An Algorithm for Use with Multiterm Lennard-Jones Potentials

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Closed analytic solutions for the two-body cluster integral are available for a limited number of simple intermolecular potential functions. These functions include the rigid sphere model, point centers of repulsion, the Sutherland model and the square well potential. All are simplified and lack sufficient flexibility to be useful for detailed thermodynamic calculations. The Lennard-Jones potential represents a degree of greater sophistication in model structure. The general Lennard-Jones potential has four variable parameters, that is, the coefficients and exponents of two terms representing attractive and repulsive forces, respectively. An infinite series solution to the cluster integral for the two-term, general potential was proposed by Lennard-Jones (*1*).

The Lennard-Jones potential can be expanded in a variety of ways. As suggested by Rowlinson (*2*), it is possible to add even powered terms to have the attractive components reflect a series of contributions for not only instantaneous dipoles, but quadrapoles, octapoles, etc., as well. We have succeeded in constructing a multiple series solution of the cluster integral for the case of the general Lennard-Jones potential with a single repulsive term and N attractive terms. This potential is represented by

$$\phi = \frac{d}{r^{\delta}} - \sum_{i=1}^{N} \frac{a_i}{r^{\alpha_i}} \tag{1}$$

New variables are defined to separately describe the attractive and repulsive components of the potential.

$$x = \frac{d}{kTr^{\delta}} \tag{2a}$$

$$y = \sum_{i=1}^{N} \frac{a_i}{kT}\left(\frac{d}{kTx}\right)^{-\alpha_i/\delta} \tag{2b}$$

The two-body cluster integral can be written for this $(N + 1)$-term potential expression in the variables x and y:

$$B = \frac{2\pi}{\delta}\left(\frac{d}{kT}\right)^{3/\delta}\int_o^{\infty}\{1 - e^{-x}e^{y}\}\, x^{-[(3+\delta)/\delta]}\, dx \tag{3}$$

Employing integral substitution and a Maclaurin series expansion for the exponential in y leads to

$$B = B_o - \frac{2\pi}{\delta}\left(\frac{d}{kT}\right)^{3/\delta}\int_o^{\infty} x^{-[(3+\delta)/\delta]}\, e^{-x}\left\{\sum_{j=1}^{N}\frac{y^j}{j!}\right\}dx \tag{4}$$

where B_o is a gamma function term

$$B_o = \frac{2\pi}{3}\left(\frac{d}{kT}\right)^{3/\delta}\Gamma\left(\frac{\delta-3}{\delta}\right) \tag{5}$$

For convenience y can be rewritten as a summation on the variable x with temperature-dependent coefficients b_i, such that

$$y = \sum_{i=1}^{N} b_i x^{\alpha_i/\delta} \tag{6a}$$

$$b_i = \frac{a_i}{kT}\left(\frac{d}{kT}\right)^{-\alpha_i/\delta} \tag{6b}$$

The revised cluster integral becomes

$$B = B_o - \frac{2\pi}{\delta}\left(\frac{d}{kT}\right)^{3/\delta}\int_o^{\infty} x^{-[(3+\delta)/\delta]}\, e^{-x}\left\{\sum_{j=1}^{\infty}\frac{\left(\sum_{i=1}^{N} b_i x^{\alpha_i/\delta}\right)^j}{j!}\right\}dx \tag{7}$$

If the inner sum of Equation (7) is raised to successive integer powers and represented by a multinomial expansion, a tractable form of the integral is generated:

$$B = B_o - \frac{2\pi}{\delta}\left(\frac{d}{kT}\right)^{3/\delta}\int_o^{\infty} x^{-[(3+\delta)/\delta]}\, e^{-x} \sum_{j=1}^{\infty}\sum_{\gamma 2=0}^{j}\sum_{\gamma 3=0}^{j}\cdots\sum_{\gamma N=0}^{j}\left[\frac{1}{\left[j-\sum_{i=2}^{N}\gamma_i\right]!\left\{\prod_{i=2}^{N}(\gamma_i!)\right\}}\left\{\prod_{i=2}^{N}(b_i x^{\alpha_i/\delta})^{\gamma_i}\right\}(b_1 x^{\alpha_1/\delta})^{j-\sum_{i=2}^{N}\gamma_i}\right] \tag{8}$$

The solution is given by

$$B = B_o - \frac{2\pi}{\delta}\sum_{j=1}^{\infty}\sum_{\gamma 2=0}^{j}\sum_{\gamma 3=0}^{j}\cdots\sum_{\gamma N=0}^{j}\left[\frac{\left(\frac{a_1}{kT}\right)^{j-\sum_{i=2}^{N}\gamma_i}\left\{\prod_{i=2}^{N}\left(\frac{a_i}{kT}\right)^{\gamma_i}\right\}}{\left[j-\sum_{i=2}^{N}\gamma_i\right]!\left\{\prod_{i=2}^{N}(\gamma_i!)\right\}}\left(\frac{d}{kT}\right)^{\left[\alpha_1\left(j-\sum_{i=2}^{N}\gamma_i\right)-\sum_{i=2}^{N}(\alpha_i\gamma_i)\right]/\delta}\Gamma\left\{\frac{\alpha_1\left[j-\sum_{i=2}^{N}\gamma_i\right]+\sum_{i=2}^{N}(\alpha_i\gamma_i)-3}{\delta}\right\}\right] \tag{9}$$

Hirschfelder, et al. (*3*) report coefficients for forty terms of the reduced series solution based on a Lennard-Jones (12-6) potential with one attractive term $(N = 1)$. The authors examined series convergence for several simple cases and observed that (a) the factorial components control the rate of convergence, and (b) at reduced temperatures as low as unity, twenty terms reduce summing error to at least three orders of magnitude less than the smallest errors in thermodynamic measurements and derived data. With this guidance, a criterion for selection of j can be adopted, that is,

$$20! < \left[j - \sum_{i=2}^{N} \gamma_i \right]! \left\{ \prod_{i=2}^{N} (\gamma_i!) \right\} \qquad (10)$$

The minimum value of j is realized when the difference across the inequality of Equation (10) is a minimum. This condition is attained with equal factorial terms, such that Equation (10) becomes

$$\left\{ \left(\frac{j_{\min}}{N} \right)! \right\}^{N} - 20! > \epsilon^{+} \qquad (11)$$

By using an approximation for the factorial, j is found to have values such as 25 for $N = 2$ and 29 for $N = 3$. For cases involving two and three attractive terms, Equation (11) generates values for j that produced acceptable convergence. Values of the second virial coefficient for methane at 200°K. were predicted by both the algorithm and direct integral solution. Results agreed to better than one part in one thousand. Table 1 is an illustration of the effect of a second attractive term taken from these predictions. Further, the limit case of $N = 1$ ($a_2/k = 0$) was checked against the method of Hirschfelder, et al. (*3*), with agreement observed to five significant figures. For the latter, an ϵ/k and σ of 147.3°K. and 3.837 Å., respectively, are equivalent to the d/k and a_1/k of Table 1.

TABLE 1. SECOND VIRIAL COEFFICIENT OF METHANE

$T = 200°$ K. $\quad B_e = -102.6$ cc./g.-mole (*4*)
$d/k = 6.00 \times 10^9$ °K., Å^{12} $\quad \delta = 12$
$a_1/k = 1.88 \times 10^6$ °K., Å^6 $\quad \alpha_1 = 6, \alpha_2 = 8$

a_2/k (°K., Å^8)	B_c (cc./g.-mole)
0	-103.9
1.33×10^4	-104.1
1.33×10^5	-105.1
1.33×10^6	-115.5

The advantage of this algorithm is reduction in computer time. Direct evaluation of the cluster integral is time consuming because of the large number of terms required to insure convergence of the exponential approximation in the repulsive region, and the large number of intervals that must be taken in the attractive tail. For the simple case of $N = 2$, time on an IBM 7040 is reduced by 50 to 90% with application of Equation (9). Benefits diminish as N increases. The number of terms necessary to a single solution of the cluster integral can be expressed in terms of $j_{\min}$:

$$S_B = \frac{(j_{\min})^N}{N!} \qquad (12)$$

At an N of five, which represents a reasonable limit on desirable expansions of the Lennard-Jones potential, about one third million terms are indicated. This is comparable in magnitude to the terms accumulated in direct cluster integral evaluation with repetitive Maclaurin series calculation of the exponential component. Thus, the algorithm appears to apply over the range of practical interest in expanded Lennard-Jones potentials.

NOTATION

a = coefficient of attractive term
B = second virial coefficient
b = coefficient of reduced attractive term
d = coefficient of repulsive term
$j_{\min}$ = minimum number of terms per series
k = Boltzmann constant
N = number of attractive terms
r = intermolecular separation
S_B = total terms in multiple series solution
T = absolute temperature
x = reduced repulsive contribution
y = reduced attractive contribution

Greek Letters

α = exponent of attractive term
δ = exponent of repulsive term
ϵ^{+} = positive infinitesimal
γ = exponent in multinomial expansion
ϕ = intermolecular potential

Subscripts

c = calculated
e = experimental
i = index of attractive term
j = index of exponential expansion

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Operational Methods for a Convective Diffusion Equation

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The purpose of this paper is to present an alternative operational method of solution for a convective diffusion equation of the type considered by Gidaspow (*1*).

Consideration will first be given to the development of