	$\gamma$	$\sigma_K(\text{\AA})$
A	117.7	3.504	147.2	0.111	3.314
N <sub>2</sub>	95.9	3.710	139.2	0.200	3.526
CH <sub>4</sub>	148.9	3.783	204.3	0.167	3.620

nard-Jones potential are selected from the available values in the literature for best agreement between the calculated results and experimental measurements. Both sets of parameters listed in Table are obtained from second virial coefficient data. By using different Lennard-Jones parameters, the computed isotherms are found to deviate only slightly from those to be presented in this work.

Numerical computations are made by using an IBM 1130 computer at West Virginia Institute of Technology. In evaluating the integrals for the calculation of  $v$  and  $(\partial v/\partial v_K)_\theta$  as defined in equations (30) and (34),  $\zeta$  is incremented in the 0.01. No significant changes can be found in the values of the integrals when half of this size is used, showing that there are no significant numerical errors in the present computed results.

Figure 2 shows the comparison between the computed and experimental compressibility factors for argon at three different temperatures. The Lennard-Jones parameters used in the computations are given by Sherwood and Prausnitz[15]. The experimental data are reported by Michels et. al.[17]. The agreement

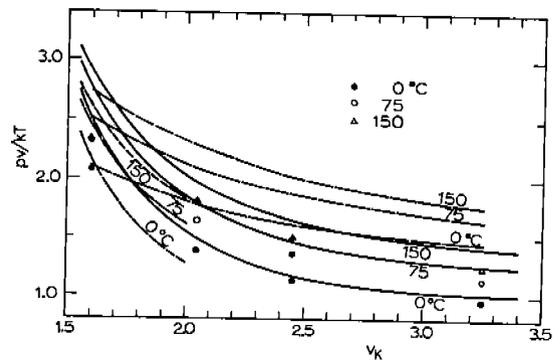


Fig. 2. Isothermal compression of argon at 0, 75, and 150°C. Present results: —,  $\gamma = 0.111$ ; ---,  $\gamma = 0.095$ . —, results by Wentorf et. al.[18] calculated from the Lennard-Jones potential. Experimental data are by Michels et. al.[17].

is satisfactory, to within 10 percent or less, for all three temperatures except at very high densities. Also compared in Figure 2 are the results

by Wentorf et. al.[18] calculated from using the Lennard-Jones potential. The inadequacy of the Lennard-Jones potential in the cell method for the description of gases at high densities is clearly demonstrated.

The results for nitrogen are shown in Figure 3. The Lennard-Jones potential are those reported by Holborn and Otto[19], and the experimental data are by Michels et. al.[20]. Again the compressibility factors calculated by Wentorf et. al. are plotted for comparison. The present work shows satisfactory results except at very high densities.

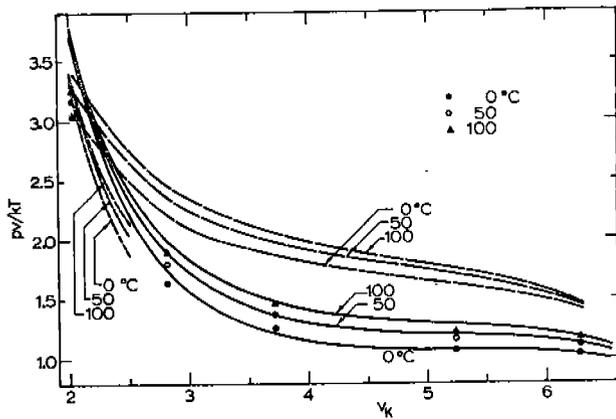


Fig. 3. Isothermal compression of nitrogen at 0, 50, and 100°C. Present work:——,  $\gamma = 0.200$ ; ----,  $\gamma = 0.185$ .——, results calculated by Wentorf et. al.[18] from Lennard-Jones potential. Experimental data are by Michels et. al.[20].

Comparison of the computed compressibility factors for methane at three different temperatures with

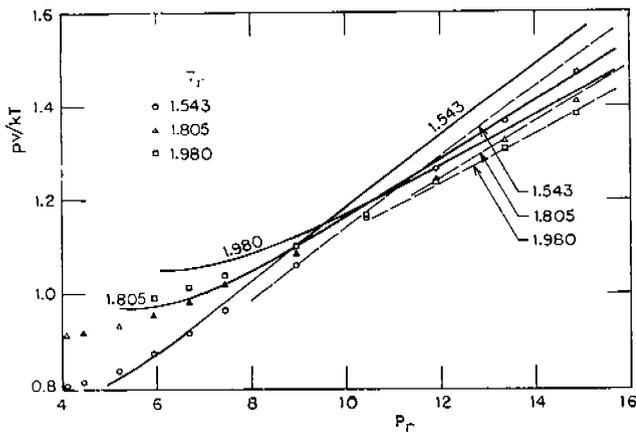


Fig. 4.  $pv/kT$  versus reduced pressure  $P_r = p/p_c$  for methane at three reduced temperatures. Present results:——,  $\gamma = 0.167$ ; ----,  $\gamma = 0.160$ . Experimental data are by Sage and Lacey[21].

experimental measurements, reported by Sage and Lacey[21], is made in Figure 4, where  $pv/kT$  is plotted against the reduced pressure  $P_r = p/p_c$  for various values of the reduced temperature  $T_r = T/T_c$  with  $p_c$  and  $T_c$  being the pressure and temperature at the critical point. The Lennard-Jones potential parameters, good for the temperature range 0-350°C, are those reported by Sherwood and Prausnitz[15]. It is seen that the cell method is inaccurate at low densities. At high densities, the calculated  $pv/kT$  are consistently higher than the experimental data. The agreement, however, is satisfactory to within a few percent up to  $P_r = 15$ .

#### CONCLUDING REMARKS

The cell method is expected to yield results the more reasonable the higher the density. This is because of that the higher the density the more probable that a molecule is imprisoned or trapped by its immediate neighbors. However, it is observed for argon and nitrogen in comparison with experiments that, at very high densities, the results of Wentorf et. al. obtained by using the Lennard-Jones potentials fair better than the present calculations. The Kihara potential parameters used in the present calculations are those derived from fitting the second virial coefficients of dilute gases. There is strong evidence that the Kihara potential determined for dilute gases can not represent correctly the effective pair potential at high densities[22]. Both the Monte Carlo calculations of McDonald and Singer[23] and the molecular dynamics calculations of Verlet [24] have provided quasi-experimental data showing that the Lennard-Jones potential, while being incorrect for gaseous argon, is in fact tolerably good in representing the effective pair potential for liquid argon. The Kihara potential reduces to the Lennard-Jones form when  $\gamma = 0$ . Since the Kihara potential has more conspicuous features conforming to the correct effective pair potential than the Lennard-Jones potential in describing dilute gases, it may be conjectured here that the former, if used as an effective pair potential for the entire range in density, must have density-dependent parameters to account for the effects of many-body interactions which is more significant the denser the fluid. The repulsive portion of the Kihara potential at small intermolecular separations is steeper than that of the true effective pair potential. The slope of this portion can be reduced by using a core size decreasing with increasing density. To demonstrate the effect of the core size on the calculated compressibility factors, a set of trial computations has been made with a smaller value of  $\gamma$ . The  $\gamma$ -value is so reduced that  $\rho = 2^{1/6}(1 - \gamma)\sigma_K$  remains constant, thus making the repulsive part at small separations less steep and the bowl of the potential broader. The results of the trial calculations at high densities of the three gases investigated are shown in their respective figures. The necessity of a density-dependent core size in the Kihara potential is clearly demonstrated. The parameters  $\epsilon$  and  $\sigma$  are likely expected to vary accordingly with density in order that the Kihara model can be used to represent the effective pair potential at high densities. At extremely high

densities, correlations between molecular motions should be small and the molecular configurations become solid-like, and the Kihara potential thus should approach the form of the Lennard-Jones potential. This probably explains the better agreement of the results by Wentorf et. al. with experiments at very high densities.

Soc., 43,16(1967).

24. Verlet, L., Phys. Rev., 159,98(1967).

#### ACKNOWLEDGEMENT

The author wishes to express his thanks to Professor B. H. Buckbee for making the graphs presented in this paper. He also wishes to acknowledge the service provided by the Computer Center at West Virginia Institute of Technology.

#### REFERENCES

1. Mayer, J. E., J. Chem. Phys., 5,67(1931).
2. Orstein, L. S., and Zernike, F., Proc. Akad. Sci. Amst., 17,793(1914).
3. Stell, G., The Equilibrium Theory of Classical Fluids, ed. Fisch, H. L., and Lebowitz, J. L., Benjamin, New York, 1964.
4. Green, H. S., Molecular Theory of Fluids, North Holland, Amsterdam, 1952.
5. Percus, J. K., and Yevick, G. J., Phys. Rev., 110,1(1958).
6. Rushbrook, G. S., and Silbert, M., Molecular Phys., 12,505(1967).
7. Rowlinson, J. S., Molecular Phys., 12,513(1967).
8. Lennard-Jones, J. E., and Devonshire, A. F., Proc. Roy. Soc., A163,53(1937); 165,1(1938).
9. Barker, J. A., Lattice Theories of the Liquid State, Pergamon Press, New York, 1963.
10. Fowler, R. H., and Guggenheim, E. A., Statistical Thermodynamics, Cambridge Univ. Press, 1949.
11. Hirschfelder, J. O., Curtiss, C. F., and Bird, R. B., Molecular Theory of Gases and Liquids, Wiley, New York, 1954.
12. Rossi, J. E., and Danon, F., Disc. Faraday Soc., 40,97(1965).
13. Rowlinson, J. S., Disc. Faraday Soc., 40,19(1965); The Thomas Alvin Boyd Lectures in Chem. Eng., Bulletin 201, Ohio State Univ., 1967. Weir, R. D., Jones, I. W., Rowlinson, J. S., and Saville, G., Trans. Faraday Soc., 63,1320(1967).
14. Kihara, T., Rev. Mod. Phys., 25,831(1953); 27,412(1955); Adv. Chem. Phys., 5,147(1963).
15. Sherwood, A. E., and Prausnitz, J. M., Chem. Phys., 41,413(1964); 41,429(1964).
16. Francis, P. G., and Luckhurst, G. R., Trans. Faraday Soc., 59,667(1963).
17. Michels, A., Wijker, H., and Wijker, H. K., Physica, 15,627(1949).
18. Wentorf, R. H., Buehler, R. J., Hirschfelder, J. O., and Curtiss, C. F., J. Chem. Phys., 18,1484(1950).
19. Holborn, L., and Otto, J., Z. Physik, 33,1(1925).
20. Michels, A., Wouters, H., and de Boer, J., Physica, 3,585(1936).
21. Sage, B. H., and Lacey, W. N., Thermodynamic Properties of the Lighter Paraffin Hydrocarbons and Nitrogen, Am. Petro. Inst., New York, 1950.
22. Rice, S. A., and Young, D. A., Disc. Faraday Soc., 43,16(1967).
23. McDonald, I. R., and Singer, K., Disc. Faraday