

Application of Lennard-Jones (n, m) potential to pure gases and gaseous mixtures

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Abstract

Reduced second virial coefficients and their first and second derivatives with respect to reduced temperature T^* are evaluated for Lennard-Jones ($4-n$) and ($5-n$) potentials over a range of $T^* = 0.3$ to 500.

Empirical equations for the reduced virial coefficients and their derivatives are presented. Force constants for $LJ(m, n)$ potential are evaluated for 28 pure substances and ten mixtures and Boyle temperature and volume for 28 pure substances are evaluated.

Key words: Virial coefficients, gaseous mixtures, Lennard-Jones potential, Boyle temperature.

1. Introduction

To evaluate the thermodynamic properties using virial equation of state, a knowledge of virial coefficients is essential. Virial coefficients may be evaluated by using a potential energy function. By using mixing rules it is possible to evaluate the thermodynamic properties of mixtures. In the present study a general Lennard-Jones potential¹, namely,

$$\phi(r) = \lambda r^{-n} - \mu r^{-m} \quad (1)$$

has been used.

Lennard-Jones² has derived an expression for the evaluation of second virial coefficients using equation (2) which can be written as

$$B^*(T^*) = \frac{B(T)}{\frac{3}{8}\pi N\sigma^3} = -\frac{3}{n} \sum_{j=0}^{\infty} \frac{1}{j!} \left(\frac{T^*}{\alpha}\right)^{(m-n)j-3/n} \Gamma\left(\frac{jm-3}{n}\right) \quad (2)$$

where

$$\alpha = \left(\frac{n}{n-m}\right) \left(\frac{n}{m}\right)^{m/(n-m)} \quad (3)$$

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2. Present work

In the present study, the second virial coefficients for $LJ(4-n)$ and $LJ(5-n)$ potentials are evaluated over a reduced temperature of 0.30 to 500.0. The temperature derivatives of the second virial coefficients are evaluated using the equations

$$B_1^*(T^*) = T^*(dB^*/dT^*) \quad (4)$$

and

$$B_2^*(T^*) = T^{*2}(d^2B^*/dT^{*2}). \quad (5)$$

2.1. Empirical equation for B^* , B_1^* and B_2^*

The values of $B^*(T^*)$, $B_1^*(T^*)$ and $B_2^*(T^*)$ evaluated are fitted to an equation of the form

$$\phi(T^*) = A + B/T^* + C/(T^*)^2 + D/(T^*)^3 + E/(T^*)^4 + F/(T^*)^5 \quad (6)$$

where ϕ is one of B_1^* , and B_2^* .

For getting a better fit, the data are fitted over two ranges, namely, $T^* = 0.3-2.10$ and $T^* = 2.0-11.0$. The second virial coefficients and their temperature derivatives and the constants of the polynomial for $B^*(T^*)$ evaluated for $LJ(4-n)$ and $LJ(5-n)$ potentials are available with the authors.

2.2. Evaluation of Boyle temperature and volume

Boyle temperature is the temperature at which the second virial coefficient is zero, and

Table I
 T_B^* and B_{1B}^* values for $(m-n)$ potential

| m | n | T_B^* | B_{1B}^* |
|-----|------|---------|------------|
| 4.0 | 5.0 | 59.29 | 0.1937 |
| 4.0 | 6.0 | 32.17 | 0.2923 |
| 4.0 | 7.0 | 22.16 | 0.3726 |
| 4.0 | 8.0 | 17.15 | 0.4383 |
| 4.0 | 10.0 | 12.27 | 0.5379 |
| 4.0 | 12.0 | 9.917 | 0.6095 |
| 4.0 | 14.0 | 8.541 | 0.6632 |
| 4.0 | 18.0 | 7.006 | 0.7383 |
| 4.0 | 20.0 | 6.533 | 0.7656 |
| 4.0 | 28.0 | 5.442 | 0.8380 |
| 5.0 | 7.0 | 9.728 | 0.5188 |
| 5.0 | 8.0 | 7.849 | 0.5794 |
| 5.0 | 9.0 | 6.687 | 0.6282 |
| 5.0 | 10.0 | 5.901 | 0.6685 |
| 5.0 | 12.0 | 4.906 | 0.7311 |
| 5.0 | 15.0 | 4.082 | 0.7968 |
| 5.0 | 20.0 | 3.385 | 0.8659 |
| 5.0 | 30.0 | 2.782 | 0.9390 |
| 5.0 | 40.0 | 2.505 | 0.9774 |

Boyle volume is the volume which corresponds to that temperature. For each value of m for $LJ(4-n)$ and $LJ(5-n)$ potentials, values of T^* and B_1^* at which the value of B^* is smaller than 10^{-7} are evaluated (Table I). Boyle temperature and volume can be evaluated using the equations:

$$T_B = T_B^* \cdot \epsilon/k \quad (7)$$

and

$$V_B = B_{1B}^* \cdot b_0. \quad (8)$$

2.3. Application of $LJ(m-n)$ potential to pure gases

The $LJ(m-n)$ potential is applied to 28 pure substances. The force constants ϵ/k and b_0 are evaluated for each potential function by a non-linear least-squares technique. From these sets the values of ϵ/k and b_0 which gave the lowest value of the sum of squares of deviation in calculated $B(T)$ values are selected as the best (Table II).

2.4. Application to mixtures

For the evaluation of force constants of mixtures, following mixing rules are used:

$$\epsilon_{ij} = (\epsilon_{ii} \cdot \epsilon_{jj})^{1/2} \quad (9)$$

$$\sigma_{ij} = (\sigma_{ii} \cdot \sigma_{jj})^{1/2} \quad (10)$$

and

$$B_m = \sum_{i=1}^n \sum_{j=1}^n x_i x_j B_{ij}. \quad (11)$$

In the present study, only binary mixtures are considered. The calculated values of B_m , the mixture second virial coefficient are evaluated for various mole fractions and potential functions. For a mixture, the potential function which gives the minimum sum of squares of deviation in calculated and experimental mixture second virial coefficients is chosen as the best (Table III).

A comparison of mixture properties evaluated by $LJ(6-12)$ potential with the $LJ(m-n)$ potential shows that the latter predicts mixture second virial coefficients better. Similar observation is found in the case of pure substances also.

The computations were made in double precision on an IBM 360/44 digital computer.

Nomenclature

| | |
|---------------------------------------|--|
| A, B, C, D, E, F | = constants in eqn (8) |
| $B(T)$ | = second virial coefficients, $\text{cm}^3 \text{mol}^{-1}$ |
| $B^*(T^*) = T^*(dB^*/dT^*)$ | = first derivative of the second virial coefficient |
| $B_1^*(T^*) = B(T)/b_0$ | = reduced second virial coefficient |
| $B_2^*(T^*) = T^{*2}(d^2B^*/dT^{*2})$ | = second derivative of the second virial coefficient |
| B_m | = mixture second virial coefficient |
| B_{ij} | = interaction second virial coefficient |
| $\phi(T^*)$ | = one of $B^*(T^*)$, $B_1^*(T^*)$, $B_2^*(T^*)$ in eqn (6) |

Table II
Force constants, Boyle temperature and volume, and potential energy functions for pure substances

| Substance | Boyle temp. (T_B , °K) | Boyle volume (cc/mole) | No. of points | Range of temp. (°K) | Potential energy function | a/k (°K) | b_0 (cc/mole) | Average deviation % | Max. deviation % | Sum of squares of deviation | Ref |
|-----------------------------|---------------------------|------------------------|---------------|---------------------|---------------------------|------------|-----------------|---------------------|------------------|-----------------------------|-----|
| Ammonia | 1355 | 23.9 | 8 | 273-573 | (12-15) | 987.7 | 21.3 | 2.16 | -8.74 | 33.4 | 3 |
| Acetone | 529.8 | 2006 | 6 | 303-403 | (9-33) | 445.3 | 1685 | 0.82 | 1.50 | 548.7 | 6 |
| Argon | 431.6 | 35.86 | 18 | 84-271 | (7-12) | 159.0 | 41.1 | 0.86 | -5.56 | 23.6 | 4 |
| Benzene | 672.4 | 868.0 | 8 | 300-440 | (7-63) | 523.0 | 750 | 0.95 | -1.58 | 844 | 3 |
| <i>n</i> -Butane | 771.7 | 382.3 | 6 | 411-511 | (4-20) | 118.1 | 499 | 0.57 | 1.23 | 18.3 | 5 |
| Carbon tetrachloride | 3222 | 71.05 | 6 | 320-420 | (5-15) | 789.4 | 89.2 | 1.17 | 2.02 | 1169 | 3 |
| Carbon tetrafluoride | 518.6 | 103.3 | 16 | 273-623 | (7-30) | 322.0 | 96.4 | 0.25 | -1.44 | 0.027 | 3 |
| Chloroform | 666.1 | 251.8 | 10 | 239-450 | (9-27) | 518.2 | 218.0 | 3.50 | 11.1 | 1228 | 6 |
| Cyclohexane | 533.9 | 1986 | 8 | 310-380 | (4-28) | 98.1 | 2370 | 0.56 | 1.34 | 448 | 3 |
| Dentorium | 114.8 | 27.59 | 14 | 123-423 | (9-72) | 120.1 | 21.43 | 0.69 | 3.68 | 0.493 | 3 |
| Diethyl ether | 549.5 | 1206 | 6 | 300-400 | (6-60) | 341.6 | 1109 | 3.34 | 6.50 | 5747 | 3 |
| Ethane | 828.1 | 72.88 | 8 | 298-473 | (7-24) | 467.7 | 70.48 | 0.37 | -0.74 | 1.36 | 7 |
| Methylchloride | 718.2 | 395.7 | 5 | 323-403 | (6-30) | 360.2 | 391.8 | 0.52 | -1.10 | 31.22 | 6 |
| <i>n</i> -Heptane | 644.6 | 1647 | 6 | 349-400 | (9-42) | 586.9 | 1343 | 0.10 | 0.19 | 14.26 | 8 |
| Hydrogensulfide | 1027 | 44.19 | 8 | 298-473 | (7-56) | 776.6 | 38.53 | 0.27 | -0.83 | 0.973 | 7 |
| Krypton | 580.4 | 47.47 | 13 | 110-600 | (6-20) | 240.9 | 60.56 | 2.71 | 23.03 | 27.80 | 3 |
| Methylchloride | 774.8 | 183.8 | 10 | 280-580 | (7-28) | 468.0 | 173.3 | 1.00 | 2.45 | 51.92 | 3 |
| Methylfluoride | 770.5 | 75.29 | 8 | 280-420 | (9-36) | 667.5 | 62.53 | 0.41 | 0.79 | 2.713 | 3 |
| Neon | 126.6 | 20.98 | 10 | 60-600 | (4-16) | 16.58 | 29.76 | 3.93 | 26.60 | 0.361 | 3 |
| Neopentane | 847.5 | 332.4 | 9 | 310-590 | (7-24) | 478.7 | 321.4 | 0.34 | 0.54 | 27.22 | 5 |
| Nitrogen | 304.9 | 50.81 | 11 | 80-250 | (7-35) | 200.4 | 46.46 | 15.9 | -51.5 | 1531 | 3 |
| <i>n</i> -octane | 661.0 | 1866 | 10 | 373-413 | (12-78) | 884.7 | 1289 | 0.55 | -3.66 | 26.31 | 9 |
| Oxygen | 418.7 | 36.10 | 10 | 90-350 | (6-30) | 210.0 | 35.75 | 1.86 | -2.13 | 3900 | 3 |
| Perfluoro <i>n</i> -hexane | 547.7 | 2414 | 6 | 308-384 | (4-24) | 93.08 | 2900 | 1.51 | 3.40 | 951.0 | 9 |
| Perfluoro <i>n</i> -pentane | 645.1 | 831.0 | 6 | 308-383 | (9-72) | 675.2 | 645.4 | 0.94 | 1.13 | 51.07 | 5 |
| Propane | 3598 | 25.72 | 13 | 260-550 | (7-24) | 551.2 | 105.6 | 0.42 | 1.13 | 18.50 | 5 |
| Sulfa-hexafluoride | 975.8 | 109.2 | 5 | 313-393 | (6-7) | 95.22 | 393.1 | 0.95 | -1.79 | 18.50 | 5 |
| Tetramethylsilane | 841.8 | 427.2 | 7 | 323-403 | (7-30) | 522.7 | 398.7 | 0.34 | -0.50 | 56.95 | 3 |

| | |
|-----------------|--|
| m, n | = parameters in Lennard-Jones potential, eqn (1) |
| N | = Avagadro's number |
| T | = temperature, °K |
| $T^* = T/(e/k)$ | = reduced temperature |
| x_i, x_j | = mole fractions of components i and j |
| T_B | = Boyle temperature, °K |
| V_B | = Boyle volume, cc/mole |

Greek letters

| | |
|------------|--|
| λ | = parameters in Lennard-Jones potential, eqn (1) |
| σ | = collision diameter, A |
| ϵ | = depth of the potential well |
| e/k | = parameter in Lennard-Jones potential, °K |
| $\phi(r)$ | = potential energy function |

References

1. JONES, J. E. *Proc. R. Soc. Lond. (A)*, 1924, **106**, 463-477.
2. LENNARD-JONES, J. E. *Physica*, 1937, **4**, 941-956.
3. DYMOND, J. H. AND SMITH, E. B. *Virial coefficients of gases—Critical compilation*, Clarendon, 1969.
4. BYRNE, M. A., JONES, M. R. AND STAVELEY, L. A. K. *Trans. Faraday Soc.*, 1968, **64**, 1747-1756.
5. HUFF, J. A. AND REED T. M. III. *J. Chem. Engng Data*, 1963, **8**, 306-311.
6. SUH, K. W. AND STORVICK, T. S. *J. Phys. Chem.*, 1967, **71**, 1450-1456.
7. KHOURY, F. AND ROBINSON, D. B. *J. Chem. Phys.*, 1971, **55**, 834-839.
8. MCGLASHAN, M. L. AND POTTER, D. J. B. *Proc. R. Soc. Lond. (A)*, 1962, **267**, 478-500.
9. GARNER, M. D. G. AND MCCOUBREY, J. C. *Trans. Faraday Soc.*, 1959, **55**, 1524-1530.
10. GUPTA, S. K. AND KING, A. D. JR. *Can J. Chem.*, 1972, **50**, 660-668.
11. SAKSENA, M. P., NAIN, V. P. S. AND SAXENA, S. C. *Indian J. Phys.*, 1967, **41**, 123-133.
12. DOUSLIN, D. R., HARRISON, R. H. AND MOORE, R. T. *J. Phys. Chem.*, 1967, **71**, 3477-3488.