The Intermolecular Potential for Spherically Symmetrical Molecules

SØREN TOXVÆRD* and EIGIL PRÆSTGAARD

Chemistry Laboratory III, H. C. Ørsted Institute, University of Copenhagen, Copenhagen, Denmark

Potential parameters for various empirical pair interaction functions have been adjusted by including in the analysis the latest available experimental data on the second virial coefficient at low temperatures. This confirms that the potential is deeper than the usual Lennard-Jones 6:12 function and that three parameter potentials reproduce experimental data adequately. The quantum effects at low temperatures are determined by a direct method which includes in the curve fitting the first two terms in the diffraction expansion as calculated for the Lennard-Jones potential 6:n. It is shown, that it is possible to reproduce the second virial coefficients from a potential having the correct values for the dipole-dipole- and dipole-quadrupole interactions.

Expressions for the classical third virial coefficient and the first correction terms for three body forces and quantum effects are derived for the Lennard-Jones 6:n potential. It is confirmed that quantum effects play a significant role.

Extensive studies in recent years of the potential energy between a pair of simple molecules have been made both experimentally and theoretically.[1] The nature of the intermolecular potential is reflected most readily by the deviation from the ideal gas law as represented by the coefficients appearing in the virial expansion, by the scattering cross sections, and by transport coefficients of dilute gases.

The exact functional form of the intermolecular potential between spherically symmetrical molecules cannot as yet be obtained from theoretical calculations. However, perturbation theory, applied to large distances of separation, gives the functional dependence of the intermolecular potential as even powers of the distance. The first two terms, $-br^{-6}$ and $-cr^{-8}$, express the induced dipole-dipole and dipole-quadrupole interaction.[2-3] Furthermore, the coefficient b can be accurately determined from spectroscopic data.[4-6]

Even though the knowledge of the potential energy function is incomplete for intermolecular distances, where perturbation theory is not applicable,

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* Present: address: Institute for Chemistry, University of Copenhagen, Rådmansgade 71, 2200 Copenhagen N, Denmark.

some information can be obtained from experimental data.[7-9] It is not possible however, to determine the functional form from the experimental data alone. This can be seen for instance from the fact, that in the simplest case of the second virial coefficient B_2 it is possible to calculate B_2 using different functions for the potential energy to the same agreement with experimentally obtained values. It has been assumed in the past, that accurate measurement of the higher virial coefficients should provide the information necessary for the determination of the functional form of the intermolecular potential. It is now established that the effects of non additive forces are too large to allow this to be done.[10]

It is therefore necessary to introduce empirical potential functions. The conditions to this function are, that they must allow values of physical quantities to be calculated in good agreement with experimental data. Furthermore the functions used should be functionally as simple as possible consistent with the requirement, that they are physically acceptable.

INTERMOLECULAR POTENTIAL FUNCTIONS

Since the inert gases obey the law of corresponding states to a fairly high degree, it can be expected, that the intermolecular potential can be represented by a function $U^*(r/r^*)$ of the same form for all the inert gases and with only two adjustable parameters A and r^*:[11]

$$U(r) = A U^*(r/r^*) \tag{1}$$

A much used potential satisfying this principle is the Lennard-Jones 12:6 function, which also gives the correct asymptotic behavior:

$$U(r) = 4 \ \varepsilon \ [(\sigma/r)^{12} - (\sigma/r)^6] \tag{2}$$

Here $-\varepsilon$ is the potential energy minimum value and σ the molecular distance, for which the potential energy is zero. It has, however, been recognized for a long time, that this potential fails to reproduce B_2 at low temperatures [12-13] and, furthermore, the coefficient b in the attractive London potential is almost twice the calculated value. The deviation between calculated and experimental values of B_2 can be reduced by treating the power of the repulsive potential as a parameter:

$$U(r) = \left(\frac{n}{n-6}\right) \left(\frac{n}{6}\right)^{6/(n-6)} \varepsilon \left[\left(\frac{\sigma}{r}\right)^n - \left(\frac{\sigma}{r}\right)^6\right] = ar^{-n} - br^{-6} \tag{3}$$

The potential (3) is the n:6 Lennard-Jones potential. This function obeys the law of corresponding states, only if n is the same for all the inert gases.

As shown in Table 1 computation of B_2 for other three parameter functions than the n:6 Lennard-Jones potential confirms that it is possible to reproduce experimental data by choosing a third parameter in addition to the two "corresponding state" parameters σ and ε. In the Kihara potential:

$$U(r) = 4 \ \varepsilon \left[\left(\frac{\sigma-2a}{r-2a}\right)^{12} - \left(\frac{\sigma-2a}{r-2a}\right)^6\right] \text{ for } r > 2a \tag{4}$$
$$\infty \qquad\qquad\qquad\qquad \text{for } r \leq 2a$$

one has chosen the hard core diameter $2a$ as the third parameter, although there is no physical reason to expect such a hard core for the inert gases.[14-15] It has, however, been assumed that the reason why the non-physical Kihara potential reproduced the experimentally obtained virial coefficients better than a two parameter potential is that this potential, when expanded in powers of a/r considers attractive terms proportional to powers higher than six.[15-16]

A simple quantum mechanical calculation of the repulsive potential indicates an exponential behaviour.[17] This is used in the exp:6 potential:

$$U(r) = \frac{\varepsilon}{1-(6/\gamma)} \left[\frac{6}{\gamma} e^{\gamma[1-(r/r_m)]} - \left(\frac{r}{r_m} \right)^{-6} \right] \text{ for } r > m \qquad (5)$$
$$\infty \qquad\qquad\qquad\qquad \text{for } r < m$$

where the parameter γ is introduced to take care of the small deviation from the corresponding state. The exp:6 potential becomes equal to the potential minimum value $-\varepsilon$ at the intermolecular distance r_m, m is that value of r for which eqn. (5) goes through a maximum. In addition to these functions we have adjusted the parameters in the Sutherland- and square well potentials:

$$U(r) = \infty \qquad \text{for } r \leq \sigma$$
$$\qquad -br^{-6} \qquad \text{for } r > \sigma \qquad (6)$$
$$U(r) = \infty \qquad \text{for } r \leq \sigma$$
$$\qquad -\varepsilon \qquad \text{for } \sigma < r < R\sigma \qquad (7)$$
$$\qquad 0 \qquad \text{for } R\sigma \leq r$$

There is excellent agreement between the B_2 obtained experimentally and the one calculated for a three parameter potential, and there would be no improvement in using more parameters in the curve fitting. Also the three parameter function gives good value for the asymptotic br^{-6} term of the potential. This term is, however, more precisely determined by calculations based on refractive index measurements.[4-6] We employed this knowledge by using the calculated value of b and adjusted a and n in the n:6 Lennard-Jones potential (3). To examine the influence of the next term $-cr^{-8}$ in the long range potential we adjust a and n in the function n:6:8

$$U(r) = ar^{-n} - br^{-6} - cr^{-8} \qquad (8)$$

where we used the otherwise determined values of b and c. For the calculation of c, see Fontana.[18]

THE SECOND VIRIAL COEFFICIENT

The classical second virial coefficient for spherically symmetrical molecules $B_2^{(0)}$ is given by the expression:

$$B_2^{(0)} = 2\pi N \int_0^\infty (1 - e^{-U(r)/kT}) \, r^2 \, dr \qquad (9)$$

Table 1. Potential parameters for argon and krypton.

Argon	Parameters: 1.	Parameters: 2.	Parameters: 3.	1.	Value: 2. (Å)	3. (K°)	rms. deviation: (cm³/mole)	References:
Sutherland:		σ	ε/k		3.002	306.9	9.53	a,b,c,d,
12:6 L-Jones:		σ	ε/k		3.545	116.5	3.22	(48 data —
n:6 L-Jones:	n	σ	ε/k	20.0	3.226	169.8	0.59	87°K to 873°K)
n:6 (quan. corr.):	n	σ	ε/k	20.5	3.224	172.7	0.59	
Kihara:	a	σ	ε/k	0.260 Å	3.256	162.0	0.62	
Square well:	R	σ	ε/k	1.65	3.034	103.3	0.61	
exp:6:	γ	r_m	ε/k	21	3.543	168.1	0.60	
n:6:8:	n		α/k	17.5		4.806×10^{11} °K·Å^n	0.72	

Krypton	Parameters: 1.	Parameters: 2.	Parameters: 3.	1.	Value: 2. (Å)	3. (°K)	rms. deviation: (cm³/mole)	References:
Sutherland:		σ	ε/k		3.134	438.6	11.87	a,d,e
12:6 L-Jones:		σ	ε/k		3.783	164.6	2.89	(30 data —
n:6 L-Jones:	n	σ	ε/k	18.0	3.490	225.3	0.60	120°K to 873°K)
n:6 (quan. corr.):	n	σ	ε/k	18.0	3.493	225.4	0.59	
Kihara:	a	σ	ε/k	0.230 Å	3.521	215.8	0.63	
Square well:	R	σ	ε/k	1.67	3.262	139.4	0.62	
exp:6:	γ	r_m	ε/k	19	3.860	222.5	0.61	
n:6:8:	n		α/k	17.5		1.803×10^{12} °K·Å^n	0.76	

For the coefficient b and c in the n:6:8 potential is used the otherwise determined values. Argon: $b = 65.7$ erg·cm⁶×10⁻⁶⁰, $c = 121$ erg·cm⁸×10⁻⁷⁶. Krypton: $b = 130.3$ erg·cm⁶×10⁻⁶⁰, $c = 274$ erg·cm⁸×10⁻⁷⁶. References: *a.* Weir, R.D., Wynn Joens, I., Rowlinson, J.S. and Saville, G. *Trans. Faraday Soc.* **63** (1967) 1320 (data for Ar at 80 82 and 84°K and for Kr at 111,112,115 and 118°K are not used). *b.* Michels, A., Wijker, H. and Wijker, Hk. *Physica* **15** (1949) 627. *c.* Michels A., Levelt, J.M. and DeGraaff W. *Physica* **24** (1958) 659. *d.* Whalley, E. and Schneider, W.G. *J. Chem. Phys.* **23** (1955) 1644. *e.* Beattie, J.A., Brierley, J.S. and Barriault, R.J. *J. Chem. Phys.* **10** (1952) 1644.

The parameters in the potential functions 2—8 were adjusted in the case of Ar and Kr by fitting the calculated $B_2^{(0)}$ to the experimentally obtained B_2. For low temperatures we only used the data of Weir, Wynn Jones, Rowlingson and Saville.[19] The adjusting was performed in the usual way by the least square criterion and minimizing the root mean square deviation (rms). Using the new measurements we found that a few of them differed markedly from the calculated values, and that none of the potential functions was able to reproduce them satisfactorily, even by taking into account the first two quantum terms in the diffraction expansion (Appendix A). We therefore excluded all the experimental data below a certain temperature, determined by the first appearing data which differed more than 3 rms. (For Ar data at 80°, 82°, and 84°K, for Kr at 111°, 112°, 115°, and 118°K, even though the measurement at 115°K agree with the calculated value. After a refitting based on the remaining data we found, that the rms deviation would be doubled by including those few points). The potential parameters determined on the remaining data are shown in Table 1; Fig. 1 shows different potential functions for argon using the potential parameters from Table 1.

From Table 1 it is seen, that one obtains a considerably better agreement between calculations and experiments by fitting a third potential parameter. Furthermore, it is seen from Fig. 1, that even though the three parameter potentials have different functional form, the adjusting of parameters in the
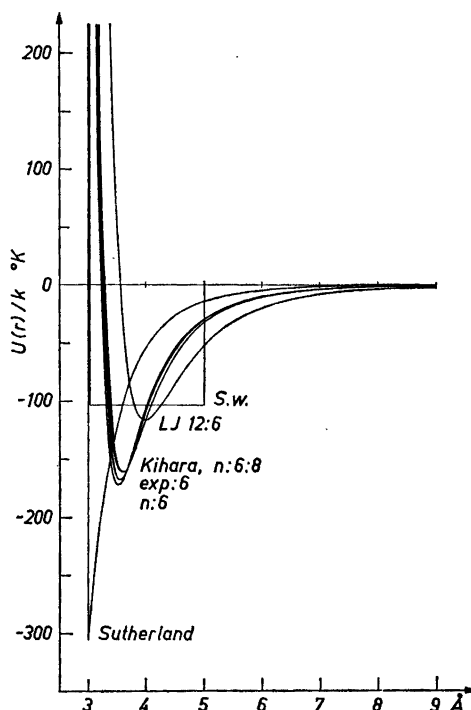

Fig. 1. The potential energy of interaction between two argon atoms for Lennard-Jones 12:6, *n*:6, Kihara, *n*:6:8, exp:6, Square-well (S.w.), and Sutherland potentials; based on $B(T)$ data.

physically reasonable functions results in nearly the same potential. This result is well known from older investigations based on other low temperature data.[12-13]

The classical expression for the second virial coefficient (9) is not sensitive to the functional form of the potential, as can be seen from the fact, that the square well potential (7) is able to reproduce B_2 as accurately as the other three parameter functions. There is, however, reason to believe, that one can determine the function for molecular distance $r < r_m (U(r_m) = -\varepsilon)$ from experimental values of B_2, if one knows the exact potential for $r > r_m$.[7] We have therefore used the otherwise determined coefficients b and c in the London potential and adjusted a and n in (8), hoping that, even though the perturbation expansion is not valid in the region $r \approx r_m$, one would obtain a stronger and more correct condition to the potential in the curve fitting. As seen from Table 1 the $n:6:8$ potential (8) reproduces B_2 almost as accurately as the potentials including three adjustable parameters. From Fig. 1 it is seen, that there is an excellent agreement between the potential (8) and the physically acceptable three parameter functions, especially the Kihara potential (4). (For Ar it was in addition possible to reproduce B_2 by including only the first term br^{-6}, but it results in systematic deviation for Kr). To get an idea of the influence of the dipole-quadrupole term $-cr^{-8}$ in the $n:6:8$ potential (8) we calculated $B_2^{(0)}$ for a $n:6$ Lennard-Jones potential using the value of a and n in the $n:6:8$ potential and found, that the dipole-quadrupole terms contributed by an amount varying between 25 % for the low temperatures region to 15 % for high temperatures. These values only show the influence of the asymptotic term $-cr^{-8}$, as it appears in formula (8), where it is extended to intermolecular separations, for which a perturbation expansion is not valid. However, the coincidence between the three parameter potentials and the $n:6:8$ potential shows that the third parameter ensures the correct asymptotic behavior as seen most clearly in the case of the Kihara potential by an expansion in powers of a/r.[15,16]

The influence of the quantum correction to the classical second virial coefficient $B_2^{(0)}$ was examined by including the first two terms in the diffraction expansion (Appendix A), calculated for a $n:6$ Lennard-Jones potential (3), in the curve fitting. At low temperatures the first term contributes 2 % for the heavy Ar atoms, whereas it only contributes a few ‰ in the case of Kr. The second term was negligible for all temperatures, for which experimental data exist. The adjusted parameters in the $n:6$ potential (3) are shown in Table 1.

THE THIRD VIRIAL COEFFICIENT

The assumption of a pairwise additive potential leads to the classical expression for the third virial coefficient $B_3^{(0)}$:

$$B_3^{(0)} = -\frac{8\pi^2 N^2}{3} \iiint_0^\infty f_{12} f_{13} f_{23} r_{12} r_{13} r_{23} \mathrm{d}r_{12} \mathrm{d}r_{13} \mathrm{d}r_{23} \qquad (10)$$

where $f_{ij} = \exp[-U(r_{ij})/kT] - 1$.

It has, however, been verified, that the nonadditive three particle potential $U(r_{12}, r_{13}, r_{23})$ contributes to the third virial coefficient by a non-negligible amount.[12,13,20] The asymptotic form of $U(r_{12}, r_{13}, r_{23})$ is known from a perturbation approximation.[21] Normally this contribution is expanded in a rapidly converging series in powers of the polarisability α (the first nonvanishing term $B_3^{(n.add.)}$ is linear in the polarisability). The short range part of $U(r_{12}, r_{13}, r_{23})$ and its effect on the third virial coefficient are only known qualitatively.[10,22]

At low temperatures it is furthermore necessary to take care of quantum effects. Considering only the first term in the diffraction expansion (Appendix A) and neglecting the short range three particle potential contribution, the third virial coefficient can be approximated by

$$B_3 = B_3^{(0)} + \alpha B_3^{(n.add.)} + (h^2/m)B_3^{(1)} \tag{11}$$

Using a $n{:}6$ Lennard-Jones potential it is possible to expand B_3 in a rapidly converging series:

$$B_3 = b_0^2 \sum_{i=0}^{\infty} T^{*-i(n-6)/n} \left[A_3^{(0)}T^{*-6/n} + \alpha^* A_3^{(n.add.)}T^{*-1+(3/n)} + \right.$$
$$\left. + (h^2/mK)A_3^{(1)}T^{*-1-(4/n)} \right] \tag{12}$$

where T^* is the reduced temperature kT/ε, $b_0 = \frac{2}{3}\pi N\sigma^3$, $\alpha^* = \alpha/\sigma^3$ and $K = 4\pi^2\sigma^2\varepsilon$.

The functional form of the coefficients $A_3^{(0)}$, $A_3^{(n.add.)}$, and $A_3^{(1)}$ are expressed in Appendix B. The coefficients were calculated for values of n varying with 0.5 between 12 and 21 and for i values up to $i=30$.

The third virial coefficient was calculated for a $n{:}6$ Lennard-Jones potential using the potential parameters determined from the analysis of the second virial coefficient. The result is shown in Figs. 2 and 3.

From Fig. 2 it is seen, that the coincidence between calculated and experimentally obtained data is improved by choosing a value of $n \approx 18-20$ in
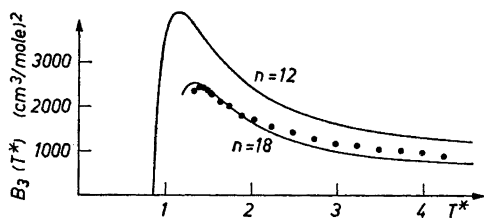

Fig. 2. The third virial cofficient B_3 for argon calculated for two values ($n=12$ and $n=18$) of the power in the $n{:}6$ Lennard-Jones potential. The parameter values are determined from the second virial coefficient. The experimental data are taken from Refs. b and c; see Table 1.
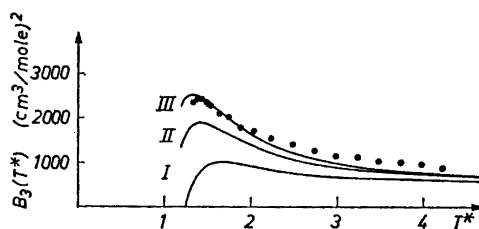
Fig. 3. Contributions to the third virial coefficient $B_3(T)$ for argon, calculated for the 18:6 Lennard-Jones potential using the parameter values determined from $B_2(T)$.

I. $B_3^{(0)}$. II. $B_3^{(0)}+\alpha B_3$(n.add.). III. $B_3^{(0)}$ $+\alpha B_3^{(n.add.)}+(h^2/m)B_3^{(1)}$.

The experimental data are taken from Refs. b and c; see Table 1.

agreement with the analysis of the second virial coefficient (see also Dymond, Rigby and Smith [13]). Fig. 3 shows the three contributions to B_3.

Even though the third virial coefficient is more sensitive to the functional form of $U(r)$, the lack of information about the short range part of the nonadditive potential makes it impossible to predict $U(r)$ from B_3, and the accuracy of the experimental data does not allow a determination of $U(r_{12}, r_{13}, r_{23})$, even though $U(r)$ was known.

CONCLUSION

Calculations of the intermolecular potential based on knowledge of B_2 over a wide temperature range confirmed that the potential is deeper than indicated by the 12:6 Lennard-Jones potential (2), since all tested three parameter potentials reproduce B_2 equally well, and those which have the correct asymptotic behavior give the same minimum.

The calculated values of B_2 get better as the parameter n in (3) is increased from 12 to 18, but this should not be taken as an indication of the steepness of the repulsive branch of the potential. The role of n in the curve-fitting is to adjust the potential minimum. This can clearly be seen from the fact, that B_2 is reproduced equally well with $n=12$ as with $n=18$, if only data above $T/T_c=1$ are used.

Calculations of the first terms in the diffraction expansion for B_2 and B_3 confirm the necessity of including quantum mechanic corrections at low temperatures to the classical expression for the virial coefficients.

APPENDIX A

The deviation from the classical expression for the virial coefficients due to quantum effects can be obtained by means of a WKB expansion in the intermediate temperature region.[21] This results in the series:

$$B_i = B_i^{(0)} + (\hbar^2/m)B_i^{(1)} + \ldots$$

For an n:6 Lennard-Jones potential it is possible to expand the classical virial coefficients and the quantum correction coefficients $B_i^{(j)}$ in rapidly converging series of gamma functions. (The expansion technique is described by Lennard-Jones [23]). For the second virial coefficient we found:

$$B_2^{(1)} = -\frac{2\pi N}{n} \sum_{i=0}^{\infty} \left(\frac{n-1+(36-6n)i}{48\,\pi^2 kT} \right) \left(\frac{b}{kT} \right)^i \left(\frac{a}{kT} \right)^{-(6i-1)/n} \frac{1}{i!}\, \Gamma\left(\frac{6i-1}{n} \right)$$

$$B_2^{(2)} = -\frac{2\pi N}{n} \sum_{i=0}^{\infty}$$

$$\left(\frac{(21+10n-9n^2+2n^3)+(504-444n-12n^2+12n^3)i+(9072-3024n+252n^2)i^2}{23040\,\pi^4(kT)^2} \right)$$

$$\left(\frac{b}{kT} \right)^i \left(\frac{a}{kT} \right)^{-(6i+1)/n} \frac{1}{i!}\, \Gamma\left(\frac{6i+1}{n} \right)$$

APPENDIX B

The coefficients $A_3^{(0)}$, $A_3^{(\text{n.add.})}$, and $A_3^{(1)}$ in the expansion (12) of the virial coefficient for the $n{:}6$ Lennard-Jones potential is:

$$A_3^{(0)}(i \neq 1) = -36\{(n/6)^{n/(n-6)}[6/(n-6)]\}^{\{i(n-6)+6\}/n}(ni!)^{-1})\Gamma[6(i-1)/n]$$

$$\int_{0.5}^{1} dy \int_{1-y}^{y} dx\ xy(\langle 6\rangle^i \langle n\rangle^{-6(i-1)/n} - \langle 6(x)\rangle^i \langle n(x)\rangle^{-6(i-1)/n}$$

$$-\langle 6(y)\rangle^i \langle n(y)\rangle^{-6(i-1)/n} - \langle 6(x,y)\rangle^i \langle n(x,y)\rangle^{-6(i-1)/n} + \langle 6\rangle)$$

$$A_3^{(0)}(i = 1) =$$

$$-36(n/6)^{6/(n-6)+1}[6/(n-6)]/n \int_{0.5}^{1} dy \int_{1-y}^{y} dx\ xy(\ln(\langle n(x)\rangle \langle n(y)\rangle / \langle n\rangle) +$$

$$x^{-6}\ln(\langle n(x)\rangle \langle n(x,y)\rangle /(x^{-n}\langle n\rangle)) + y^{-6}\ \ln(\langle n(y)\rangle \langle n(x,y)\rangle /(y^{-n}\langle n\rangle)))$$

$$A_3^{(\text{n.add.})} =$$

$$27[(n/6)^{n/(n-6)}6/(n-6)]^{\{i(n-6)-3\}/n+1}(ni!)^{-1}\Gamma[(6i+3)/n]$$

$$\int_{0.5}^{1} dy \int_{1-y}^{y} dx(xy)^{-2}(3\ \cos\theta_1\cos\theta_2\cos\theta_3 + 1)\langle 6\rangle^i \langle n\rangle^{-(6i+3)/n}$$

$$A_3^{(1)} =$$

$$3(n/6)^{\{i(n-6)+4\}/(n-6)}(6/(n-6))^{\{i(n-6)+4\}/n}\ (ni!)^{-1}\ \Gamma[(6i-4)/n]$$

$$\int_{0.5}^{1} dy \int_{1-y}^{y} dx\ xy\ \{(6i+n-4)(6i-4)(\langle n,n\rangle\langle n\rangle^{-(6i-4)/n-2}\langle 6\rangle^i - \langle 6\rangle) -$$

$$12i(6i-4)\{\langle n,6\rangle\langle n\rangle^{-(6i-4)/n-1}\langle 6\rangle^{i-1} - \langle 6\rangle) + 36i(i-1)$$

$$(\langle 6,6\rangle\langle n\rangle^{-(6i-4)/n}\langle 6\rangle^{i-2} - \langle 6\rangle)\}$$

where following bracket notation has been used:

$$\langle n\rangle = x^{-n} + y^{-n} + 1$$
$$\langle a(b)\rangle = 1 + b^{-a}$$
$$\langle a(b,c)\rangle = b^{-a} + c^{-a}$$
$$\langle a,b\rangle = \langle a+b+2\rangle + 1/4(x^{-a-2} + x^{-b-2})(x^2 - y^2 + 1) + 1/4(y^{-a-2} + y^{-b-2}).$$
$$(-x^2 + y^2 + 1) + 1/4(x^{-a-2}y^{-b-2} + x^{-b-2}y^{-a-2})(x^2 + y^2 - 1)$$

θ_1, θ_1 and θ_3 are the inner angles of a triangle with the corresponding sides $x,y,1$.

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