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

LITERATURE CITED

1. Lennard-Jones, J. E., *Proc. Royal Society, London,* **106A**, 463, (1924).
2. Rowlinson, J. S., *Eng. Exp. Sta. Bull.,* **201**, Ohio State Univ. (1967).
3. Hirschfelder, J. O., C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley, New York, (1954).
4. Din, F., "Thermodynamic Functions of Gases," Vol. 2, Butterworths, London, (1962).

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 a generalized finite integral transform which can then be specialized to handle a variety of problems. The starting point for the analysis is the ordinary differential equation

$$\alpha_2 d^2y/dz^2 + \alpha_1 dy/dz + \lambda^2 y = 0 \tag{1}$$

with the boundary conditions

$$a_1 y(a) - a_2 dy(a)/dz = 0 \tag{2}$$

$$b_1 y(b) - b_2 dy(b)/dz = 0 \tag{3}$$

where α_1, α_2, λ^2, a_1, a_2, b_1 and b_2 are constants to be specified or determined. The general solution to Equation (1) is easily determined as

$$y(z) = c_1 e^{q_1 z} + c_2 e^{q_2 z} \tag{4}$$

where

$$q_{1,2} = \frac{-\alpha_1 \pm (\alpha_1^2 - 4\alpha_2\lambda^2)^{1/2}}{2\alpha_2} \tag{5}$$

The constants c_1 and c_2 are determined by substitution of Equation (4) in the boundary conditions, Equations (2) and (3) which gives

$$a_{11}c_1 + a_{12}c_2 = 0 \tag{6}$$

$$a_{21}c_1 + a_{22}c_2 = 0 \tag{7}$$

where a_{11}, a_{12}, a_{21} and a_{22} are defined in the section on notation. Equations (6) and (7) will have nontrivial solutions only if

$$a_{11}a_{22} - a_{12}a_{21} = 0 \tag{8}$$

which determines the permissible values (eigenvalues) for λ. The solution to Equation (1) in terms of the arbitrary constant c_1 is therefore

$$y(z) = c_1 \left(e^{q_1 z} - \frac{a_{11}}{a_{12}} e^{q_2 z} \right) \tag{9}$$

Since Equation (1) can be written as a Sturm-Liouville equation

$$\frac{d}{dz}\left(e^{(\alpha_1/\alpha_2)z} \frac{dy}{dz} \right) + (\lambda^2/\alpha_2) e^{(\alpha_1/\alpha_2)z} y = 0$$

the $y(z)$ given by Equation (9) are orthogonal with respect to the weighting function

$$(1/\alpha_2) e^{(\alpha_1/\alpha_2)z}$$

and we can consider an infinite series expansion of an arbitrary function $f(z)$ in terms of the $y(z)$

$$f(z) = \sum_{n=1}^{\infty} c_n \left(e^{q_{1n} z} - \frac{a_{11}}{a_{12}} e^{q_{2n} z} \right) \tag{10}$$

where q_{1n} and q_{2n} are given by Equation (5) for a particular eigenvalue, λ_n, given by Equation (8). The c_n of Equation (10) are obtained through the orthogonality mentioned previously and therefore a finite transform, $\overline{f}(\lambda_n)$, of $f(z)$ can be defined as

$$\overline{f}(\lambda_n) = \int_a^b f(z) e^{(\alpha_1/\alpha_2)z} \left(e^{q_{1n} z} - \frac{a_{11}}{a_{12}} e^{q_{2n} z} \right) dz \tag{11}$$

with the inverse

$$f(z) = \sum_{n=1}^{\infty} \frac{\overline{f}(\lambda_n) \left(e^{q_{1n} z} - \frac{a_{11}}{a_{12}} e^{q_{2n} z} \right)}{\int_a^b e^{(\alpha_1/\alpha_2)z} \left\{ e^{q_{1n} z} - \frac{a_{11}}{a_{12}} e^{q_{2n} z} \right\}^2 dz} \tag{12}$$

The transform pair, Equations (11) and (12), serves as the starting point for the solution of the multidimensional convective diffusion equation:

$$\partial T/\partial t = \partial^2 T/\partial x^2 + \partial^2 T/\partial y^2 + \partial^2 T/\partial z^2 - N_{Pe}\, \partial T/\partial z + f(x, y, z, t) \tag{13}$$

For the Dirichlet problem in which the temperature $T(x, y, z, t)$ is specified at the boundaries, we take $a_1 = b_1 = 1$ and $a_2 = b_2 = 0$ in Equations (2) and (3); the system boundaries are taken as $z = 0$ and $z = L$ so $a = 0$, $b = L$. To obtain a transform for the constant-coefficient partial differential operator $\partial^2/\partial z^2 - N_{Pe}\, \partial/\partial z$, we take $\alpha_1 = -N_{Pe}$, $\alpha_2 = 1$ in Equation (1). Then Equations (5) and (8) reduce to

$$q_{1,2} = N_{Pe}/2 \pm i(\lambda^2 - N^2_{Pe}/4)^{1/2} \tag{14}$$

$$e^{q_2 L} - e^{q_1 L} = e^{N_{Pe}L/2} \{ e^{i(\lambda^2 - N^2_{Pe}/4)^{1/2} L} - e^{-i(\lambda^2 - N^2_{Pe}/4)^{1/2} L} \} = 0 \tag{15}$$

Equation (15) has the roots (eigenvalues)

$$\lambda^2_n = N^2_{Pe}/4 + (n\pi/L)^2, \quad n = 1, 2, 3 \ldots.$$

The corresponding eigenfunctions are easily obtained from Equation (9):

$$y_n(z) = 2i e^{N_{Pe} z/2} \sin(\beta_n z) \tag{16}$$

where $\beta_n = n\pi/L$, $n = 1, 2, 3 \ldots\ldots$ The required transform pair is therefore

$$\overline{f}(\beta_n) = F_z\{f(z)\} = \int_0^L f(z) e^{-N_{Pe} z/2} \sin(\beta_n z) dz \tag{17}$$

$$f(z) = F_z^{-1}\{\overline{f}(\beta_n)\} = \frac{2}{L} \sum_{n=1}^{\infty} \overline{f}(\lambda_n) e^{N_{Pe} z/2} \sin(\beta_n z) \tag{18}$$

Two additional transform pairs are of particular interest:

$$F_z\{\partial^2 y/\partial z^2 - N_{Pe}\, \partial y/\partial z\} = \beta_n \{y(0) - (-1)^n e^{-N_{Pe}L/2} y(L)\} - (\beta_n^2 + N^2_{Pe}/4)\overline{y}(\beta_n) \tag{19}$$

$$F_z\{1\} = \frac{\beta_n}{N^2_{Pe}/4 + \beta_n^2} \{1 - (-1)^n e^{-N_{Pe}L/2}\} \tag{20}$$

Equations (17) to (20) can now be used to develop the solution to Equation (13) directly.

Consider for example the auxiliary conditions

$$T(0, y, z, t) = T(a_1, y, z, t) = 0 \tag{21}$$

$$T(x, 0, z, t) = T(x, a_2, z, t) = 0 \tag{22}$$

$$T(x, y, 0, t) = f_0(x, y, t) \tag{23}$$

$$T(x, y, 1, t) = f_1(x, y, t) \tag{24}$$

$$T(x, y, z, 0) = g(x, y, z) \tag{25}$$

If successive transforms of $T(x, y, z, t)$ with respect to x, y, and z are defined as [Transformed quantities are now denoted by their arguments and the bar (¯) of Equation (17) has been dropped.]

$$T(\beta_l, y, z, t) = F_x\{T(x, y, z, t)\} \quad (N_{Pe} = 0) \tag{26}$$

$$T(\beta_l, \beta_m, z, t) = F_y\{T(\beta_l, y, z, t)\} \quad (N_{Pe} = 0) \tag{27}$$

$$T(\beta_l, \beta_m, \beta_n, t) = F_z\{T(\beta_l, \beta_m, z, t)\} \tag{28}$$

then the application of these three transforms to Equations (13) and (21) to (24) using Equation (19) gives

$$dT(\beta_l, \beta_m, \beta_n, t)/dt + (\beta_l^2 + \beta_m^2 + \beta_n^2 + N^2_{Pe}/4) T(\beta_l, \beta_m, \beta_n, t)$$

$$= \beta_n\{f_0(\beta_l, \beta_m, t) - (-1)^n e^{-N_{Pe}/2} f_1(\beta_l, \beta_m, t)\} + f(\beta_l, \beta_m, \beta_n, t) \quad (29)$$

If finally a Laplace transform of $T(\beta_l, \beta_m, \beta_n, t)$ is defined as

$$T(\beta_l, \beta_m, \beta_n, s) = L_t\{T(\beta_l, \beta_m, \beta_n, t) \quad (30)$$

application of this transform to Equations (25) and (29) gives

$$T(\beta_l, \beta_m, \beta_n, s) = \frac{g(\beta_l, \beta_m, \beta_n)}{s + (\beta_l^2 + \beta_m^2 + \beta_n^2 + N^2_{Pe}/4)} + \frac{\beta_n\{f_0(\beta_l, \beta_m, s) - (-1)^n e^{-N_{Pe}/2} f_1(\beta_l, \beta_m, s)\}}{s + (\beta_l^2 + \beta_m^2 + \beta_n^2 + N^2_{Pe}/4)} + \frac{f(\beta_l, \beta_m, \beta_n, s)}{s + (\beta_l^2 + \beta_m^2 + \beta_n^2 + N^2_{Pe}/4)} \quad (31)$$

$T(x, y, z, t)$ can then easily be obtained by applying to Equation (31) successive inversions of the transforms defined by Equations (30), (28), (27), and (26). The final result is quite lengthy so some special cases will be considered:

Case I: $f_0(x, y, t) = f_1(x, y, t) = g(x, y, z) = 0$

$$f(x, y, z, t) = f_x(x) f_y(y) f_z(z) f_t(t)$$

The product function transforms to

$$f(\beta_l, \beta_m, \beta_n, s) = f_x(\beta_l)\, f_y(\beta_m) f_z(\beta_n) f_t(s)$$

Inversion of Equation (31) then gives

$$T(x, y, z, t) = \int_0^t \left\{ \left[\frac{2}{a_1} \sum_{l=1}^{\infty} f_x(\beta_l) e^{-\beta_l^2(t-\tau)} \sin(\beta_l x) \right] \cdot \left[\frac{2}{a_2} \sum_{m=1}^{\infty} f_y(\beta_m) e^{-\beta_m^2(t-\tau)} \sin(\beta_m y) \right] \cdot \left[2 \sum_{n=1}^{\infty} f_z(\beta_n) e^{-(\beta_n^2 + N^2_{Pe}/4)(t-\tau)} e^{N_{Pe}z/2} \sin(\beta_n z) \right] \cdot f_t(\tau) \right\} d\tau \quad (32)$$

The product property of this solution is evident. Also if the term $e^{-(N^2_{Pe}/4)(t-\tau) + N_{Pe}z/2}$ is factored out of the series in z, the change of variable used by Gidaspow is immediately suggested since the remaining series in z is identical to the two preceding series in x and y. Clearly from Equation (31) similar product solutions will result if f_0, f_1, and g are product functions.

Case II: Case I with $f_x(x) = 2$, $f_y(y) = 2$, $f_z(z) = 2$, $f_t(t) = 1$ which is the nonhomogeneous function considered by Gidaspow. From Equation (20)

$$f_x(\beta_l) = 4/\beta_l, \quad l = 1, 3, 5 \ldots. \quad (N_{Pe} = 0)$$

$$f_y(\beta_m) = 4/\beta_m, \quad m = 1, 3, 5 \ldots. \quad (N_{Pe} = 0)$$

$$f_z(\beta_n) = \frac{2\beta_n}{N^2_{Pe}/4 + \beta_n^2}\{1 - (-1)^n e^{-N_{Pe}/2}\}, \quad n = 1, 2, 3 \ldots.$$

Substitution in Equation (32) gives

$$T(x, y, z, t) = \frac{256}{a_1 a_2} \sum_{\substack{l=1,\\3,5..}}^{\infty} \sum_{\substack{m=1,\\3,5..}}^{\infty} \sum_{\substack{n=1,\\2,3..}}^{\infty} \frac{1}{\beta_l \beta_m} \frac{\beta_n}{N^2_{Pe}/4 + \beta_n^2} \{1 - (-1)^n e^{-N_{Pe}/2}\} \frac{\sin(\beta_l x)\sin(\beta_m y)\sin(\beta_n z)\, e^{N_{Pe}z/2}}{\beta_l^2 + \beta_m^2 + \beta_n^2 + N^2_{Pe}/4} (1 - e)^{-(\beta_l^2 + \beta_m^2 + \beta_n^2 + N^2_{Pe}/4)t} \quad (33)$$

Note that the eigenvalues in z (or n) are $\beta_n = n\pi$, $n = 1, 2, 3 \ldots.$ and not $\beta_n = (2n + 1)\pi$, $n = 0, 1, 2, \ldots.$ as implied by Gidaspow in his Equations (9) and (10).

Case III: Case I with $f_x(x) = \delta(x - x')$, $f_y(y) = \delta(y - y')$, $f_z(z) = \delta(z - z')$, $f_t(t) = \delta(t - t')$

From Equation (17),

$$f_x(\beta_l) = \sin(\beta_l x') \quad (N_{Pe} = 0)$$

$$f_y(\beta_m) = \sin(\beta_m y') \quad (N_{Pe} = 0)$$

$$f_z(\beta_n) = e^{-N_{Pe}z'/2} \sin(\beta_n z')$$

and Equation (32) becomes

$$T(x, y, z, t) = \left[\frac{2}{a_1} \sum_{l=1}^{\infty} e^{-\beta_l^2(t-t')} \sin(\beta_l x')\sin(\beta_l x) \right] \cdot \left[\frac{2}{a_2} \sum_{m=1}^{\infty} e^{-\beta_m^2(t-t')} \sin(\beta_m y')\sin(\beta_m y) \right] \cdot \left[e^{N_{Pe}/2(z-z') - N^2_{Pe}/4(t-t')}\; 2 \sum_{n=1}^{\infty} e^{-\beta_n^2(t-t')} \sin(\beta_n z')\sin(\beta_n z) \right]$$

which is just the product of the Green's functions for the one-dimensional problems in x, y, and z. Again the change of variable used by Gidaspow is suggested by this solution.

The generalized transform, Equations (11) and (12) can clearly be applied to the convective diffusion equation with Neumann or convective (radiation) boundary conditions which are included in boundary conditions (2) and (3). The more general parabolic partial differential equation with constant coefficients considered by Gidaspow with the three types of boundary conditions can also be handled by the generalized transform. In the case of cylindrical coordinates, a Hankel transform (2) would also be used.

NOTATION

- $a_{11} = a_1 e^{q_1 a} - a_2 q_1 e^{q_1 a}$
- $a_{12} = a_1 e^{q_2 a} - a_2 q_2 e^{q_2 a}$
- $a_{21} = b_1 e^{q_1 b} - b_2 q_1 e^{q_1 b}$
- $a_{22} = b_1 e^{q_2 b} - b_2 q_2 e^{q_2 b}$
- $\beta_l = l\pi/a_1$, $l = 1, 2, 3 \ldots.$ (except in Case II)
- $\beta_m = m\pi/a_2$, $m = 1, 2, 3 \ldots.$ (except in Case II)
- $\beta_n = n\pi$, $n = 1, 2, 3 \ldots.$

LITERATURE CITED

1. Gidaspow, D., *AIChE J.*, 13, 810 (1967).
2. Sneddon, I. N., "Fourier Transforms," Chap. 2, pp. 82-91, McGraw-Hill, New York, (1951).