ELSEVIER

Physica A 290 (2001) 92–100

PHYSICA A

www.elsevier.com/locate/physa

Second virial coefficient for the Lennard–Jones potential

P. Vargas[a,b,*], E. Muñoz[a], L. Rodriguez[c]

[a]Departamento de Física, Universidad Técnica F. Santa María, Casilla 110-V, Valparaíso, Chile
[b]Max-Planck Institut für Festkörperforchung, D-70569 Stuttgart, Germany
[c]Departamento de Física, Universidad de Santiago de Chile, Casilla 307, Santiago-2, Chile

Received 29 December 1999; received in revised form 1 May 2000

Abstract

The second virial coefficient for the $(12-6)$ Lennard–Jones potential and its first and second temperature derivatives are explicitely derived. All coefficients can be explicitly written as a linear combination of four modified Bessel functions which can be evaluated for every temperature with high degree of numerical accuracy. Detailed comparisons with the classical series expansion for the coefficient and its temperature derivatives are made. The use of these analytical, simple and closed formulae can be very valuable when using experimental p–V–T data to fit a Lennard–Jones potential.

PACS: 5.20.−y; 5.70.Ce; 5.20.Jj

1. Introduction

Many books on statistical mechanics (see, for instance, Refs. [1–6]) have a chapter devoted to imperfect gases, in which the virial expansion of the equation of state in terms of density is derived. Explicit evaluation of the second virial coefficient is given only in simple cases such as hard spheres and square well potentials [1–5]. However, closed forms for the second virial coefficient using different potentials can be found in the literature. Buckingham potential formula is modified in terms of Whittaker functions [7], Lennard–Jones $(2n-n)$ and Woolley potential in terms of parabolic cylinder functions [8,9], Sutherland and particular Mie potentials in terms of generalized hypergeometric functions [10,11]. Also, extensive numerical calculation for the

* Correspondence address. Departamento de Física, Universidad Técnica F. Santa María, Casilla 110-V, Valparaíso, Chile. Fax: +56-32-797656.
E-mail address: pvargas@fis.utfsm.cl (P. Vargas).

0378-4371/01/$ - see front matter
PII: S0378-4371(00)00362-9

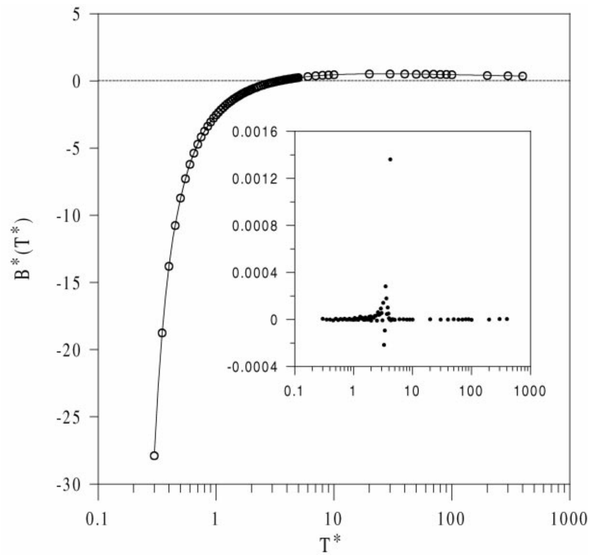

Fig. 1. Second virial coefficient as a function of reduced temperature, as given by Eq. (3) (full-line). Tabulated data from Ref. [2] are also plotted (open circles). The inset shows the percent error between the values obtained using the analytical formula and the tabulated ones.

Lennard–Jones (12−6) potential [6,12,13] as well as its first derivatives have been done in the past [6].

Although parabolic cylinder, hypergeometric and Whittaker functions are easily programmable, their numerical evaluation can be more involved than working interpolating values from tabulated functions. However, a simple analytical closed form is very useful, especially at low temperatures where the series expansion of the virial coefficient converges very slowly. Also simple formula is desirable, for instance, to study the inversion temperatures for real gases in expansion [14].

In this letter we derive an alternative, simpler, analytical form for the second virial coefficient for the Lennard–Jones (12−6) potential, and, for the first time, derive explicit closed forms for its first and second temperature derivative from which the zero-pressure Joule–Thompson coefficient is evaluated.

2. Method

If u, the intermolecular potential between two particles, only depends on the relative separation, r, between them the second virial coefficient is commonly given by the following expression [1–6] (Fig. 1):

$$B(T) = -2\pi \int_0^\infty [\mathrm{e}^{-u(r)/kT} - 1] r^2 \, \mathrm{d}r \,. \tag{1}$$

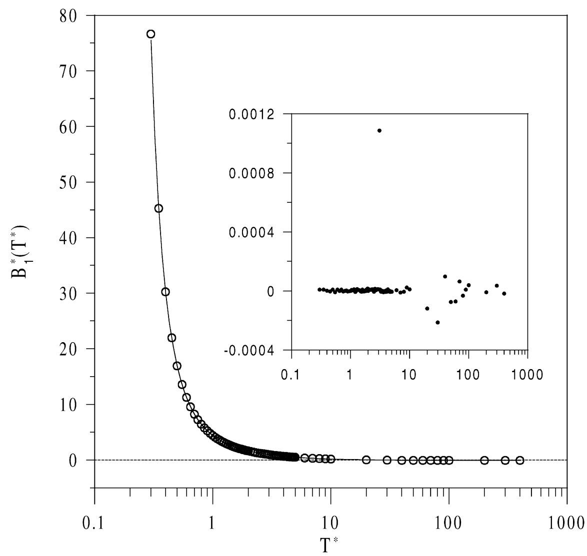

Fig. 2. First temperature derivative of the second virial coefficient as a function of reduced temperature, as given by Eq. (4) (full-line). Tabulated data from Ref. [2] are also plotted (open circles). The inset shows the percent error between the values obtained using the analytical formula and the tabulated ones.

Provided that $u(r)$ approaches zero faster than $1/r^3$, necessary condition for existence of the virial, integration by parts of Eq. (1) gives an equivalent expression

$$B(T) = -\frac{2\pi}{3kT}\int_0^{\infty} \frac{\mathrm{d}u(r)}{\mathrm{d}r}\, \mathrm{e}^{-u(r)/kT} r^3\, \mathrm{d}r\,. \tag{2}$$

Then, if $u(r)$ is the Lennard–Jones (12−6) potential

$$u(r) = 4\varepsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\}$$

and making the following substitution $x = r/\sigma$ and $T^* = kT/\varepsilon$, the expression for the second virial coefficient of Eq. (2) reads

$$B(T^*) = -\left(\frac{2\pi\sigma^3}{3}\right)\frac{4}{T^*}\int_0^{\infty}\left\{-12\left(\frac{1}{x}\right)^{12} + 6\left(\frac{1}{x}\right)^{6}\right\} \mathrm{e}^{-4/T^*\{(1/x)^{12}-(1/x)^6\}} x^2\, \mathrm{d}x\,.$$

By defining $B^*(T^*) = B(T^*)/(2\pi\sigma^3/3)$, substituting, $u = 1/x^3$, and after some straightforward algebraic manipulations (see Appendix A) we obtain the following dimensionless form for the second virial coefficient (Figs. 2 and 3):

$$B^*(T^*) = \frac{8}{\sqrt{2T^*}}\, \mathrm{e}^{1/T^*}\int_0^{\infty}(u^2-1)\, \mathrm{e}^{-(1/T^*)(u^2-1)^2}\, \mathrm{d}u\,.$$

In Appendix B we demonstrate that the function $P(z)$, defined as

$$P(z) \equiv \int_0^{\infty}(u^2-1)\, \mathrm{e}^{-2z(u^2-1)^2}\, \mathrm{d}u\,,$$

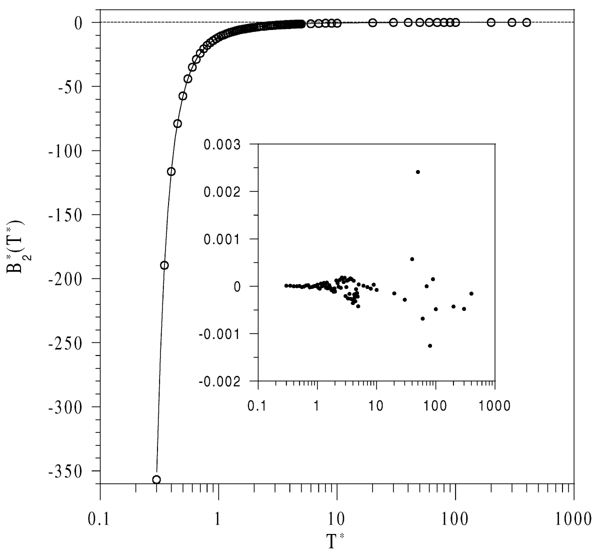

Fig. 3. Second temperature derivative of the second virial coefficient as a function of reduced temperature, as given by Eq. (5) (full-line). Tabulated data from Ref. [2] are also plotted (open circles). The inset shows the percent error between the values obtained using the analytical formula and the tabulated ones.

is a linear combination of four modified Bessel functions [15]:

$$P(z) = \tfrac{1}{8}\pi\, \mathrm{e}^{-z}(I_{-3/4}(z) - I_{-1/4}(z) - I_{1/4}(z) + I_{3/4}(z))\,.$$

Then, it turns out, by replacing $z=1/2T^*$, the second virial coefficient for the Lennard–Jones (12−6) potential has the following analytically closed expression:

$$B^*(T^*) = \frac{\sqrt{2}\pi}{2T^*}\,\mathrm{e}^{1/2T^*}\left(I_{-3/4}\left(\frac{1}{2T^*}\right) + I_{3/4}\left(\frac{1}{2T^*}\right)\right.$$
$$\left. -I_{1/4}\left(\frac{1}{2T^*}\right) - I_{-1/4}\left(\frac{1}{2T^*}\right)\right)\,. \tag{3}$$

It is now a trivial matter, using the recurrence formulas for the modified Bessel function (see 9.6.26 of Abramowitz and Stegun [15]), to derive the following expressions for the temperature derivatives, and zero-pressure Joule–Thompson coefficient (Fig. 4).

$$B_1^*(T^*) \equiv T^*\frac{\mathrm{d}B^*(T^*)}{\mathrm{d}T^*}\,,$$

$$B_1^*(T^*) = -\frac{1}{8T^*}\sqrt{2}\pi e^{1/2T^*}\left(I_{3/4}\left(\frac{1}{2T^*}\right) + I_{-3/4}\left(\frac{1}{2T^*}\right)\right.$$
$$\left. -3I_{1/4}\left(\frac{1}{2T^*}\right) -3I_{-1/4}\left(\frac{1}{2T^*}\right)\right),$$

$$B_2^*(T^*) \equiv T^{*2}\frac{\mathrm{d}^2B^*(T^*)}{\mathrm{d}T^{*2}} = T^*\frac{\mathrm{d}B_1^*(T^*)}{\mathrm{d}T^*} - B_1^*(T^*)\,, \tag{4}$$

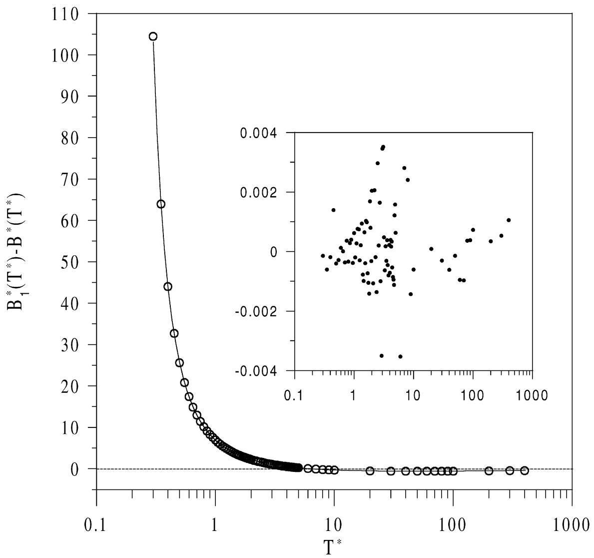

Fig. 4. $B_1^*(T^*) - B^*(T^*)$ (reduced zero-pressure Joule–Thompson coefficient) as a function of reduced temperature, as given by Eq. (1) and Eq. (2) (full-line). Tabulated data from Ref. [2] are also plotted (open circles). The inset shows the percent error between the values obtained using the analytical formula and the tabulated ones.

$$B_2^*(T^*) = \frac{\pi}{16\sqrt{2}T^{*2}} e^{1/2T^*} \left[(-4+5T^*) \left(I_{3/4}\left(\frac{1}{2T^*}\right) + I_{-3/4}\left(\frac{1}{2T^*}\right) \right) \right.$$
$$\left. -(4+21T^*) \left(I_{-1/4}\left(\frac{1}{2T^*}\right) + I_{1/4}\left(\frac{1}{2T^*}\right) \right) \right] . \quad (5)$$

Zeros for the different thermodynamical functions are in $T^* = 3.417\,928\,023$, $25.152\,573\,456$, $48.289\,836\,984$ and $6.430\,798\,472$ for B^*, B_1^*, B_2^*, and $B_1^* - B^*$, respectively.

3. Results

Figs. 1–4 illustrate the tabulated second virial coefficients and zero-pressure Joule–Thompson coefficient as given by Hirschfelder et al. [6] in their Table I-B (open circles), together with the analytical expressions given in Eqs. (3)–(5) (full line curves). For a given reduced temperature T^*, the percent error in the case of the second virial coefficient is defined as $100 \times [\text{exact}(B^*) - \text{tabulated}(B^*)]/\text{exact}(B^*)$. Same definition applies for the other functions and they are shown as insets in each figure. We see that the overall behavior coincides almost perfectly in all temperature ranges. Maximum differences are found in the derivatives which are nevertheless less than 0.004%. These results clearly demonstrate the high quality of the numerical work performed almost 50 years ago.

4. Conclusion

Second virial coefficient for the Lennard–Jones $(12-6)$ potential, as well as its first and second temperature derivatives have been derived for the first time from simple and closed formulas. We expect the expression as given in Eqs. (1)–(3) will be of great help in fitting a Lennard–Jones $(12-6)$ potential from experimental data. Nowadays they can be easily evaluated in every temperature range with high-numerical accuracy using the modified Bessel functions which come precompiled in the majority of numerical library packages or scientific softwares.

Acknowledgements

This work was supported by the Dirección de Investigación Científica y Tecnológica (DICYT) from the Universidad de Santiago de Chile, FONDECYT under contrat 1990812 and the Max-Planck Institut für Festkörperphysik, Stuttgart, Germany.

Appendix A

According to the text definition, we have

$$B^*(T^*) = -\frac{4}{T^*}\int_0^\infty \left\{-12\left(\frac{1}{x}\right)^{12} + 6\left(\frac{1}{x}\right)^6\right\} \mathrm{e}^{-(4/T^*)\{(1/x)^{12}-(1/x)^6\}} x^2\,\mathrm{d}x\,.$$

By making the substitution $u = 1/x^3$ we obtain

$$B^*(T^*) = \frac{8}{T^*}\int_0^\infty (2u^2-1)\,\mathrm{e}^{-4/T^*(u^4-u^2)}\,\mathrm{d}u\,,$$

and now, making $u = x/\sqrt{2}$ we finally get the desired expression:

$$B^*(T^*) = \frac{8}{\sqrt{2}T^*}\,\mathrm{e}^{1/T^*}\int_0^\infty (u^2-1)\,\mathrm{e}^{-1/T^*(u^2-1)^2}\,\mathrm{d}u\,.$$

Appendix B

We recall the integral representation of the modified Bessel function I_ν (see formula 9.6.20 of Abramowitz and Stegun [15]).

$$I_\nu = \frac{1}{\pi}\int_0^\pi \mathrm{e}^{z\cos t}\cos\nu t\,\mathrm{d}t - \frac{\sin\pi\nu}{\pi}\int_0^\infty \mathrm{e}^{-z\cosh t-\nu t}\,\mathrm{d}t\,.$$

Then it follows that

$$\int_0^\infty \mathrm{e}^{-z\cosh t}\sinh\nu t\,\mathrm{d}t = \frac{\pi}{2\sin\pi\nu}(I_\nu + I_{-\nu}) - \frac{1}{\sin\pi\nu}\int_0^\pi \mathrm{e}^{z\cos t}\cos\nu t\,\mathrm{d}t \tag{6}$$

which we will use for the demonstration.

We have to evaluate analytically $P(z)$ defined as

$$P(z) \equiv \int_0^\infty (u^2 - 1)\,\mathrm{e}^{-2z(u^2-1)^2}\,\mathrm{d}u\,.$$

By substituting $x = u^2$ it follows that

$$P(z) = \frac{1}{2}\int_0^\infty \frac{(u-1)}{\sqrt{u}}\,\mathrm{e}^{-2z(u-1)^2}\,\mathrm{d}u\,.$$

Let us first separate $P(z)$ as a summation of two terms. The interval splitting $[0,2]$ and $[2,\infty]$ will be clear later in the demonstration:

$$\begin{aligned}P(z) &= \frac{1}{2}\int_0^2 \frac{(u-1)}{\sqrt{u}}\,\mathrm{e}^{-2z(u-1)^2}\,\mathrm{d}u + \frac{1}{2}\int_2^\infty \frac{(u-1)}{\sqrt{u}}\,\mathrm{e}^{-2z(u-1)^2}\,\mathrm{d}u\\ &= P_1(z) + P_2(z)\,.\end{aligned}$$

In the last term, we do the following transformation, which is valid for $u > 2$:

$$(u-1)^2 = \frac{1}{2} + \frac{1}{2}\cosh t = \cosh^2\frac{t}{2}\,,$$

$$u = 1 + \cosh\frac{t}{2}\ (u > 2)\,,$$

$$2(u-1)\,\mathrm{d}u = \tfrac{1}{2}\,\mathrm{d}t\sinh t\,.$$

Then,

$$\begin{aligned}P_2(z) &= \frac{1}{2}\int_2^\infty \frac{(u-1)}{\sqrt{u}}\,\mathrm{e}^{-2z(u-1)^2}\,\mathrm{d}u = \frac{1}{8\sqrt{2}}\,\mathrm{e}^{-z}\int_0^\infty \frac{\sinh t}{\cosh t/4}\,\mathrm{e}^{-z\cosh t}\,\mathrm{d}t\,,\\ &= \frac{1}{2\sqrt{2}}\,\mathrm{e}^{-z}\int_0^\infty \sinh\frac{t}{4}\cosh\frac{t}{2}\,\mathrm{e}^{-z\cosh t}\,\mathrm{d}t\\ &= \frac{1}{4\sqrt{2}}\,\mathrm{e}^{-z}\int_0^\infty \left(\sinh\frac{3t}{4} - \sinh\frac{t}{4}\right)\mathrm{e}^{-z\cosh t}\,\mathrm{d}t\,.\end{aligned}$$

Now, doing the following transformation in the first term, $P_1(z)$, valid for $0 < u < 2$,

$$(u-1)^2 = \frac{1}{2} + \frac{1}{2}\cos t = \cos^2\frac{t}{2}\,,$$

$$u = 1 + \cos\frac{t}{2}\ (0 < u < 2)\,,$$

$$2(u-1)du = -\tfrac{1}{2}\,\mathrm{d}t\sin t\,,$$

Then

$$\begin{aligned}P_1(z) &= -\frac{1}{8}\int_{2\pi}^0 \frac{\sin t}{\sqrt{1+\cos t/2}}\,\mathrm{e}^{-2z((1/2)+(1/2)\cos t)}\,\mathrm{d}t = \frac{\mathrm{e}^{-z}}{8\sqrt{2}}\int_0^{2\pi} \frac{\sin t}{\cos t/4}\,\mathrm{e}^{-z\cos t}\,\mathrm{d}t\,,\\ &= \frac{\mathrm{e}^{-z}}{2\sqrt{2}}\int_0^{2\pi} \sin\frac{t}{4}\cos\frac{t}{2}\,\mathrm{e}^{-z\cos t}\,\mathrm{d}t = \frac{\mathrm{e}^{-z}}{4\sqrt{2}}\int_0^{2\pi}\left(\sin\frac{3t}{4} - \sin\frac{t}{4}\right)\mathrm{e}^{-z\cos t}\,\mathrm{d}t\,.\end{aligned}$$

These expressions lead to the following expression for $P(z)$:

$$P(z)=\frac{e^{-z}}{4\sqrt{2}}\left(\int_0^{2\pi}\left(\sin\frac{3t}{4}-\sin\frac{t}{4}\right)e^{-z\cos t}\,dt\right.$$
$$\left.+\int_0^{\infty}\left(\sinh\frac{3t}{4}-\sinh\frac{t}{4}\right)e^{-z\cosh t}\,dt\right).$$

From the derived expression for the modified Bessel functions of Eq. (6), using as particular cases $v=\frac{3}{4}$, and $\frac{1}{4}$ we get

$$\int_0^{\infty} e^{-z\cosh t}\sinh\frac{3t}{4}\,dt=\frac{1}{2}\pi\sqrt{2}(I_{3/4}+I_{-3/4})-\sqrt{2}\int_0^{\pi} e^{z\cos t}\cos\frac{3t}{4}\,dt,$$

$$\int_0^{\infty} e^{-z\cosh t}\sinh\frac{t}{4}\,dt=\frac{1}{2}\pi\sqrt{2}(I_{1/4}+I_{-1/4})-\sqrt{2}\int_0^{\pi} e^{z\cos t}\cos\frac{t}{4}\,dt.$$

Therefore by replacing them in the $P(z)$ expression, we have

$$P(z)=\frac{e^{-z}}{4\sqrt{2}}\left(\int_0^{2\pi}\left(\sin\frac{3t}{4}-\sin\frac{t}{4}\right)e^{-z\cos t}\,dt+\frac{1}{2}\pi\sqrt{2}(I_{3/4}+I_{-3/4})\right.$$
$$\left.-\sqrt{2}\int_0^{\pi} e^{z\cos t}\cos\frac{3t}{4}\,dt-\frac{1}{2}\pi\sqrt{2}(I_{1/4}+I_{-1/4})+\sqrt{2}\int_0^{\pi} e^{z\cos t}\cos\frac{t}{4}\,dt\right)$$
$$=\frac{e^{-z}}{4\sqrt{2}}\left(Q(z)+\frac{1}{2}\pi\sqrt{2}(I_{3/4}(z)+I_{-3/4}(z))-\frac{1}{2}\pi\sqrt{2}(I_{1/4}(z)+I_{-1/4}(z))\right).$$

To see that $Q=0$, let us write

$$Q=\int_0^{2\pi}\left(\sin\frac{3t}{4}-\sin\frac{t}{4}\right)e^{-z\cos t}\,dt-\sqrt{2}\int_0^{\pi} e^{z\cos t}\left(\cos\frac{3}{4}t-\cos\frac{t}{4}\right)dt.$$

and substituting $t=x+\pi$ in the first integral and then expanding the trigonometrical functions, we have

$$Q=\int_{-\pi}^{\pi}\left(\sin\left(\frac{3t}{4}\right)\cos\frac{3\pi}{4}+\cos\left(\frac{3t}{4}\right)\sin\frac{3\pi}{4}\right.$$
$$\left.-\sin\left(\frac{t}{4}\right)\cos\frac{\pi}{4}-\cos\left(\frac{t}{4}\right)\sin\frac{\pi}{4}\right)e^{z\cos t}\,dt$$
$$-\sqrt{2}\int_0^{\pi} e^{z\cos t}\left(\cos\frac{3t}{4}-\cos\frac{t}{4}\right)dt.$$

Odd functions give zero in the integrals from $[-\pi,\pi]$, then by transforming the integrals of the even functions in the $[-\pi,\pi]$ interval by twice the same integrals in the $[0,\pi]$ interval, we get

$$Q=\sqrt{2}\int_0^{\pi}\left(\cos\frac{3t}{4}-\cos\frac{t}{4}\right)e^{z\cos t}\,dt$$
$$-\sqrt{2}\int_0^{\pi} e^{z\cos t}\left(\cos\frac{3}{4}t-\cos\frac{1}{4}t\right)dt=0.$$

Thus, we have proved that

$$P(z) = \frac{\pi\, e^{-z}}{8}((I_{3/4}(z) + I_{-3/4}(z)) - (I_{1/4}(z) + I_{-1/4}(z)))\,.$$

References

[1] M.C. McQuarrie, Statistical Thermodynamics, Harper & Row, New York, 1976.
[2] R.P. Feynman, Statistical Mechanics, a Set of Lectures, Benjamin, New York, 1972.
[3] S. Ma, Statistical Mechanics, World Scientific, Singapore, 1985.
[4] C.V. Heer, Statistical Mechanics, Kinetic Theory and Stochastic Processes, Academic Press, New York, 1972.
[5] M. Plischke, B. Bergensen, Equilibrium Statistical Physics, 2nd Edition, World Scientific, Singapore, 1994.
[6] J.O. Hirschfelder, C.F. Curtiss, R.B. Bird, Molecular Theory of Gases and Liquids, Wiley, New York, 1954.
[7] S.F. Ragab, A.A. Helmy, T.L. Hassanein, M.A. El-Naggar, J. Low-Temp. Phys. 111 (1998) 447.
[8] H. Guérin, J. Phys. B 26 (1993) L693.
[9] A.J.M. Garrett, J. Phys. A 13 (1980) 379.
[10] D. Levi, M. de Llano, J. Chem. Phys. 63 (1975) 4561.
[11] E. Ley-Koo, M. de Llano, J. Chem. Phys. 65 (1976) 3802.
[12] L.F. Epstein, G.M. Roe, J. Chem. Phys. 19 (1951) 1320.
[13] J.A. Barker, P.J. Leonard, A. Pompe, J. Chem. Phys. 44 (1966) 4206.
[14] D. Huang, Physica A 256 (1998) 30.
[15] M. Abramowitz, I.A. Stegun (Eds.), Handbook of Mathematical Functions, U.S. National Bureau of Standards, 1964; Dover, New York, 1965.