ON THE REPRESENTATION OF THREE-BODY NON-ADDITIVE INTERACTIONS IN SOLIDS

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ABSTRACT. An attempt has been made to represent the three-body non-additive interactions empirically by a function which approximately represents the results obtained by quantum mechanical calculations. The results show that the Jansen's formula as such can not be utilized for the calculation of the second order crystal properties and the third virial coefficient of gases.

INTRODUCTION

The problem of representing the simultaneous interaction between more than two atoms or molecules has not yet been solved satisfactorily. The first attempt in this direction was made by Axilrod (1951) who obtained the interaction between three non-overlapping distributions of charge in the third-order perturbation theory. This so-called triple-dipole effect decreases the attraction compared to an addditive sum-over pairs for an equilateral configuration of atoms and increases it for a linear array. The same type of third-order effect was evaluated by Muto (1943) for an oscillator model and later extended by Midzuno and Kihara (1956). These results have been applied to the calculation of the stability of inert gas solids and to the third virial coefficients of gases. The net effect summed over the hcp and the fcc lattices, however, favour the cubic configuration for the inert gas solids but its magnitude is too small to take care of the small pair potential difference between the two structures. Sherwood and Prausnitz (1964) have recently calculated the non-additive three-body contributions to the third virial coefficients of gases as obtained from the triple-dipole effect. Their calculations, however, reveal that at least for the dense gases it is essential to consider the non-additive repulsive forces in addition to the triple-dipole effect.

The first order forces (exchange, chemical or valence) which predominate at smaller inter-atomic distances are of the many-body type (Margenau 1939). These forces were evaluated for an equilateral triangle and a linear array of three helium atoms by Rosen (1953) and Shostak (1955) using molecular orbitals. Subsequently Jansen (1962, 1963) obtained the tri-atomic first-order and second-order three-body interaction for heavy rare gases by using a Gaussian effective electron model given by

$$\rho(r) = (\beta/\pi^{\frac{1}{2}})^3 \exp\left(-\beta^2 r^2\right), \qquad \qquad \dots \text{ (1)}$$

where r is the distance from the effective electron to its nucleus, β is a parameter

and $\rho(r)$ is the charge distribution of effective electron. His results for the three-body interaction in first order, agree in sign with those of Rosen (1953) for helium. It should be pointed out that for the equilateral triangle configuration the relative three-body energy formula of Jansen remains almost constant for increasing inter-atomic distances (in terms of the dimensionless parameter βr) whereas the Rosen formula shows an exponential decrease. In the second-order the contribution to the relative three-body component is the sum of the effects due to diatomic and triatomic exchanges. Jansen's calculations explain satisfactorily the fcc structure and the enegy of vacancy formation in solid argon (Jansen, 1963). Due to mathematical difficulties the quantum-mechanical calculations are not suitable for applying to a general case and for considering the effect on various properties. It seems that, at present the only way to consider simultaneously the effects of three-body interactions in both the attractive and the repulsive parts is to use a pair potential with the parameters adjusted to the theoretical results obtained for three-body interactions.

DETERMINATION OF THE THREE-BODY NON-ADDITIVE INTERACTION FUNCTION

The three-body non-additive interaction ϕ_{non} may be written as,

$$\phi_{non} = \phi_{total} - \tfrac{1}{2} \sum_{i \neq j} \phi_{ij}, \qquad (2)$$

where ϕ_{total} represents the total interaction energy between three molecules forming a triangle and in the second term on the r.h.s. of eqn. (2), the summation extends over all the three pairs of the molecules. It has been shown by Kihara (1958) that the three-body non-additive interaction in the attractive part can be represented as

$$\phi_{non} = v(r_{12}\, r_{13}\, r_{23})^{-3}(1 + 3 \cos\theta_1 \cos\theta_2 \cos\theta_3), \qquad \ldots \quad (3)$$

where $$v = \frac{\tilde{\ }}{4}\, \alpha\mu,$$

α is the polarizability and μ is the coefficient of two-body dispersion energy varying as r^{-6}. No convenient expression for ϕ_{non} including both the repulsive and the attractive parts is available. However, it is found that an expression

$$\phi_{non} = -\omega(r_{12}^{*}r_{13}^{*}r_{23}^{*})^{-3}(1 + 10 \cos\theta_1 \cos\theta_2 \cos\theta_3) \tfrac{1}{2} \sum_{i \neq j} \phi_{ij} \qquad (4)$$

represents fairly well the quantum mechanically obtained results by Jansen (1962, 1963) (Fig. 1). r_{ij}^{*} in the above equation are the reduced intermolecular distances. It is possible to determine ω from the cohesive energy in the solid state. The three-body non-additive contributions to the cohesive energy per lattice-point in a fcc lattice considering only the nearest neighbours are given by

$$\Delta E_{coh}/N = 8\Delta_{60} + 4\Delta_{90} + 8\Delta_{120} + 2\Delta_{180}, \qquad (5)$$

where

$$\Delta_\theta = -\omega(r_{12}{}^*r_{13}{}^*r_{13}{}^*)^{-3}(1+10\cos\theta_1\cos\theta_2\cos\theta_3)\sum_{i\neq j}^{3}\phi_{ij} \qquad \dots (6)$$

On the basis of the core-potential (Sherwood and Prausnitz 1964),

$$\phi(r) = 4\epsilon\left[\left(\frac{\sigma-2a}{r-2a}\right)^{12} - \left(\frac{\sigma-2a}{r-2a}\right)^{6}\right], \qquad \dots (7)$$
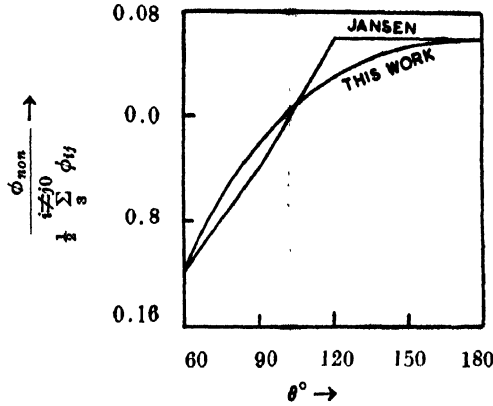

Fig. 1. The variation of $\phi_{non}/\frac{1}{3}\sum_{i\neq j}^{3}\phi_{ij}$ vs θ for solid argon.

(The interatomic distances are the nearest neighbour distances).

where a is the core radius, σ is the value of r for which $\phi(r) = 0$ and ϵ is the maximum energy of attraction, the pair cohesive energy per atom is given by

$$E'_{coh}/N = 2\epsilon\left[C_{12}\left(\frac{\sigma-2a}{d_0-2a}\right)^{12} - C_6\left(\frac{\sigma-2a}{d_0-2a}\right)^{6}\right] \qquad \dots (8)$$

In the above expression C_{12} and C_6 are lattice sums for the fcc structure and d_0 is the distance of nearest neighbour.

The cohesive energy per atom corrected for the three-body interaction is then

$$E_{coh}/N = E'_{coh}/N + 8\Delta_{60} + 4\Delta_{90} + 8\Delta_{120} + 2\Delta_{180}. \qquad \dots (9)$$

The value of ω calculated from eqn. (9) for inert gases are recorded in table I along with the force parameters (Sherwood and Prausnitz 1964) used in the calculation. The core-potential has been used due to its flexibility as shown by Barker (1964).

TABLE I

Gases	a^*	σÅ	$\epsilon/k°K$	d_0Å	L_0 cal/mol	ω	$\dfrac{\Delta E_{coh}/N}{\phi_{ij}(do)}$
Ar	0.125	3.314	147.2	3.756	1846	0.350	1.708
Kr	0.150	3.521	215.6	3.991	2666	0.400	1.679
Xe	0.175	3.878	298.8	4.335	3828	0.453	1.722

†Pollook, L., (1964) Rev. Mod. Phys., **36**, 748,

RESULTS AND DISCUSSION

In order to check the adequacy of eqn. (4), we have calculated the Debye characteristic temperature (Hirschfelder, Curtiss and Bird, 1954) given by

$$\theta_D(d_0) = \left(\frac{5}{3} \right)^{\frac{1}{2}} \frac{h\nu(d_0)}{k} \qquad \ldots \quad (9)$$

where the fundamental frequency $\nu(d_0)$ for a molecule of mass m, moving in three-dimensional potential well corrected for three-body non-additive interaction on the core-potential is

$$\nu^2(d_0) = \frac{\epsilon}{\pi^2 m(\sigma - 2a)^2} \left[22(C_{14} - A) \left(\frac{\sigma - 2a}{d_0 - 2a} \right)^{14} - 5(C_8 - A) \left(\frac{\sigma - 2a}{d_0 - 2a} \right)^8 \right] \quad (10)$$

in which

$$A = \frac{\Delta E_{coh}/N}{\phi_{ij}(d_0)} \qquad \ldots \quad (11)$$

The calculated and the experimental values of θ_D (Pollock, 1964) are given in Table II along with the values obtained on pair-potential ($A = 0$) and values determined from crystal properties (Singh and Barua, 1967). It can be seen from Table II that by considering three-body non-additive interaction the agreement between the experimental and the calculated values of θ_D becomes worse than that obtained on the pair-potential. However, no reliable quantitative conclusion on the three-body overlap forces based on the Jansen formulas which explain f.c.c. structure of inert gas solids with remarkable success, can be drawn from this simple analysis which shows a negative result (Table II). Recently, Bullough, Glyde, and Venables (1966) have measured the stacking fault energy in solid argon and have found it to be 1/15th of the value predicted by the Jansen formulas. It may be pointed out that the parameters for the pair-potential obtained from the crystal properties at 0°K represent the experimental θ_D value quite satisfactorily (Singh and Barua, 1967). This leads one to believe that the success of the additivity hypothesis may be due to an unexplained cancellation of the non-additive effects in the successive orders of the perturbation theory.

One of the best properties suitable for the study of non-additive interactions and which does not depend on more than three-body forces is the third virial coefficient of gases. In performing the theoretical calculation of the third virial coefficient $C(T)$, one must take into account of the following three types of three-body interactions;

(a) the first-order triple overlap exchange interaction (Jansen, 1962),

(b) the second-order single-overlap exchange interaction (Jansen and Mc-Ginnies 1956) and

(c) the thrid-order triple-dipole interaction (Axilord and Teller, 1943).

The effect of the triple-dipole interaction on the third virial coefficient has been investigated by several workers (Koba, Kaneko and Kihara, 1956; Graben and Present 1962; Sherwood and Prausnitz 1964). In applying the Jansen formulas which include the interaction of types (a) and (b) to the theoretical calculation of non-additive third virial coefficient, Graben, Present and McCulloch (1966) find that Jansen's choice of the Gaussian parameter β is unreasonably large. The sensitive dependence of the non-additive correction to $C(T)$ on the parameter β limits the scope applying Jansen formulas as such in estimating the total non-additive effects in $C(T)$.

On the above arguments it seems that the Gaussian model and the Jansen formulas at best can be utilized to find a functional form of the non-additive correction of the types (a) and (b). In the present paper we have attempted in this direction and have found that the eqn. (4) which is independent of the parameter β is very close to the Jansen formulas.

TABLE II

Substance	Debye Temp. (°K) at 0°K θ_{Do} Exptl.	Debye Temp. (°K) at 0°K θ_{Do} calculated from		
		Pair-Potential	Three-body	Crystal Properties
Ar	93.3	67.7	62.3	94.1
Kr	71.7	52.7	48.6	72.4
Xe	55.0*	52.8	48.7	64.8

*This value is expected to be about 65°K (Pollock 1964).

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