

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 β^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

$$A = -kT \ln Z \quad (1)$$

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

$$\equiv \frac{Q_N}{\Lambda^{3N}}, \quad \Lambda^2 = \frac{h^2}{2\pi m kT} \quad (3)$$

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

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

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

$$p = \rho KT [1 + B_2(T)\rho + B_3(T)\rho^2 + \dots] \quad (5)$$

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

$$B_m = -\frac{m}{m+1} \cdot \frac{1}{Vm!} \int \dots \int \sum_{1 \leq i < j \leq m+1} f_{ij}(r_{ij}) dr_1 \dots dr_{m+1} \quad (6)$$

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

$u(r_{ij})$ 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 :

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

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

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

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

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

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

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

Consider the integral

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

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

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

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

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

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

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

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

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

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

$$G(r_{13}) = -2\beta\mu \times \frac{16}{r_{13}^3} \pi \int_{1-2\eta_0}^1 d\eta \int_1^{\eta+2\eta_0} \frac{(\xi-\eta)}{(\xi+\eta)^5} d\xi, \quad \eta_0 = \frac{\sigma}{r_{13}}$$

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

$$G(R) = -2\beta\mu \times \frac{16}{R^3} \pi \left[\frac{1}{64} \left(\frac{R}{R+\sigma} \right)^2 - \frac{1}{64} \left(\frac{R}{R-\sigma} \right)^2 - \frac{1}{96} \left(\frac{R}{R+\sigma} \right)^3 + \frac{1}{96} \left(\frac{R}{R-\sigma} \right)^3 \right] \quad (\lambda+1)\sigma \leq R \leq \infty \quad (15)$$

Similarly, we have for the second case

$$G(R) = -2\beta\epsilon C_1(R) - 2\beta\mu C_2(R) \quad (\lambda-1)\sigma \leq R \leq (\lambda+1)\sigma \quad (16)$$

where

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

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

The third case is obvious

$$G(R) = -2\beta\epsilon \times \frac{4}{3} \pi \sigma^3 \quad 2\sigma \leq R \leq (\lambda-1)\sigma \quad (19)$$

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

$$G(R) = C_3(R) - 2\beta\epsilon C_4(R) + \beta^2\epsilon^2 C_5(R) + 2\beta^2\epsilon\mu C_6(R) + 2\beta^2\mu^2 C_7(R) \quad 0 \leq R \leq 2\sigma \quad (20)$$

where

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

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

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

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

$$C_7(R) = \frac{1024\pi}{R^3} \left[\frac{35(\lambda\sigma)^2 R}{2048(R+\lambda\sigma)^3} + \frac{525(\lambda\sigma)R^2}{12288(R+\lambda\sigma)^3} + \frac{385}{12288} \left(\frac{R}{R+\lambda\sigma} \right)^3 + \frac{35}{8192} \frac{R^4}{(\lambda\sigma)(R+\lambda\sigma)^3} - \frac{7}{8192} \frac{R^5}{(\lambda\sigma)^2(R+\lambda\sigma)^3} + \frac{7}{24576} \frac{R^6}{(\lambda\sigma)^3(R+\lambda\sigma)^3} - \frac{1}{8192} \frac{R^7}{(\lambda\sigma)^4(R+\lambda\sigma)^3} + \frac{1}{16384} \left(\frac{R}{\lambda\sigma} \right)^8 - \frac{35}{2048} \ln \left| \frac{R+\lambda\sigma}{\lambda\sigma} \right| \right] \quad (25)$$

The third virial coefficient is given by

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

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

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

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 $\lambda \geq 3$ which 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 $0 \leq R \leq (\lambda-1)\sigma$. For the third case, terms up to β^2 are needed when $\lambda \leq 2$ because of the form of the function $f(R)$ but for $2 \leq \lambda \leq 3$ terms linear in β are sufficient. The result for the third case is

$$G(R) = F_1(R) - 2\beta\epsilon F_2(R) - 2\beta\mu F_3(R) + \beta^2\epsilon^2 F_4(R) + 2\beta^2\epsilon\mu F_5(R) + 2\beta^2\mu^2 F_6(R) \quad (\lambda-1)\sigma \leq R \leq 2\sigma \quad (28)$$

where

$$F_1(R) = C_3(R) \quad (29)$$

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

$$F_3(R) = C_2(R) \quad (31)$$

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

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

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

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 $\lambda \leq 2$, $2 \leq \lambda \leq 3$ are taken care of. The final results show that $B_3(T)$ has the same

expression (27) for $2 \leq \lambda \leq 3$, so that this expression stands for $\lambda \geq 2$.

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

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

Expression (27) for $\lambda \geq 2$ coincides with expression (35) for $\lambda \leq 2$, 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 is 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-well potential⁽⁹⁾ considering only terms up to β^2 .

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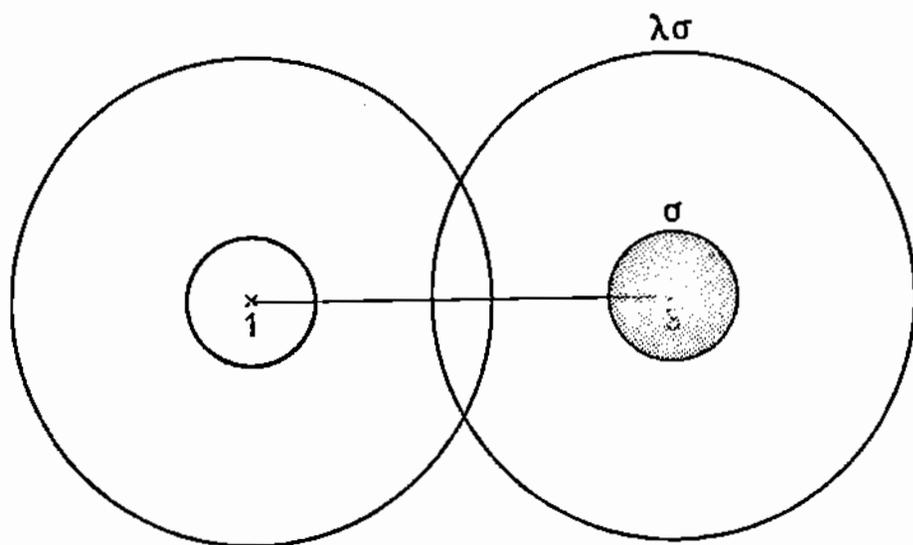


Fig. I

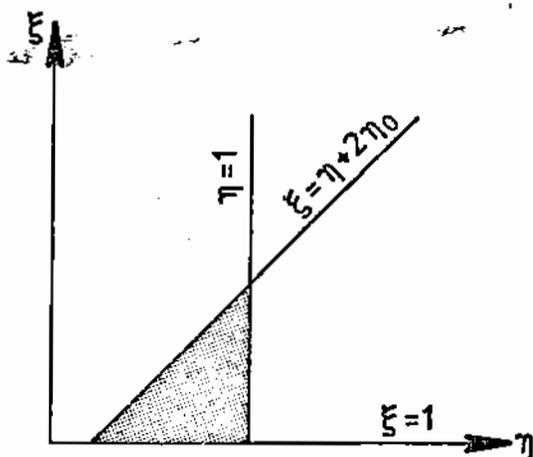


Fig. II