HIGH TEMPERATURE THIRD VIRIAL COEFFICIENT FOR SQUARE-WELL PLUS VAN DER WAALS POTENTIAL

M. Boghdadi

Department of Mathematics, Assiut University, Egypt

ABSTRACT

As a function of the absolute temperature T, the third virial coefficient in the case of a square-well plus Van der Waals potential is evaluated up to terms in $\beta^2 (\beta = \frac{1}{KT})$. Suitable variables are used which simplify considerably the integrations involved. The result obtained is valid only at high temperatures and low densities.

INTRODUCTION

As is well known(1), the thermodynamic properties of a system modelled by a canonical ensemble are related to the interactions of particles in the system through the partition function

$$A = -kT \ln Z \tag{1}$$

where $$Z = \frac{1}{N!\Lambda^{3N}} \int \cdots \int e^{-U(\underline{r}_1,\ldots,\underline{r}_N)/kT} \, d\underline{r}_1 \ldots d\underline{r}_N \tag{2}$$

$$\equiv \frac{Q_N}{\Lambda^{3N}} \quad , \quad \Lambda^2 = \frac{h^2}{2\pi mKT} \tag{3}$$

and A is the Helmholtz free energy of the system composed of N particles. The integral Q_N is known as the configurational partition function. Having determined A as a function of T, V, N all thermodynamic functions can follow. For example, the pressure p of the system is given by

$$p = -\left(\frac{\partial A}{\partial V}\right)_T \quad \text{or} \quad pV = KT\left(\frac{\partial \ln Q_N}{\partial \ln V}\right)_T \tag{4}$$

It is possible[2] to develop $\ln Q_N$ as a power series in the number density $\rho \equiv \frac{N}{V}$. This allows an equation of state to be written as the virial expansion

$$p = \rho KT[1+B_2(T)\rho+B_3(T)\rho^2+\ldots\ldots] \tag{5}$$

where B_2, B_3, ... are the second, third, ... virial coefficients which are expressed in terms of Mayer's f-bond functions[2]

$$B_m = -\frac{m}{m+1}\cdot\frac{1}{Vm!}\int\cdots\int \sum_{1\leq i<j\leq m+1}^{irr}\prod f_{ij}(r_{ij})\,d\underline{r}_1\ldots d\underline{r}_{m+1} \tag{6}$$

$$f_{ij}(r_{ij}) = e^{-\beta u(r_{ij})} - 1 \tag{7}$$

$u(r_{ij})$ is the pair-wise additive interaction potential between particles i and j, and $\beta = \frac{1}{KT}$. The virial expansion (5) with the virial coefficients given by (6) is valid only at low densities. Since this virial series was developed a considerable amount of attention was devoted to methods of evaluating the virial coefficients B_m. However, there are two difficulties in evaluating these virial coefficients. Firstly, the number of the f-functions in the integrand of (6) grows rapidly with m which makes it rather difficult to evaluate the integrals for large m even for simplified potential functions. Secondly, the form of the pair potential $u(r_{ij})$ for (quasi)[3] realistic potentials such as the Lennard-Jones (12-6) potential complicates the evaluation of B_m even for small m. As a consequence of the first difficulty, attention was focused on evaluating the first few manageable terms in the series (5). The second difficulty was treated in such a way as to deal with more tractable potentials such as the hard sphere[(4),(5)] (HS), square-well[(6),(7)] (SW) and other simplified forms for the potential. Though these are not real potentials, still important from the point of view of perturbation theory[(8)] which is the most recent successful technique of equilibrium statistical mechanics. This theory is a mathematical means of expanding the configurational partition function Q_N of an original system around a relatively simple reference system whose properties are known. This reference system is usually chosen to be the (HS) one. In our paper, we choose for the pair potential energy a square-well plus a Van der Waals potential. This potential has all the characteristics of a real one, a hard repulsive core and a long range attractive tail. Suitable variables had been used which simplify the integrals considerably where the number of dimensionality of the integrals are reduced by one. As a consequence of expanding the f-functions in power series in β, the third virial coefficient is also obtained as a power series in β which is truncated after terms in β^2 because of the tedious integrals encountered in higher terms.

THE THIRD VIRIAL COEFFICIENT

The assumption of a pair-wise additive potential leads to the classical expression for the third virial coefficient B_3:

$$B_3 = -\frac{2}{3}\frac{1}{2V}\iiint f(r_{12})f(r_{13})f(r_{23})\; d\underline{r}_1 d\underline{r}_2 d\underline{r}_3 \qquad (8)$$

where the f-function is defined by (7). Our model is characterised by having the potential $u(r)$. defined as

$$\begin{aligned} u(r) &= \infty & r<\sigma \\ &= -\varepsilon & \sigma<r<\lambda\sigma \\ &= -\frac{\mu}{r^6} & r>\lambda\sigma \end{aligned} \qquad (9)$$

σ is the rigid-core diameter of the molecules and ε is the depth of the well. The coefficient μ satisfies the relation

$$\frac{(\mu/\varepsilon)}{\sigma^6} = \lambda^6 \qquad (10)$$

Expanding in powers of β, the function $f(r)$ will have the following forms:

$$\begin{aligned} f(r) &= -1 & r<\sigma \\ &= \beta\varepsilon + \tfrac{1}{2}\beta^2\varepsilon^2 + \ldots & \sigma<r<\lambda\sigma \\ &= \frac{\beta\mu}{r^6} + \tfrac{1}{2}\frac{\beta^2\mu^2}{r^{12}} & r>\lambda\sigma \end{aligned} \qquad (11)$$

Consider the integral

$$G(r_{13}) \equiv \int f(r_{12})f(r_{23})d\underline{r}_2 \tag{12}$$

We first assume that $\lambda \geqslant 3$. Consider the four different cases:

$$(\lambda+1)\sigma \leqslant r_{13} \leqslant \infty$$
$$(\lambda-1)\sigma \leqslant r_{13} \leqslant (\lambda+1)\sigma$$
$$2\sigma \leqslant r_{13} \leqslant (\lambda-1)\sigma$$
$$0 \leqslant r_{13} \leqslant 2\sigma$$

In the first three cases we retain only terms linear in β for $G(r_{13})$ if the third virial coefficient is to be truncated after terms in β^2 since $f(r_{13})$ in these three cases contains terms at least linear in β . We introduce the variables ξ , η defined as

$$\frac{2}{r_{13}} r_{12} = \xi+\eta \quad ; \quad \frac{2}{r_{13}} r_{23} = \xi-\eta \quad . \tag{13}$$

ξ = constant gives an ellipse and η = constant gives a hyperbola. The element of volume $d\underline{r}_2$ in these variables is thus given by

$$d\underline{r}_2 = \frac{1}{4}\pi r_{13}^3 (\xi^2-\eta^2) \; d\xi \; d\eta \tag{14}$$

and the integrals $G(r_{13})$ over the three-dimensional volume in each case are transformed into integrals over the corresponding areas in the ξ-η plane . For example, considering the first of these cases we have (see Fig.I),

$$G(r_{13}) = -2 \int_{\substack{\text{dotted} \\ \text{volume}}} \frac{\beta\mu}{r_{12}^6} \, d\underline{r}_2$$

On using (13), the integral is now taken over the dotted area in the $\xi-\eta$ plane (see Fig.II)

$$G(r_{13}) = -2\beta\mu \times \frac{16\pi}{r_{13}^3} \int_{1-2\eta_o}^{1} d\eta \int_{1}^{\eta+2\eta_o} \frac{(\xi-\eta)}{(\xi+\eta)^5} d\xi \quad , \quad \eta_o = \frac{\sigma}{r_{13}}$$

Carrying out the integral and setting $r_{13} \equiv R$, we get

$$G(R) = -2\beta\mu \times \frac{16\pi}{R^3}\left[\frac{1}{64}\left(\frac{R}{R+\sigma}\right)^2 - \frac{1}{64}\left(\frac{R}{R-\sigma}\right)^2 - \frac{1}{96}\left(\frac{R}{R+\sigma}\right)^3 + \frac{1}{96}\left(\frac{R}{R-\sigma}\right)^3\right]$$

$$(\lambda+1)\sigma \leqslant R \leqslant \infty \qquad (15)$$

Similarly, we have for the second case

$$G(R) = -2\beta\varepsilon\, C_1(R) - 2\beta\mu\, C_2(R) \qquad (\lambda-1)\sigma \leqslant R \leqslant (\lambda+1)\sigma \qquad (16)$$

where

$$C_1(R) = \frac{1}{4}\pi R^3\left[-(\lambda^2-1)^2\left(\frac{\sigma}{R}\right)^4 + \frac{8}{3}(1+\lambda^3)\left(\frac{\sigma}{R}\right)^3 - 2(1+\lambda^2)\left(\frac{\sigma}{R}\right)^2 + \frac{1}{3}\right] \qquad (17)$$

$$C_2(R) = \frac{16\pi}{R^3}\left[\frac{1}{64}\left(\frac{R}{R+\sigma}\right)^2 - \frac{1}{96}\left(\frac{R}{R+\sigma}\right)^3 - \frac{1}{64}\left(\frac{R}{\lambda\sigma}\right)^4 + \frac{1}{24}\left(\frac{R}{\lambda\sigma}\right)^3 - \frac{2\lambda^2-1}{64\lambda^2}\left(\frac{R}{\lambda\sigma}\right)^2\right] \qquad (18)$$

The third case is obvious

$$G(R) = -2\beta\varepsilon \times \frac{4}{3}\pi\sigma^3 \qquad 2\sigma \leqslant R \leqslant (\lambda-1)\sigma \qquad (19$$

In the fourth case we have to evaluate $G(R)$ up to terms in β^2 since $f(R)$ has the value -1 when $0 \leqslant R \leqslant \sigma$. Proceeding as in the first case we obtain the result

$$G(R) = C_3(R)-2\beta\varepsilon C_4(R)+\beta^2\varepsilon^2 C_5(R)+2\beta^2\varepsilon\mu C_6(R)+2\beta^2\mu^2 C_7(R)$$

$$0 \leqslant R \leqslant 2\sigma \qquad (20)$$

where

$$C_3(R) = \frac{4}{3}\pi\sigma^3 - \pi\sigma^2 R + \frac{\pi}{12} R^3 \qquad (21)$$

$$C_4(R) = \pi\sigma^2 R - \frac{\pi}{12} R^3 \qquad (22)$$

$$C_5(R) = \frac{4}{3}\pi(\lambda^3-1)\sigma^3-\pi(\lambda^2+2)\sigma^2 R+\frac{\pi}{4}R^3 \qquad (23)$$

$$C_6(R) = \frac{16\pi}{R^3}\Big[\frac{1}{64}\Big(\frac{R}{R+\lambda\sigma}\Big)^2 - \frac{1}{96}\Big(\frac{R}{R+\lambda\sigma}\Big)^3 - \frac{1}{64}\Big(\frac{R}{\lambda\sigma}\Big)^2 + \frac{1}{24}\Big(\frac{R}{\lambda\sigma}\Big)^3 - \frac{1}{64}\Big(\frac{R}{\lambda\sigma}\Big)^4\Big] \qquad (24)$$

$$C_7(R) = \frac{1024\pi}{R^9}\Big[\frac{35(\lambda\sigma)^2 R}{2048(R+\lambda\sigma)^3} + \frac{525(\lambda\sigma)R^2}{12288(R+\lambda\sigma)^3} + \frac{385}{12288}\Big(\frac{R}{R+\lambda\sigma}\Big)^3$$

$$+ \frac{35}{8192}\frac{R^4}{(\lambda\sigma)(R+\lambda\sigma)^3} - \frac{7}{8192}\frac{R^5}{(\lambda\sigma)^2(R+\lambda\sigma)^3}$$

$$+ \frac{7}{24576}\frac{R^6}{(\lambda\sigma)^3(R+\lambda\sigma)^3} - \frac{1}{8192}\frac{R^7}{(\lambda\sigma)^4(R+\lambda\sigma)^3}$$

$$+ \frac{1}{16384}\Big(\frac{R}{\lambda\sigma}\Big)^8 - \frac{35}{2048}\ln\Big|\frac{R+\lambda\sigma}{\lambda\sigma}\Big|\Big] \qquad (25)$$

The third virial coefficient is given by

$$B_3(T) = -\frac{1}{3}\int f(R)\ G(R)\ \cdot\ 4\pi R^2 dR \tag{26}$$

where $G(R)$ is readily obtained for the four different cases and $f(R)$ is to have the appropriate value in each case according to equation (11) and that all terms up to β^2 are to be considered in each case. Carrying out the integrations for each of the four cases and summing them up we finally obtain

$$\begin{aligned} B_3 &= \frac{5}{18}\pi^2\sigma^6 - \frac{17}{18}\pi^2\sigma^6\beta\varepsilon + \frac{1}{36}\pi^2\sigma^6\beta^2\varepsilon^2(64\lambda^3-36\lambda^2-113) \\ &+ \frac{\pi^2\beta^2\varepsilon\mu}{18\lambda^4(\lambda+1)^3}[-12\lambda^6-30\lambda^5-22\lambda^4+33\lambda^3+51\lambda^2+5\lambda-9] \\ &+ \frac{2}{3}\pi^2\beta^2\varepsilon\mu\ \ln(\frac{\lambda+1}{\lambda}) + \frac{\pi^2\beta^2\mu^2}{36\sigma^6\lambda^8(\lambda+1)^4(\lambda+2)^2}[-840\lambda^{13}-6300\lambda^{12} \\ &- 18760\lambda^{11} - 28070\lambda^{10} - 21728\lambda^9 - 7644\lambda^8 - 568\lambda^7 + 83\lambda^6 \\ &+ 142\lambda^4 + 316\lambda^3 + 353\lambda^2 + 180\lambda + 36] \\ &+ \frac{70\pi^2\beta^2\mu^2}{3\sigma^6}\ln(\frac{\lambda+1}{\lambda}) \qquad , \quad \lambda\geq 3 \end{aligned} \tag{27}$$

We assume now $\lambda\leq 3$ and consider the four different cases

$$\begin{aligned} (\lambda+1)\sigma &\leq r_{13} \leq \infty \\ 2\sigma &\leq r_{13} \leq (\lambda+1)\sigma \\ (\lambda-1)\sigma &\leq r_{13} \leq 2\sigma \\ 0 &\leq r_{13} \leq (\lambda-1)\sigma \end{aligned}$$

The first two cases are exactly the same as those for $\lambda\geq 3$ whic yield the same results for $G(R)$ equations (15), (16)-(18).

terms in β^2 which is obvious for the fourth case and yields the same expression (20) with $0 \leqslant R \leqslant (\lambda-1)\sigma$. For the third case, terms up to β^2 are needed when $\lambda \leqslant 2$ because of the form of the function $f(R)$ but for $2 \leqslant \lambda \leqslant 3$ terms linear in β are sufficient. The result for the third case is

$$G(R) = F_1(R) - 2\beta\varepsilon F_2(R) - 2\beta\mu F_3(R) + \beta^2\varepsilon^2 F_4(R) + 2\beta^2\varepsilon\mu F_5(R) + 2\beta^2\mu^2 F_6(R) \qquad (\lambda-1)\sigma \leqslant R \leqslant 2\sigma \tag{28}$$

where

$$F_1(R) = C_3(R) \tag{29}$$

$$F_2(R) = \pi[\tfrac{1}{2}(1-\lambda^2)\sigma^2 R + \tfrac{2}{3}(\lambda^3-1)\sigma^3 - \tfrac{1}{4}(\lambda^2-1)^2 \frac{\sigma^4}{R}] \tag{30}$$

$$F_3(R) = C_2(R) \tag{31}$$

$$F_4(R) = \pi[-\tfrac{1}{2}(1-\lambda^2)\sigma^2 R - \tfrac{2}{3}(\lambda^3-1)\sigma^3 + \tfrac{3}{4}(\lambda^2-1)^2 \frac{\sigma^4}{R}] \tag{32}$$

$$F_5(R) = \frac{16\pi}{R^3}[\frac{1}{64}(\frac{R}{R+\lambda\sigma})^2 - \frac{1}{64}(\frac{R}{R+\sigma})^2 - \frac{1}{96}(\frac{R}{R+\lambda\sigma})^3 + \frac{1}{96}(\frac{R}{R+\sigma})^3 + \frac{\lambda^2-1}{64\lambda^2}(\frac{R}{\lambda\sigma})^2] \tag{33}$$

$$F_6(R) = \frac{\pi}{720}[\frac{36R}{(\lambda\sigma)^{10}} - \frac{80}{(\lambda\sigma)^9} - \frac{8\sigma}{R(R+\sigma)^9} - \frac{36\sigma^2}{R(\lambda\sigma)^{10}} - \frac{1}{R(R+\sigma)^8} + \frac{45}{R(\lambda\sigma)^8}] + C_7(R) \tag{34}$$

With $G(R)$ in hand, the third virial coefficient $B_3(T)$ given by (26) can be obtained by choosing the appropriate form for the function $f(R)$ equation (11) and in such a way that all terms up to β^2 are considered and cases $\lambda \leqslant 2$, $2 \leqslant \lambda \leqslant 3$ are taken care of. The final results show that $B_3(T)$ has the same expression (27) for $2 \leqslant \lambda \leqslant 3$, so that this expression stands for $\lambda \geqslant 2$.

For $\lambda \leqslant 2$, the result is given by

$$
\begin{aligned}
B_3(T) = \frac{5}{18}\pi^2\sigma^6 &+ \frac{\pi^2\sigma^6\beta\varepsilon}{18}[-\lambda^6+18\lambda^4-32\lambda^3+15] \\
&+ \frac{\pi^2\beta\mu}{18\lambda^3}[-5\lambda^3+36\lambda-32] + \frac{\pi^2\beta\mu}{3}\ln\left(\frac{\lambda}{2}\right) \\
&+ \frac{\pi^2\sigma^6\beta^2\varepsilon^2}{36}[-5\lambda^6+90\lambda^4-96\lambda^3-36\lambda^2+47] \\
&+ \frac{\pi^2\beta^2\varepsilon\mu}{18\lambda^4(\lambda+1)^4(2\lambda-1)^2}[-40\lambda^{10}-168\lambda^9+78\lambda^8+596\lambda^7 \\
&\qquad + 150\lambda^6-624\lambda^5-287\lambda^4+228\lambda^3 \\
&\qquad + 108\lambda^2-32\lambda-9] \\
&+ \frac{2}{3}\pi^2\beta^2\varepsilon\mu\ln\left(\frac{\lambda+1}{2}\right) \\
&+ \frac{\pi^2\beta^2\mu^2}{27648\lambda^9(\lambda+1)^4(\lambda+2)^2\sigma^6}[\lambda^{15}-645112\lambda^{14}-4838374\lambda^{13} \\
&\qquad - 14407636\lambda^{12}-21557719\lambda^{11}-16687084\lambda^{10} \\
&\qquad - 5871356\lambda^9-442368\lambda^8+50688\lambda^7+13312\lambda^6 \\
&\qquad + 191944\lambda^5+318464\lambda^4+190976\lambda^3 \\
&\qquad - 59392\lambda^2-108544\lambda-32768] \\
&+ \frac{70\pi^2\beta^2\mu^2}{9\sigma^6}[3\ln(\lambda+1)-\ln(4\lambda)] \qquad \lambda \leqslant 2 \qquad (3
\end{aligned}
$$

Expression (27) for $\lambda \geqslant 2$ coincides with expression (35) for $\lambda \leqslant 2$, at $\lambda = 2$ as it should be . As the third virial coefficient $B_3(T)$ is obtained only up to terms in β^2 , it i valid only at high temperatures. Our potential reduces to the square-well one by putting $\mu = 0$. In this case, the third virial coefficient $B_3(T)$ equations (27) and (35) reduces to the well-known third virial coefficient for square-qell potential(9) considering only terms up to β^2 .

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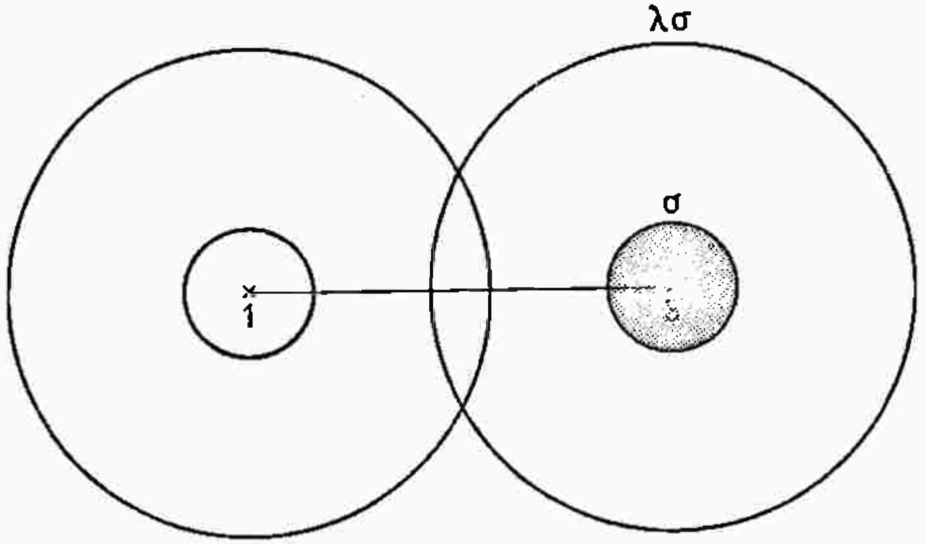

Fig. I

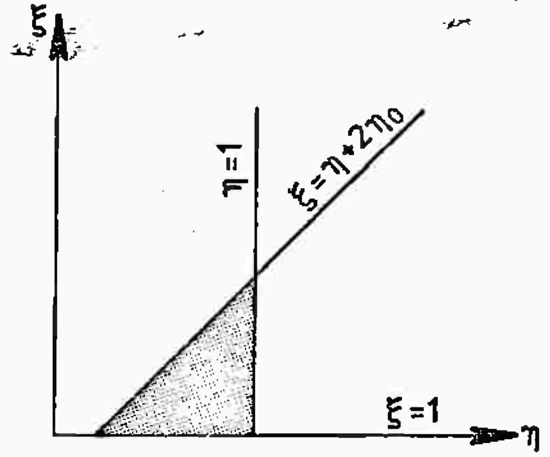

Fig. II