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Nonpairwise Interactions and Vacancy Formation Energies in Simple Molecular Solids[†]

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A method is given for summing all orders of nonpairwise contributions to the van der Waals interaction energy of a substitutional impurity in a monatomic molecular crystal using a Lorentz oscillator model as an approximation. The nonpairwise contribution to the energy of removing an atom from the lattice is obtained as a limiting case. Applied to rare-gas solids, the model suggests vacancy formation energies reduced from the two-body values, but insufficiently to give complete agreement with experiment.

I. INTRODUCTION

Calculations using two-body model potentials for the interactions between rare-gas atoms yield third virial coefficients in disagreement with experiment,[1] and predict vacancy formation energies in solid argon and krypton about equal to the cohesive energy per atom,[2–4] while observed thermal vacancy concentrations[5,6] suggest much smaller values. Also, the two-body potentials generally employed predict stability for the hexagonal close-packed (hcp) solid relative to the face-centered cubic (fcc),[7,8] contrary to observation. The possibility of explaining these apparent discrepancies between theory and experiment in terms of nonpairwise contributions to the cohesive energies of rare-gas solids has been widely examined.

Jansen *et al.*[9] consider nonpairwise interactions involving three-atom electron exchange in the overlap region; they obtain rather large three-body contributions (25% of the cohesive energy) that decisively stabilize the fcc lattice, reduce the two-body vacancy formation energy by as much as 47%,[10] and reportedly produce large relaxations around vacancies.[11] Swenberg[12,13] points out, however, that Jansen's effective one-electron Gaussian wave functions give unrealistically large nearest-neighbor overlaps, and that Gaussians with more realistic width parameters produce negligible three-body effects in Jansen's theory. Other possible difficulties with Jansen's approach have also been discussed.[14]

Nonpairwise contributions to the van der Waals interaction energy alone have also been considered. When interatomic overlaps are neglected and a multipole expansion used, the van der Waals interactions among rare-gas atoms are found to be pairwise additive to second order in perturbation theory,[14] and a three-body "triple-dipole" interaction arises in third order.[15–18] The triple-dipole interaction favors the fcc structure, but insufficiently to decisively stabilize it,[18] and Burton[19] shows that it decreases the vacancy formation energy in solid argon, although insufficiently to give agreement with experiment. The triple-dipole interaction also reduces the discrepancies between observed and calculated third virial coefficients in gaseous argon and krypton,[1,20,21] and its possible effects on other rare-gas properties have also been considered.[22–25] Present's calculation[26] suggests that this interaction might be much more significant than three-body interactions arising from overlap and exchange at normal lattice separation.

Higher-order nonpairwise van der Waals interactions have been calculated by treating the system approximately as an array of Lorentz oscillators,[27–34] each with appropriate polarizability, under the assumption that the van der Waals interactions are insensitive to the detailed electronic structure of the interacting atoms. Calculations[31] based on this approach suggest that the nonpairwise parts of the van der Waals interaction summed to all orders still favor, but cannot decisively stabilize, the cubic lattice. This method appears not to have been applied to higher-order effects on the vacancy formation energy.

Now the two-body calculated hcp-fcc energy difference is only about 0.01% of the cohesive energy in rare-gas solids and arises from differences in coordination number beyond the second nearest neighbors. Even a small arbitrary change in the two-body potential at these distances can reverse the energy difference without changing properties such as calculated virial coefficients, for example.[35] The discrepancy between observed and two-body calculated vacancy formation energies is, however, quantitatively more striking, and it can in fact be shown[19] that the n-body contribution to the vacancy formation energy is n-1 times as great as to the sublimation energy per atom. Furthermore, the nth-*order* contribution to the van der Waals energy (which contains n-*body* interactions, among others) falls off rather slowly with increasing n for the heavier rare gases.[31] It is therefore of considerable relevance to determine how well nonpairwise van der Waals interactions, summed to all orders, can explain the observed vacancy formation energies. We attempt to answer this question in the context of a Lorentz oscillator model for the van der Waals part of the interaction.

The van der Waals energy of a lattice of identical Lorentz oscillators is discussed briefly in Sec. II and the treatment extended in Sec. III to the case of a substitutional impurity characterized by a modified polarizability α_I. In the limit $\alpha_I \to 0$, the van der Waals energy of removing an atom from the lattice is obtained. The effects of nonpairwise van der Waals interactions on vacancy formation energies in simple molecular solids are treated in Sec. IV using this model an an approximation, and the numerical calculation using parameters appropriate to rare-gas solids are presented in Secs. V and VI.

II. MODEL FOR PERFECT CRYSTAL

Consider N isotropic Lorentz oscillators located at $\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_N$, and each having mass m, charge e, frequency ω_0, and polarizability $\alpha_0 = e^2/m\omega_0^2$. Assuming only nonretarded dipole-dipole interactions[36] between the oscillators, the Hamiltonian of the system is

$$H_0 = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i=1}^{N} \tfrac{1}{2} m\omega_0^2 q_i^2 + \tfrac{1}{2} e^2 \sum_{i=1}^{N} \sum_{j=1}^{N}{}' \vec{q}_i \cdot \overleftrightarrow{T}_{ij} \cdot \vec{q}_j \quad , \tag{1}$$

where $\vec{q}_i$ and $\vec{p}_i$ are, respectively, the position and momentum operators for the oscillator at $\vec{R}_i$, and $\overleftrightarrow{T}_{ij}$ is the dipole tensor whose components are 0 if $i=j$, and

$$T_{ij}^{\mu\nu} = (\delta_{\mu\nu} R_{ij}^2 - 3R_{ij}^{\mu} R_{ij}^{\nu})/R_{ij}^5 ,$$

with

$$\vec{R}_{ij} = \vec{R}_i - \vec{R}_j \quad \text{if } i \neq j .$$

Diagonalization of (1) can be effected by the usual methods for a system of coupled oscillators, with

$$\mathfrak{D}_{ij}^{\mu\nu} = [\delta_{ij}\delta_{\mu\nu} + (e^2/m\omega_0^2)\, T_{ij}^{\mu\nu}]\,\omega_0^2 \quad ,$$

the dynamical matrix. For the case of a Bravais lattice with periodic boundary conditions defined on a unit volume, the transformation

$$\begin{aligned} \vec{p}_{\vec{k}} &= N^{-1/2} \sum_i e^{-i\vec{k}\cdot\vec{R}_i} \vec{p}_i \quad , \\ \vec{q}_{\vec{k}} &= N^{-1/2} \sum_i e^{i\vec{k}\cdot\vec{R}_i} \vec{q}_i \quad , \\ \overleftrightarrow{T}(\vec{k}) &= (4\pi N)^{-1} \sum_i{}' e^{i\vec{k}\cdot\vec{R}_i} \overleftrightarrow{T}_{0i} \end{aligned} \tag{2}$$

partially diagonalizes H_0:

$$H_0 = \sum_{\vec{k}} \frac{\vec{p}_{\vec{k}}^{\,\dagger} \cdot \vec{p}_{\vec{k}}}{2m} + \frac{m}{2} \sum_{\vec{k}} \vec{q}_{\vec{k}}^{\,\dagger} \cdot \left(\omega_0^2 \overleftrightarrow{E} + \frac{4\pi N e^2}{m} \overleftrightarrow{T}(\vec{k}) \right) \cdot \vec{q}_{\vec{k}} \quad .$$

The van der Waals interaction energy is then the change in zero point energy arising from the dipole-dipole couplings of (1). With $\mathcal{T}$ the $3N \times 3N$ matrix having elements $\mathcal{T}_{ij}^{\mu\nu} = T_{ij}^{\mu\nu}$, $\epsilon_s(\vec{k})$ the sth eigenvalue of $4\pi\overleftrightarrow{T}(\vec{k})$, and $\omega_s(\vec{k})$ the sth eigenfrequency of wave number $\vec{k}$ for the system, the van der Waals energy is readily found to be[31]

$$W_C = \tfrac{1}{2}\hbar \sum_{s=1}^{3} \sum_{\vec{k}\in B} [\omega_s(\vec{k}) - \omega_0] \tag{3a}$$

$$= \tfrac{1}{2}\hbar\omega_0 \sum_{s=1} \sum_{\vec{k}\in B} \{[1 + \epsilon_s(\vec{k})]^{1/2} - 1\} \tag{3b}$$

$$= -\tfrac{1}{2}\hbar\omega_0 \sum_{n=2}^{\infty} \frac{(2n)!\,\alpha_0^n}{(2n-1)(n!)^2 2^{2n}} (-1)^n \operatorname{Tr}(\mathcal{T}^n) \; , \tag{3c}$$

where the $\vec{k}$ sum is over the first Brillouin zone. The first two nonvanishing contributions to (3c) are the pairwise van der Waals interaction

$$W_2 = -\frac{1}{2!} \sum_{i,j}{}' \frac{C_2}{R_{ij}^6} \quad , \tag{4}$$

and the triple-dipole interaction

$$W_3 = \frac{1}{3!} \sum_{i,j,k}{}' C_3 \times \frac{R_{ij}^2 R_{jk}^2 R_{ki}^2 - 3(\vec{R}_{ij}\cdot\vec{R}_{jk})(\vec{R}_{jk}\cdot\vec{R}_{ki})(\vec{R}_{ki}\cdot\vec{R}_{ij})}{R_{ij}^5 R_{jk}^5 R_{ki}^5} , \tag{5}$$

with $C_3 = 9\alpha_0^3\hbar\omega_0/16$ and $C_2 = 3\alpha_0^2\hbar\omega_0/4$. It is seen by expressing $\mathrm{Tr}(\mathcal{T}^n)$ as a lattice sum that the nth-order contribution to (3b) for $n > 3$ contains both n-body and k-body contributions with $k < n$. Equations (3c)–(5) hold also for an arbitrary array of Lorentz oscillators. A detailed discussion of Eq. (3) and numerical methods for evaluating W_C are given by Lucas.[31]

III. VAN DER WAALS ENERGY OF SUBSTITUTIONAL IMPURITY

The effects of a substitutional impurity can be treated in the context of the Lorentz-oscillator model by adding

$$H' = \tfrac{1}{2}m(\omega_I^2 - \omega_0^2)q_I^2 \tag{6}$$

to H_0 of (1), corresponding to a change in polarizability of the Ith oscillator. Rayleigh's theorems[37] then imply that the resultant change in each of the $3N$ eigenfrequencies is either zero or of the same sign as $\omega_I^2 - \omega_0^2$, and that no more than three eigenfrequencies are shifted out of their band. Besides changing the ground-state energy by modifying the $\omega_s(\vec{k})$ in (3a), H' changes the energy of the corresponding system of noninteracting oscillators by $\frac{3}{2}\hbar(\omega_I - \omega_0)$. The change in van der Waals energy of the system is then

$$\Delta W_z = \Delta W - \tfrac{3}{2}\hbar(\omega_I - \omega_0) ,$$

where ΔW is the value of (3a) calculated with the perturbed $\omega_s(\vec{k})$; the sum of W_C/N for the perfect lattice and ΔW_z is then the van der Waals interaction energy of the impurity with the host crystal.

To calculate ΔW, let $\mathfrak{M}_0(\omega)$ be the $3N\times 3N$ matrix with components

$$\mathfrak{M}_0(\omega)_{ij}^{\mu\nu} = (\omega_0^2 - \omega^2)\delta_{ij}\delta_{\mu\nu} + (e^2/m)T_{ij}^{\mu\nu}$$

$$= \mathfrak{D}_{ij}^{\mu\nu} - \omega^2\delta_{ij}\delta_{\mu\nu} ,$$

and let $\mathfrak{M}(\omega) = \mathfrak{M}_0(\omega) + \Delta\mathfrak{M}$ be the corresponding matrix for the perturbed system, so that

$$\Delta\mathfrak{M}_{ij}^{\mu\nu} = (\omega_I^2 - \omega_0^2)\delta_{ij}\delta_{\mu\nu}\delta_{Ii} .$$

Then the secular equation determining the eigenfrequencies is

$$\det\mathfrak{M}(\omega) = \det\mathfrak{M}_0(\omega)\cdot\det\Delta(\omega) = 0 , \tag{7}$$

with

$$\Delta(\omega) = \underline{1} + \mathfrak{M}_0^{-1}(\omega)\cdot\Delta\mathfrak{M} . \tag{8}$$

Now for a function $f(z)$ that is regular on and within a closed contour C in the complex plane, is nonzero on C, and has zeros $z_1, z_2, \ldots, z_k$ of order $m_1, m_2, \ldots, m_k$, respectively, within C,[38]

$$\sum_{i=1}^{k} m_1 z_i = \frac{1}{2\pi i}\oint_C z\frac{1}{f(z)}\frac{df(z)}{dz}\,dz .$$

Then from (7) and (8),

$$\Delta W = \tfrac{1}{2}\hbar\left\{\sum[\textit{positive zeros of } \mathfrak{M}(\omega)] - \sum[\textit{positive zeros of } \mathfrak{M}_0(\omega)]\right\}$$

$$= \frac{\hbar}{4\pi i}\oint_C z\,d[\ln\det\Delta(z)] ,$$

where C enclosed all the positive eigenfrequencies of the system and no others. When C is taken to consist of the imaginary axis from iR to $-iR$ and the semicircle of radius R in the right half-plane, in the limit $R\to\infty$,

$$\Delta W = -(\hbar/4\pi)\int_{\omega=-\infty}^{\infty}\omega\, d[\ln\det\Delta(i\omega)]$$

$$= (\hbar/2\pi)\int_0^{\infty}\ln[\det\Delta(i\omega)]d\omega . \tag{9}$$

The function $\ln[\det\Delta(i\omega)]$ is readily evaluated. Noting from (8) that

$$\Delta(\omega)_{ij}^{\mu\nu} = \delta_{ij}\delta_{\mu\nu} + \frac{\omega_I^2 - \omega_0^2}{\omega_0^2 - \omega^2}[(\underline{1} + \alpha(\omega)\mathcal{T})^{-1}]_{iI}^{\mu\nu}\delta_{Ij} ,$$

with $\alpha(\omega) = e^2/m(\omega_0^2 - \omega^2)$ and $\underline{1}_{ij}^{\mu\nu} \equiv \delta_{ij}\delta_{\mu\nu}$, it is seen that, except for the 3×3 submatrix $\Delta(\omega)_{II}^{\mu\nu}$, $\Delta(\omega)$ is reducible to a unit matrix by adding appropriate multiples of its columns, and therefore

$$\ln\det\Delta(i\omega) = \ln\det\left[\underline{1} + \frac{\omega_I^2 - \omega_0^2}{\omega_0^2 + \omega^2}(\underline{1} + \alpha(i\omega)\mathcal{T})^{-1}\right]_I , \tag{10}$$

where $[\cdots]_I$ denotes the 3×3 matrix $[\cdots]_{II}^{\mu\nu}$. Since by cubic symmetry $[\mathcal{T}^n]_I$ is a multiple of the unit matrix, expansion of (10) gives, for ΔW of (9),

$$\Delta W = \frac{3}{2}\hbar\frac{1}{\pi}\int_0^{\infty}\ln\left\{1 + \frac{\omega_I^2 - \omega_0^2}{\omega^2 + \omega_0^2} \times[1 + \alpha(i\omega)^2(\mathcal{T}^2)_{II}^{11} - \alpha(i\omega)^3(\mathcal{T}^3)_{II}^{11} + \cdots]\right\}d\omega . \tag{11}$$

To evaluate ΔW_z, note that when α_0 is small enough for the $\alpha_0^n\mathcal{T}^n$ terms to be neglected, (11) has the value $\frac{3}{2}\hbar(\omega_I - \omega_0)$, so subtracting

$$\frac{3}{2}\hbar\frac{1}{\pi}\int_0^{\infty}\ln\left\{1 + \frac{\omega_I^2 - \omega_0^2}{\omega^2 + \omega_0^2}\right\}d\omega$$

from (11), we find

$$\Delta W_z = \frac{3}{2}\hbar\frac{1}{\pi}\int_0^{\infty}\ln\left\{1 + \frac{\omega_I^2 - \omega_0^2}{\omega^2 + \omega_I^2}[\alpha(\omega)^2(\mathcal{T}^2)_{II}^{11} - \cdots\ ]\right\}d\omega. \tag{12}$$

The sum of ΔW_z and W_C/N calculated from (3) is then the desired van der Waals interaction energy of the impurity with the lattice.

The quantities $[\mathcal{T}^n]_{II}^{1,1}$ in (12) are related to $\epsilon_s(k)$ by

$$[\mathcal{T}^n]_{II}^{1,1} = \left[\sum_{s=1}^{3}\sum_{\vec{k}\in B}\vec{\mathrm{T}}(\vec{k})^n e^{i\vec{k}\cdot(\vec{R}_I - \vec{R}_I)}\right]^{1,1} = \frac{1}{3}\sum_{s=1}^{3}\sum_{\vec{k}\in B}\epsilon_s(\vec{k})^n . \tag{13}$$

The $\epsilon_s(\vec{k})$ for any $\vec{k}$ are, in turn, readily computed using the summation formula given by Lucas[31] for $\overleftrightarrow{T}(\vec{k})$.

IV. VACANCY FORMATION ENERGY

In the context of the Lorentz oscillator model, the van der Waals energy to remove an atom from the lattice is the difference ΔW_z in van der Waals energy of the system with $\alpha_I = \alpha_0$ and with $\alpha_I = 0$. Since this involves letting $\omega_I \rightarrow \infty$, the changes produced in both the ΔW and $\frac{3}{2}\hbar(\omega_I - \omega_0)$ contributions to ΔW_z are infinite, the divergence in ΔW being associated with the three localized mode frequencies split off from the band. In the limit $\omega_I \rightarrow \infty$, the van der Waals removal energy is found from (12) to be

$$\Delta W_R = \tfrac{3}{2}\hbar\omega_0 I_R$$

with

$$I_R = \frac{1}{\pi}\int_0^\infty \ln\left[1 + \sum_{k=2}^{\infty} \frac{(-\alpha_0)^k}{(1+\xi^2)^k}\,(\mathcal{T}^k)^{1,1}_{II}\right] d\xi \;. \tag{14}$$

The $\alpha_0^n(\omega)\mathcal{T}^n$ terms are each rather small ($\lesssim 0.1$), and expanding the logarithm to first order in the $\mathcal{T}^k$ sum,

$$\Delta W_R \approx \tfrac{1}{2}\hbar\omega_0 \sum_{n=2}^{\infty} n \frac{(2n)!(-\alpha_0)^n}{(2n-1)(n!)^2 2^{2n}} \frac{\mathrm{Tr}(\mathcal{T}^n)}{N} \equiv \tfrac{3}{2}\hbar\omega_0 I_N \;. \tag{15}$$

By comparison of (15) with (3c), the nth-order contribution to ΔW_{R} is seen in this approximation to be n times the nth-order contribution to $-W_C$. It can be shown that whenever the cohesive energy is given by some n-body additive interaction[19] summed over all distinct sets of n atoms and over all n, then the n-body contribution to the removal energy is $-n$ times its contribution to cohesive energy, so that (15) also obtains in the approximation of identifying the nth-order contribution to (3b) with the n-body contribution.

The vacancy formation energy E_V for a rare-gas crystal can be treated in terms of the following sequence of operations:

(a) Add an extra atom to the surface without changing the cohesive energy per atom. The energy change is $\Delta E_1 = -W/N$, with W/N (<0) the cohesive energy per atom.

(b) Remove an atom from the bulk of the crystal, with energy change ΔE_2.

Then apart from lattice relaxation and vibrational energy changes, $E_V = \Delta E_1 + \Delta E_2$. Assuming the interaction energy to be given in terms of a (12;6) pairwise interatomic model potential plus the nonpairwise part of the W_C from (3a), we find

$$\Delta E_1 = \frac{1}{2N}\sum_{i,j}{}' \left(\frac{A}{R_{ij}^{12}} - \frac{B}{R_{ij}^{6}} + \frac{C_2}{R_{ij}^{6}}\right) + \tfrac{3}{2}\hbar\omega_0 I_C \;,$$

where $W_C = \frac{3}{2}\hbar\omega_0 I_C$. Similarly,

$$\Delta E_2 = -\sum_{j}{}' \left(\frac{A}{R_{j}^{12}} - \frac{B}{R_{j}^{6}} + \frac{C_2}{R_{j}^{6}}\right) + \tfrac{3}{2}\hbar\omega_0 I_R \;,$$

so that

$$E_V = -W/N + (8C_3/3\alpha_0^3)(2I_C + I_{\mathrm{R}}) \;, \tag{16}$$

using $16C_3/9\alpha_0^3$ for the multiplicative $\hbar\omega_0$. In the case where only two-body interactions are considered in evaluating I_C and I_R [cf. Eqs. (4) and (15)], E_V in (16) reduces to $-W/N$ and the removal energy ΔE_2 (or W_R) to -2 times the cohesive energy per atom W/N (W_C/N).

V. CALCULATION

To evaluate $\Delta E_1 + \Delta E_2$, the $\overleftrightarrow{T}(\vec{k})$ were calculated using Lucas's summation formula[31] on a uniform mesh of increment $\delta k = 0.05\,(2\pi/a_0)$ (with a_0 the lattice constant) in $\frac{1}{48}$ of the Brillouin zone to which the remaining points in the zone are related by cubic symmetry. The $\epsilon_s(\vec{k})$ were then determined from the $\overleftrightarrow{T}(\vec{k})$ and a three-dimensional Simpson's rule integration used to evaluate I_C in (3b) and the $[\mathcal{T}^n]^{1,1}_{II}$ in (13) for $n = 1, 11$. Using these latter coefficients, I_R in (14) and I_N in (15) were evaluated by numerical integration, and these results were in turn used to calculate $\Delta E_1 + \Delta E_2$ of (16). In these calculations α_0 was chosen as the free atomic polarizability and the multiplicative constant $3\hbar\omega_0/2$ ($= 8C_3/3\alpha_0^3$) was then chosen to give a C_3 in agreement with that calculated[39] from observed and estimated oscillator strengths. Such a choice of parameters also reproduces the C_2 calculated[39] from observed and estimated oscillator strengths to within 10%. The energy $-W/N$ was taken as the latent heat of sublimation per atom.

VI. RESULTS AND CONCLUSIONS

Some of the results are summarized in Table I. It is seen that I_N gives rather good agreement with I_R and that, while higher-order contributions do fall off slowly, the effects on I_R of keeping terms

TABLE I. Van der Waals contribution to the energy of removing an atom from the lattice. Values of I_R calculated by retaining powers of up to the nth are listed for various n. Also listed are the two-body value I_2, and I_N obtained by the approximate evaluation of I_R discussed in the text.

	n	Argon	Krypton	Xenon
I_R	2	0.006 867 5	0.010 829	0.017 907
I_R	3	0.006 238 8	0.009 587	0.015 281
I_R	4	0.006 473 5	0.010 171	0.016 873
I_R	5	0.006 425 5	0.010 021	0.016 345
I_R	6	0.006 440 0	0.010 078	0.016 604
I_R	11	0.006 437 0	0.010 064	0.016 493
I_2		0.006 928 3	0.010 979	0.018 316
I_N	11	0.006 488 1	0.010 189	0.016 866

TABLE II. Calculated vacancy formation energies. L_0 is the latent heat of sublimation and $E_V = \Delta E_1 + \Delta E_2$ is the vacancy formation energy calculated without relaxation or vibrational contributions.

	L_0 (cal/mole)	E_V (cal/mole)	$(E_V - L_0)/L_0$
Ar	1850[a]	1742	−0.06
Kr	2666[a]	2509	−0.06
Xe	3830[a]	3506	−0.08

[a] G. K. Horton and J. W. Leech, Proc. Phys. Soc. (London) 82, 816 (1963).

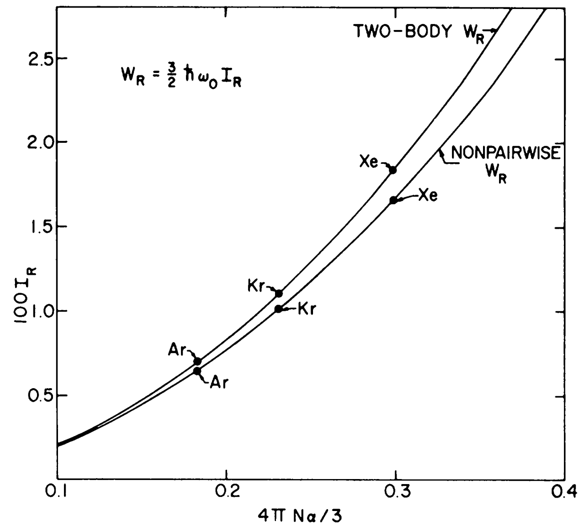

FIG. 1. Removal energies in units of $3\hbar\omega_0/2$. Shown as functions of $4\pi N\alpha_0/3$ are W_R calculated for nonpairwise interactions only and W_R calculated for all orders of interaction.

beyond T^4 are too small to be significant. It is also seen from Fig. 1 that the total nonpairwise contribution to I_R increases rapidly from argon to xenon, but even in xenon it accounts for no more than a 10% reduction from the I_R that includes only two-body van der Waals interactions. The effects of nonpairwise interactions are further reduced in E_V(Table II) these values being only 6 to 8% lower than L_0.

These results may be compared with the data in Table III. In thermal equilibrium at temperature T, the fraction of vacant sites is $\exp(-g_V/kT)$, where k is the Boltzmann constant and g_V is the Gibbs free energy of vacancy formation given by $E_V - T\delta S + p\delta V$ with δS the entropy of vacancy formation and the work term $p\delta V \approx 0$. Although the g_V's based on observed vacancy concentrations show significant disagreement with each other, they are all significantly lower and are associated with much higher thermal vacancy concentrations than two-body calculated values. The observed reductions from two-body calculated values are

TABLE III. Vacancy formation free energies and vacancy concentrations in rare-gas solids. The values given by Glyde and Venables and by Cotterill and Doyama are based on two-body potentials; all others are experimental.

	Source	g_V (cal/mole)	T (°K)	$g_V(T)$ (cal/mole)	Mole fraction vacancies
Argon	Smith and Chapman[a]	≥1100	81.7 83.8		≤0.0012 ≤0.0013
	van Witzenburg[b]		83.3		0.0037
	Beaumont *et al.*[c]	1280−3.4 RT	83.8	713.8	0.0138
	Foreman and Lidiard[d]			747.4	0.011
	Glyde and Venables[e]	2100−3.21 RT	80.0 83.8	1591 1567	0.00004 0.00008
Krypton	Losee and Simmons[f]	1780 ± 200 − 2 RT	115	1323 ± 200	0.0031
	Beaumont *et al.*[c]	1770−3.4 RT	115	993	0.013
	Cotterill and Doyama[g]	$E_V = 2630$			

[a] B. L. Smith and J. A. Chapman, Phil. Mag. 15, 739 (1967).

[b] W. van Witzenburg, Phys. Letters 25A, 293 (1967).

[c] R. H. Beaumont, H. Chihara, and J. A. Morrison, Proc. Phys. Soc. (London) 78, 1462 (1961).

[d] A. J. E. Foreman and A. B. Lidiard, Phil. Mag. 8, 97 (1963).

[e] See Ref. 6.

[f] D. L. Losee and R. O. Simmons, Phys. Rev. 172, 934 (1968).

[g] See Ref. 4.

much larger than would result in the present calculation through nonpairwise effects on E_V. We therefore conclude that within the context of the model used in estimating the effects of nonpairwise van der Waals interactions on the vacancy formation energy, these effects reduce the vacancy formation energy, but insufficiently to give satisfactory agreement between theory and experiment.

The remaining discrepancies might involve other effects than those treated here, such as polarization of the atoms around a vacancy[40] or nonpairwise interactions associated with overlap and exchange.[9] It should also be kept in mind that although the overlaps between nearest-neighbor rare-gas atoms in the solid are small, the atomic excited states that are mixed with the ground state by the dipole-dipole couplings actually involve rather large overlaps (~ 0.5 for nearest-neighbor $4p$ wave functions in Ar) and the collective excited states of the solid can be treated quantitatively in terms of a Frenkel exciton model only with difficulty.[41] Such considerations are not properly included in this and other calculations that treat the van der Waals interactions in rare-gas solids as those involving well-separated atoms.

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