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INTERACTIONS BETWEEN MOLECULES ADSORBED ON A SURFACE

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August 1959

ABSTRACT

The intermolecular potential energy between two inert gas molecules is considerably altered when these molecules are next to a solid surface as in physical adsorption. The change in the interaction is evidenced by the additional long range repulsion that is often observed between the molecules of a monolayer and also by the additional attractions that must play a role in multilayer formation.

In this article, the "two molecule-surface potential" is derived from quantum mechanical third order perturbation theory. It is shown that this potential consists of two parts just as the energy giving the van der Waals attraction of a single molecule to a surface does. The first part exists only when the surface has a net electrostatic field and this is equivalent to the classical polarization effect. The second part arises from the fluctuations of the surface fields and is of the same origin as the "dispersion" forces. The third order energy, i.e., the new intermolecular interaction caused by the surface, is directly related to the zero-coverage heat of adsorption and except for this experimental quantity, the results do not require specific assumptions about the surface. Thus, the theory is applicable to either metal or insulator surfaces. When both the two molecule-surface and the one

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molecule-surface interactions are available experimentally (for example, from the application of virial coefficients treatment in physical adsorption) the electrostatic field of the surface can be estimated.

The "fluctuation" or "dispersion" part of the third order energy is shown to yield a repulsion between two molecules in a "monolayer" that amounts to 20 - 40% of the gas phase Lennard - Jones potential minimum, ϵ_0 . The same energy yields an additional attraction of about 10 - 20% of ϵ_0 when the two molecules are on top of one another as in multilayer formation. The theory is applicable also when more than two molecules at a time need be considered on the surface.

INTERACTIONS BETWEEN MOLECULES ADSORBED ON A SURFACE

A) Introduction

Physical adsorption is characterized by relatively weak forces as compared to chemisorption and it might be considered a process in which both the adsorbed molecules and the adsorbent surface remain quite unchanged. Thus the Van der Waals forces that cause physical adsorption can be understood for the most part through the use of quantum mechanical perturbation theory. The theory of these forces between molecules has been reviewed by Margenau¹ and some recent

¹H. Margenau, Revs. Mod. Phys., 11, 1 (1939).

considerations by Pitzer.² Extensive reviews on the forces that

²K. S. Pitzer, "Advances in Chemical Physics," Vol. II, Interscience Publs., N. Y., (1959); or see K. S. Pitzer, UCRL-8395 (Sept., 1958).

cause physical adsorption also exist.^{3,4}

³J. H. de Boer, Advances in Catalysis, VIII, 29 (1956).

⁴S. Brunauer, "The Adsorption of Gases and Vapors," Princeton University Press, Princeton (1945); p. 180.

Some interesting phenomena such as the formation of monolayers and multilayers on an adsorbent involve the forces between adsorbed molecules themselves as well as with the surface. Such forces can be investigated through the application of statistical mechanics to experimental measurements especially in physical adsorption, and although this is difficult when the adsorbate is dense, it becomes particularly suitable in the dilute case, i.e. relatively high temperature adsorption making use of a theory similar to the virial coefficients treatment of imperfect gases.⁵ By such a method it

⁵a) W. A. Steele and G. D. Halsey, Jr., J. Chem. Phys., 22, 979 (1954); see also, b) M. P. Freeman, J. Phys. Chem., 62, 729 (1958).

is possible to investigate the adsorption of essentially one molecule, two molecules, etc. at a time on a surface and the potential energies of interaction involved in each case.⁵

Such experimental evidence has long shown^{3,5b} that two inert gas atoms adsorbed into a monolayer display a rather different potential energy between themselves as compared to their energy when they are in the gas phase, i.e. the presence of the surface apparently causes a new long range repulsion to appear between the two molecules of the monolayer and this repulsion tends to counter-balance their usual London attraction. On the other hand, in multilayer formation additional attractions must exist. These

observations are not explainable in terms of second order perturbation theory of long range forces. This theory predicts that the total interaction between a system of adsorbed molecules and the surface must be "pairwise additive;" hence the interaction between molecules would be unaltered.¹ The repulsion in the monolayer has usually been ascribed³ to the dipoles permanently induced in the non-polar molecules by an electrostatic field that is known to be present on metal⁶ and charcoal³

⁶J. C. P. Mignolet, Rec. Trav. Chim., 74, 701 (1955).

surfaces. The magnitude of these induced dipoles can be inferred³ from the non-ideal behavior of the adsorbed two-dimensional gas if the entire additional repulsion in the presence of the surface is attributed to this classical electrostatic effect. However the values so obtained usually seem to be too high in comparison to the estimates from measured contact potentials⁶ and work function lowering.⁷

⁷G. Ehrlich and F. G. Hudda, J. Chem. Phys., 30, 493 (1959).

It is apparent that part of the "many-body" repulsion must be caused by a mechanism other than ordinary electrostatic polarization.

Many-body forces between spherical, inert molecules have been investigated quite extensively. When overlap effects are negligible these forces arise for the most part from the "triple-dipole" interaction in third order perturbation theory. These "three-body" forces have been reviewed extensively, along with their application

to the third virial coefficient of an imperfect gas, by Kihara.⁸

⁸T. Kihara, "Advances in Chemical Physics," Vol. I, Interscience
 Publs., N. Y. (1958); p. 267; "Triple-dipole" energy was first
 discussed by B. M. Axilrod and E. Teller, J. Chem. Phys., 11, 299
 (1943); Axilrod, Ibid., 19, 719 (1951).

A recent discussion with reference to colloidal particles has been
 given by Sparnaay.⁹ Although the three-body force between three

⁹M. J. Sparnaay, Physica, 25, 217 (1959).

molecules is quite small, it is to be expected that forces of
 similar origin should become appreciable, as compared to the
 interaction between two molecules, when the third body is a large
 surface.

If the two molecules overlap, then even in second order
 perturbation appreciable many-body forces should arise as shown
 by Jansen and McGinnies¹⁰ for three atoms. However, we shall

¹⁰L. Jansen, R. T. McGinnies, Phys. Rev., 104, 961 (1956).

assume that this effect is part of the change that must take
 place in the short-range repulsive region of the intermolecular

potential and concern ourselves with non-overlap, long range interactions.

Higher order perturbations have been studied by Bade¹¹ using

¹¹W. L. Bade, J. Chem. Phys., 27, 1280, 1284 (1957); 28, 282 (1958).

the simple Drude or harmonic oscillator model. It is found that for a system of a few molecules the perturbation series converges quite rapidly and more will be said about convergence in Section C.

In the following we shall give a general derivation of some forces that arise between spherical (hence non-polar) molecules in the presence of a semi-infinite solid "surface" (metal or insulator) based on a third order perturbation treatment. Since in this order the energy is "triple-wise" additive¹¹ (see end of Section C) it will be necessary to consider only the system of two molecules and the surface. We shall show that, just as in the case of Van der Waals' energy between one molecule and the surface,³ the energy of two molecules and the surface is composed of an "electrostatic" part and a quantum-mechanical "fluctuation" or "dispersion" part. Moreover, it will be found that each part of the "three-body" energy can be related directly to the corresponding part of the one molecule adsorption energy. Thus it is often possible to obtain the potential energy of interaction between two molecules, physically adsorbed on a surface, in terms of the experimental

zero-coverage heat of adsorption, $\underline{U}_0$. On the other hand the present treatment enables one to estimate the "electrostatic" fraction of $\underline{U}_0$, when both $\underline{U}_0$ and the "surface intermolecular potential" are available experimentally. The intimate connection between these two energies makes it necessary to discuss first the van der Waals energy of a single molecule on a surface with comments on the application of some of the existing theories before going into the derivation of the "two molecule-surface" potential.

B) Second Order Energy

Let us consider the most general derivation of the van der Waals attraction energy between a spherical, non-polar molecule such as a rare gas atom and any solid which extends from minus to plus infinity in the x and y directions, defining the surface plane, and is semi-infinite in the perpendicular z direction. We shall use straightforward perturbation theory. If the adsorbed molecule is not too large, the perturbation can be written as

$$J = -\mu_1 \cdot F_1 \quad (1)$$

where μ_1 is the instantaneous dipole moment of the molecule and F_1 is the instantaneous electric field produced by all the electrons and nuclei of the solid at the center of molecule, 1 . The unperturbed Hamiltonian is simply:

$$H^0 = H_1 + H_s \quad (2)$$

i.e. sum of the parts describing the molecule and the surface separately.

Where overlap is negligible, the system will be represented by

$$\psi^0 = \psi_1^0 \psi_s^0, \quad (3)$$

i.e. the product of unperturbed wave functions for the molecule and the surface. When (1) is applied as the perturbing potential on (2) and (3), the first order energy vanishes. But the second order energy becomes

$$E_{1s}^{(2)} = \sum_{(\rho, \tau) \neq 0} \frac{|\langle \infty | \mu_1 \cdot \vec{F}_1 | \rho \tau \rangle|^2}{\delta_{\rho\rho} + \delta_{\tau\tau}} \quad (4)$$

where ρ , τ refer to the various unperturbed energy states of the molecule and the "surface" (meaning the semi-infinite solid) respectively, and δ 's denote the excitation energies to these various states. Now, if we assume that the δ 's can be replaced by some "mean excitation energies" and use the relations

$$\sum_{\rho=0}^{\infty} |\langle 0 | \mu_1 | \rho \rangle|^2 = \langle 0 | |\mu_1|^2 | 0 \rangle = \langle |\mu_1|^2 \rangle_{\infty} \quad (5)$$

$$\text{and } \alpha_1 = \alpha_1^{\text{ext}} \approx 2 \frac{\langle \mu_{1x}^2 \rangle_{\infty}}{\delta_1} \quad (6)$$

for a spherical molecule, Eq. (4) becomes

$$E_{1s}^{(2)} \approx - \frac{\alpha_1}{2} |\langle 0 | \vec{F}_1 | 0 \rangle|^2 - \frac{\alpha_1}{2} \left(\frac{\delta_1}{\delta_1 + \delta_s} \right) \sum_{\tau \neq 0} |\langle 0 | \vec{F}_1 | \tau \rangle|^2 \quad (7)$$

The first term is simply the electrostatic polarization of the molecule due to a net field $\langle \vec{F}_1 \rangle_{\infty}$ over the surface. This field would be zero if the solid were uniform up to its surface, as is roughly the case for

an insulator. But on a metal it arises from an effective dipole layer¹² on the surface caused by electron leakage through the surface

¹²W. G. Pollard, Phys. Rev., 61, 740(A), (1942).

barrier.¹³ The second term corresponds to the usual "dispersion"

¹³K. Huang and G. Wyllie, Proc. Phys. Soc. (London), 62, 180 (1949).

type of force. The physical meaning of this force becomes clearer if we write

$$\begin{aligned} \left\langle |F_{\sim 1}|^2 \right\rangle_{\tau} &= \sum_{\tau=0}^{\infty} \left| \left\langle \circ | F_{\sim 1} | \tau \right\rangle \right|^2 = \left\langle |F_{\sim 1}|^2 \right\rangle_{\infty} - \left| \left\langle F_{\sim 1} \right\rangle_{\infty} \right|^2 \\ &= \left\langle \left| F_{\sim 1} - \left\langle F_{\sim 1} \right\rangle_{\infty} \right|^2 \right\rangle_{\infty} \quad (8) \end{aligned}$$

Thus the second term of Eq. (7) may be looked upon as arising from the additional polarization of the molecule due to the non-vanishing of the mean square of the fluctuations of the "surface" electric field about its average value. And of course, when the thermal motion of the nuclei in the solid is negligible, these fluctuations are due primarily to the quantum motion of the electrons. In fact, Eq. (8) can be written¹⁴ in terms of first and second order density matrices

¹⁴J. Bardeen, Phys. Rev., 58, 727 (1940).

for the electrons after making the Born-Oppenheimer approximation, in a form most useful when the solid is a metal. However we must be cautious with this interpretation of the second term of Eq. (7) due to the presence of the factor $(\delta_1/(\delta_1 + \delta_s))$. If for a metal the free electron model is adopted and δ_s assumed negligible compared to δ_1 , as was done by Prosen and Sachs,¹⁵ this factor is unity making

¹⁵E. J. R. Prosen and R. G. Sachs, Phys. Rev., **61**, 70 (1942).

the above interpretation correct, i.e. only the molecule is polarized. However, the presence of a quite large δ_s as in insulators and real metals, in effect accounts for the polarization of the "surface" in turn by the molecule.

Now, all the formulas^{3,4} that are used for either insulators or metals can be shown to follow directly or indirectly from the general expression Eq. (7). When the "surface" is an insulator, Eq. (8) can be evaluated by summing (or integrating) the contributions from each molecule or section that makes up the solid considering these as fluctuating dipoles. Then the over-all van der Waals attraction can be obtained directly from one of the formulas¹⁻⁴ which give the intermolecular dispersion energy (such as London's, Kirkwood-Miller's, etc.) using empirical quantities such as polarizabilities and diamagnetic susceptibilities. Although a metal should be treated in terms of metallic electrons and it seems at first thought that it could not be divided into sections, the consideration of electron

correlation¹⁴ has been shown to lead to essentially the same result as though the metal behaved as an insulator made up of sections of oscillating dipoles.¹⁶ With these considerations in mind, an estimate

¹⁶H. Margenau and W. G. Pollard, Phys. Rev., 60, 128 (1941).

of the total potential between one molecule and the surface (and the heat of adsorption) can be obtained by assuming the usual Lennard-Jones [12-6] potential, frequently used in imperfect gas theory,¹⁷ to

¹⁷See for example:

Hirschfelder, Curtiss and Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York (1954).

hold between a portion of the solid and the molecule and integrating.¹⁸

¹⁸T. L. Hill, J. Phys. Chem., 63, 456 (1959).

The result which we shall need later is

$$U(R) = \frac{3}{2\sqrt{5}} U_0 \left[\left(\frac{r_0}{R} \right)^3 - \frac{1}{15} \left(\frac{r_0}{R} \right)^9 \right] , \quad (9)$$

$$U_0 = - \frac{2\sqrt{5}}{9} \pi n \epsilon_0 r_0^3 ,$$

with R the distance from the molecule to the surface and ϵ_0 , r_0 the parameters of the Lennard-Jones [12-6] potential.¹⁷ Notice that at the minimum, R_0 , the attractive portion of energy is simply 1.5 times U_0 ,

the heat of adsorption at zero coverage.

The magnitude of the van der Waals attraction between a molecule and a surface can be estimated by the use of the "non-metallic" or metallic type formulas some of which we have cited above. (These formulas will be mentioned here only by name; the reader is referred to the general references given for details.) Such estimates are usually found to yield values for the heats of adsorption,^{4,19}

¹⁹R. A. Pierotti and G. D. Halsey, Jr., J. Phys. Chem., 63, 680 (1959).

however, which are too low. A similar situation has existed in the comparison of observed and calculated van der Waals attractions between two molecules.²⁰ Recently, however, in connection with London forces

²⁰K. S. Pitzer, "Quantum Chemistry," Prentice Hall, N. Y., (1954); p. 339.

it has been shown^{2,21} that the trouble often lies in the δ 's, the

²¹W. E. Donath, University of California, Ph. D. thesis (1958) and UCRL-8385 (July 21, 1958).

"mean excitations energies." These also occur in Eq. (7) and in most of the specific formulas mentioned above. In adsorption as well as

in intermolecular dispersion energies the δ 's are usually assumed to be approximately equal to the ionization potentials, I . Recent considerations show^{2,20,21} that in more than two electron atoms electron correlation raises the δ by a factor of about 2.1 higher than I . It must be pointed out here that the use of this proper δ (for the molecules and possibly for the solid) will bring the "insulator-type" adsorption energy formulas such as London's into quite good agreement with experiment. Slater-Kirkwood formula^{2,19} involves N , the number of electrons in the outer shell of molecules, instead of δ ; here N should be regarded as an empirical parameter and "effective" values used.² Kirkwood-Müller formula^{2,4,19} does not contain any of these "parameters" and although it is strictly valid for spherical systems,² it is still quite successful in adsorption.¹⁹ In the rest of this article, we shall use the appropriate molecular δ 's (2.1 I) instead of I wherever they occur.

The formulas derived from Eq. (7) and Eq. (8) strictly for metals^{14,16} also predict heats which are too small.¹⁹ Here the increase in δ_1 has a smaller effect on $E_{1s}^{(2)}$. However, it should be recalled that the δ 's appearing as the main feature in both Bardeen's¹⁴ and Margenau and Pollard's¹⁶ formulas were derived¹⁴ for monovalent metals neglecting the effect of the periodic potential of the lattice and the effect of the polarizability of the ion cores. Thus, such formulas should not be applied to, for instance, transition metals that have incomplete d -shells and might show very large "inner core" effects.

The low values predicted for the heats of adsorption by the theories above, in the way that they are often applied, have induced discussion⁶ of another type of force, i.e. the "charge-transfer"²² force as contributing to van der Waals adsorption on

²²R. S. Mulliken, J. Am. Chem. Soc., 74, 811 (1952).

metals. However, in view of the lack of a sufficiently quantitative treatment of these forces in adsorption and considering the preceding discussion, we shall assume that van der Waals attraction of non-polar molecules to metals as well as to insulators is given primarily by $E_{is}^{(2)}$ of Eq. (7).

C) The Third Order Energy

Now, if instead of a single molecule on the "surface" several molecules are considered, no new effects arise in the non-overlap second order perturbation. The potential energy of the system is simply the sum of London attractions¹ between molecules and their individual van der Waals attractions to the surface as given by Eq. (7). To see the effect of the surface on the long range interaction between molecules we must turn to the third order term of the perturbation series. If, as we had done for the second order term in Eq. (1), we consider the adsorbed molecules to be quite small, and after expanding the instantaneous potential of the molecules in multipole series in the usual fashion,¹ take only the leading dipole terms, the interaction operator between two molecules and the surface becomes

$$J = - \mu_1 \cdot F_1 - \mu_2 \cdot F_2 + \mu_1 \cdot T_{12} \cdot \mu_2 \quad (10)$$

where again F_1 and F_2 are the instantaneous electric fields produced at the centers of the molecules 1 and 2 respectively, by a given distribution of all the electrons and nuclei that make up the solid. μ 's are the instantaneous dipole moments of the molecules (here we always mean inert gas atoms or other small quasi-spherical molecules) given by $e \sum_i \vec{r}_i$, i.e. summing the radius vectors of all the electrons of a given atom. The last term of Eq. (10) is the dipole-dipole operator for the interaction between two molecules with the tensor, T_{12} , given by

$$\underline{\hat{r}}_{12} = (\underline{\hat{I}} - 3 \underline{\hat{r}}_{12} \underline{\hat{r}}_{12}) / r_{12}^3 \quad ; \quad (11)$$

$\underline{\hat{r}}_{12}$ is the unit vector along $\underline{r}_{12}$, the distance between the two molecules as shown in Fig. 1.

With the $\underline{J}$ of Eqs. (10) or (1) the third order energy becomes:²³

²³In general $\underline{E}^{(3)}$ will have an additional term which is different in different perturbation theories (see: Morse and Feshbach, "Methods of Theoretical Physics," Vol. II, McGraw Hill Co., N. Y.; (1953)); however this term vanishes in our case because of the dipole selection rules.

$$E^{(3)} = \sum_{n \neq 0} \sum_{m \neq n, 0} \frac{\langle 0 | \underline{J} | n \rangle \langle n | \underline{J} | m \rangle \langle m | \underline{J} | 0 \rangle}{(E_0 - E_n)(E_0 - E_m)} \quad (12)$$

This energy vanishes for one molecule and the surface, i.e. for $\underline{J}$ given by Eq. (1). If on the other hand, Eq. (10) is substituted into Eq. (12), each matrix element there, can be written as a sum of three terms and since the eigenstates of the system are taken in the product form as in Eq. (3) (with each factor forming an orthonormal set) a typical matrix element is of the form

$$\begin{aligned} \langle o | J | n \rangle = & - \langle oo | \mu_1 \cdot E_1 | \rho \tau \rangle \delta_{o\sigma} - \langle oo | \mu_2 \cdot E_2 | \sigma \tau \rangle \delta_{o\rho} \\ & + \left(\langle o | \mu_1 | \rho \rangle \cdot T_{12} \cdot \langle o | \mu_2 | \sigma \rangle \right) \delta_{o\tau} \quad (13) \end{aligned}$$

where again o , ρ , J label the various eigenstates of molecules 1 and 2 and the entire solid (including all the nuclei and electrons that make it up), respectively. (The $\delta_{o\sigma}$, etc. are Kronecker deltas only here and should not be confused with the excitation energies in Eq. (4), Eq. (5) and in the forthcoming equations.) Then, multiplying out such matrix elements in Eq. (12) and using the dipole selection rules for spherical molecules,²⁴ it can be seen that only certain combinations

²⁴Landau, Lifschitz, "Non-relativistic Quantum Mechanics," Addison-Wesley Publ. Co., Reading, Massachusetts (1958).

of transitions giving rise to such terms as

$$\sum_{\tau \neq o} \sum_{\sigma' \neq o} \frac{\langle \mu_1 \rangle_{o\rho} \cdot \langle E_1 \rangle_{o\tau} \langle \mu_2 \rangle_{o\sigma'} \cdot \langle E_2 \rangle_{\tau o} \langle \mu_1 \rangle_{\rho o} \cdot T_{12} \cdot \langle \mu_2 \rangle_{\sigma' o}}{\left[\delta_1(o\rho) + \delta_s(o\tau) \right] \left[\delta_1(o\rho) + \delta_2(o\sigma') \right]}, \quad (14)$$

with $\delta_1(o\rho) = E_1^o - E_1^\rho$ and similarly δ_s for the surface, contribute to the sum (Eq. (12)). The derivation follows along quite similar lines to that given by Kihara⁸ for three molecules. There are two types of terms designated by transitions such as

and

in which only the ground state of the solid is involved, and six types of terms corresponding to different double transitions in each matrix element, such as

The numerators of these six are all equivalent (Eq. (14)) but four of the denominators (of the form $(\delta_1 + \delta_2)(\delta_1 + \delta_s)$) are different from the other two (of the form $(\delta_1 + \delta_s)(\delta_2 + \delta_s)$). After using "mean excitation energies" and polarizabilities for the molecules (Eqs. (5) and (6)) as had been done for $E_{1s}^{(2)}$ previously, the result is:

$$E_{12s}^{(3)} = \frac{\alpha_1^2}{r_{12}^3} \left[\langle \tilde{F}_1 \rangle_{oo} \cdot \langle \tilde{F}_2 \rangle_{oo} - 3 \langle \tilde{F}_1 \rangle_{oo} \cdot \hat{\tilde{L}}_{12} \hat{\tilde{L}}_{12} \cdot \langle \tilde{F}_2 \rangle_{oo} \right] \quad (15a)$$

$$+ \frac{\alpha_1^2}{2r_{12}^3} \frac{(2\delta_1 + \delta_s) \delta_1}{(\delta_1 + \delta_s)^2} \sum_{\tau \neq 0} \left(\langle \tilde{F}_1 \rangle_{o\tau} \cdot \langle \tilde{F}_2 \rangle_{\tau o} - 3 \langle \tilde{F}_1 \cdot \hat{\tilde{L}}_{12} \rangle_{o\tau} \langle \hat{\tilde{L}}_{12} \cdot \tilde{F}_2 \rangle_{\tau o} \right)$$

$$\text{or} \quad E_{12s}^{(3)} \equiv E_{e.s.}^{(3)} + E_{fl.}^{(3)} \quad (15b)$$

where for convenience we have assumed molecules 1 and 2 to be identical.

In arriving at this result use has been made of relations of the type:

$$\sum_{p \neq 0} \langle \mu_1 \rangle_{op} \cdot \mathbf{T}' \cdot \langle \mu_1 \rangle_{po} = \sum_{p \neq 0} \langle \mu_1 \rangle_{op} \langle \mu_1 \rangle_{po} : \mathbf{T}' = \langle \mu_{1x} \rangle_{oo}^2 \mathbf{I} : \mathbf{T}' ;$$

$$\mathbf{T}' = \langle \mathbf{F}_1 \rangle \langle \mathbf{F}_2 \rangle + \mathbf{T}_{12} ; \quad (17)$$

$$\mathbf{I} : \mathbf{T}' = \text{Trace } \mathbf{T}' = \left(\langle \mathbf{F}_1 \rangle \cdot \langle \mathbf{F}_2 \rangle - 3 \langle \mathbf{F}_2 \cdot \hat{\ell}_{12} \times \mathbf{F}_1 \cdot \hat{\ell}_{12} \rangle \right) / r_{12}^3$$

and $\mathbf{r}$ in Eq. (15) still refers to an eigenstate of the semi-infinite solid as a whole.

The meaning of Eq. (15) is similar to that of Eq. (7) discussed previously. Again the first part, $E_{\text{e.s.}}^{(3)}$ (e.s. for electrostatic) exists only when the surface possesses a net average electrostatic field, $\langle \mathbf{F} \rangle_{oo}$, and within the approximation of Eq. (6), i.e. the substitution of atomic polarizability into Eq. (16), it is the same as the classical interaction between two permanently induced dipoles and already has been considered by de Boer.³ The second part $E_{\text{fl.}}^{(3)}$ involving the sum

$$\begin{aligned} \langle \mathbf{F}_1 \cdot \mathbf{F}_2 - 3 \mathbf{F}_1 \cdot \hat{\ell}_{12} \hat{\ell}_{12} \cdot \mathbf{F}_2 \rangle_{\mathbf{r}} &= \sum_{\tau \neq 0} \left(\langle \mathbf{F}_1 \rangle_{o\tau} \cdot \langle \mathbf{F}_2 \rangle_{\tau o} - \right. \\ &\quad \left. 3 \langle \mathbf{F}_1 \cdot \hat{\ell}_{12} \times \hat{\ell}_{12} \cdot \mathbf{F}_2 \rangle_{\tau o} \right) \quad (18) \end{aligned}$$

$$\begin{aligned} &= \left(\langle \mathbf{F}_1 \cdot \mathbf{F}_2 \rangle_{oo} - 3 \langle \mathbf{F}_1 \cdot \hat{\ell}_{12} \hat{\ell}_{12} \cdot \mathbf{F}_2 \rangle_{oo} \right) - \left(\langle \mathbf{F}_1 \rangle_{oo} \cdot \langle \mathbf{F}_2 \rangle_{oo} \right. \\ &\quad \left. - 3 \langle \mathbf{F}_1 \rangle_{oo} \cdot \hat{\ell}_{12} \hat{\ell}_{12} \cdot \langle \mathbf{F}_2 \rangle_{oo} \right) \end{aligned}$$

is again of the "dispersion" or "fluctuation" type. When δ_s is small, it represents the interaction resulting from the additional simultaneous polarization of the molecules by the in phase fluctuations of the "surface" fields at the points 1 and 2.

The "electrostatic" or average fields in Eq. (15) must be in the z-direction (see Fig. 1) whenever they exist, on account of the symmetry in the xy-plane, so that the electrostatic energy in Eq. (15a) is given by

$$E_{e.s.}^{(3)} = \frac{\alpha_1^2}{r_{12}^3} \left\langle F_1^z \right\rangle_{\infty} \left\langle F_2^z \right\rangle_{\infty} (1 - 3 \cos^2 \theta) \quad (19)$$

and similarly we have from Eq. (7)

$$E_{e.s.}^{(2)} = - \frac{\alpha_1}{2} \left\langle F_1^z \right\rangle_{\infty}^2 \quad (20)$$

When one of these energies is known the other is obtainable by the appropriate elimination of $\left\langle F^z \right\rangle_{\infty}$'s.³

On insulators Eq. (19) and (20) are usually unimportant³ and "fluctuation" energies constitute the primary effects. On metal and charcoal surfaces both e.s. and fl. energies must be taken into account. The discussion of $E^{(3)}$ and $E^{(2)}$ in relation to one another when e.s. terms are not negligible will be deferred until the end of this section, i.e. until after a detailed derivation of what we have called the "fluctuation" energy between adsorbed molecules, to which we now turn:

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Fig. 1. Coordinates used in the general derivation of $\underline{E}^{(3)}$.

The "fluctuation" parts of Eqs. (7) and (15a) are given by

$$E_{fl.}^{(2)} = - \frac{\alpha_1}{2} \frac{\delta_1}{\delta_1 + \delta_s} \left\langle | \underline{F}_1 |^2 \right\rangle_{\tau} \quad (21a)$$

$$\left\langle | \underline{F}_1 |^2 \right\rangle_{\tau} = \left\langle (F_1^z)^2 \right\rangle_{\tau} + 2 \left\langle (F_1^x)^2 \right\rangle_{\tau} \quad (21b)$$

and

$$E_{fl.}^{(3)} = \frac{\alpha_1^2}{r_{12}^3} \frac{\delta_1(2\delta_1 + \delta_s)}{2(\delta_1 + \delta_s)^2} \left(\left\langle \underline{F}_1 \cdot \underline{F}_2 \right\rangle_{\tau} - 3 \left\langle \underline{F}_1 \cdot \hat{\underline{l}}_{12} \hat{\underline{l}}_{12} \cdot \underline{F}_2 \right\rangle_{\tau} \right) \quad (22)$$

where the summations over the eigenstates of the solid not including the $\tau = 0$ ground state have been indicated by $\left\langle \right\rangle_{\tau}$. Eq. (21b) follows from the equivalence of the $\underline{x}$ and $\underline{y}$ coordinates over the "surface."

In terms of the coordinates shown in Fig. 1, Eq. (22) becomes

$$E_{fl.}^{(3)} = \frac{\alpha_1^2}{r_{12}^3} \frac{\delta_1(2\delta_1 + \delta_s)}{2(\delta_1 + \delta_s)^2} \left[\left\langle F_1^x F_2^x \right\rangle_{\tau} (1 - 3 \sin^2 \theta) + \left\langle F_1^y F_2^y \right\rangle_{\tau} + \left\langle F_1^z F_2^z \right\rangle_{\tau} (1 - 3 \cos^2 \theta) - 3 \sin \theta \cos \theta \left\langle F_1^x F_2^z + F_1^z F_2^x \right\rangle_{\tau} \right] \quad (23)$$

θ denoting the angle between $\hat{\underline{l}}_{12}$ and the normal to the surface. The coordinate axes have been so chosen that z is along the normal and the $\underline{x} \underline{z}$ - plane contains $\hat{\underline{l}}_{12}$ (Fig.1). Notice also that e.g. $\left\langle F_1^x F_2^z \right\rangle_{\tau}$ is identical with $\left\langle F_1^z F_2^x \right\rangle_{\tau}$ i.e. the expectation

value over the ground state of the solid, because $\langle F_1^x \rangle_{00}$ is zero. (See Eqs. (8) and (18)). Eq. (23) can be simplified considerably by noting that $\langle F_1^x F_2^z \rangle_{00}$ and $\langle F_1^z F_2^x \rangle_{00}$ vanish because F^x is an odd function in all the x-coordinates involved (i.e. all electrons and nuclei of the solid). In addition the matrix elements, $\langle F_1^x F_2^x \rangle_\tau, \dots$ can be replaced to a good approximation by the corresponding quantities $\langle F_1^x F_2^x \rangle_\tau, \dots$ (Fig. 1); i.e. the points 1 and 2 can be brought on top of one another along the normal to the surface passing through the mid-point m of r₁₂. This approximation can be partly justified in the following manner:

Since the states of the solid, $\psi_0, \psi_\tau, \dots$, form an orthonormal set, we have as in Eq. (18)

$$\langle F_1^z F_2^z \rangle_\tau = \sum_{\tau' \neq 0}^{\infty} \langle F_1^z \rangle_{0\tau'} \langle F_2^z \rangle_{\tau'0} \quad (24)$$

and similarly for x and y. Now because of translational symmetry the over-all eigenstates describing the solid must be of generalized Bloch function form; i.e.

$$\psi_\tau = e^{i \mathbf{k}_\tau \cdot \mathbf{R}} u_\tau(\mathbf{R}) \quad (25)$$

where R denotes the coordinates of all the electrons and nuclei, $\mathbf{k}_\tau$ is a generalized wave vector and u_τ a periodic function of R depending on the symmetry of the solid. Thus the matrix elements such as $\langle F_1^z \rangle_{0\tau}$ will be of the form:

$$\langle F_1^z \rangle_{0\tau} = \int e^{i \mathbf{k}'_\tau \cdot \mathbf{R}} F_1^z u_0^* u_\tau d\mathbf{R}. \quad (26)$$

F_1^2 is the sum of the instantaneous electric fields of all the electrons and nuclei in the solid, and these electrons and nuclei may be assumed to be quite uniformly distributed at all instances. This assumption allows us to consider F_1 as a nearly "periodic" operator in the sense that if all the electrons and nuclei were to be translated by a lattice constant in the x or y directions, it would remain quite unchanged. In this case, according to group theory, only those matrix elements (Eq. (26)) for which the $k'_y(x,y)$ equals zero would be nonvanishing.^{25,26} Even though this selection rule is not

²⁵N. F. Mott, H. Jones, "The Theory of the Properties of Metals and Alloys," Reprinted by Dover Publ. Inc., N. Y.; (1936); p. 59.

²⁶M. Tinkham, "Advanced Quantum Mechanics of Atoms, Molecules and Solids," A. S. U. C. Store, University of California, Berkeley (1958); p. 94.

rigorously applicable here because F_1 is not really a "periodic" operator, nevertheless it suggests that the greatest contribution to Eq. (24) will come from excitations for which the generalized wave vector $k(x,y)$ in the $x y$ plane is approximately unchanged. It is interesting to note that even when the crude free-electron approximation is made when the solid is a metal, a similar conclusion can be shown¹⁵ to follow; in this case where the assumption of the periodicity of F_1 cannot be made at all, Eq. (26) reduces to a single electron matrix element involving ordinary one electron Bloch functions.

Nevertheless it is found¹⁵ that even these matrix elements have appreciable values only when the changes in the wavelength (in the x y plane) of an electron are small compared with the reciprocal of a distance of the order of a lattice constant. (See Eq. (14) of Reference (15)).

If then, it is further assumed that d (Fig. 1) is either much smaller, than or approximately equal to a lattice constant of the "surface," the origin of the coordinates for the wave functions in Eq. (26) can be shifted from 1 and 2 to 1' or 2' respectively and in view of the translational properties just discussed, one gets

$$\left\langle F_1^x F_2^x \right\rangle_\tau = \sum_{\tau \neq 0}^{\infty} \left\langle F_1^x \right\rangle_{0\tau} \left\langle F_2^x \right\rangle_{\tau 0} \approx \sum_{\tau \neq 0}^{\infty} \left\langle F_{1'}^x \right\rangle_{0\tau} \left\langle F_{2'}^x \right\rangle_{\tau 0} = \left\langle F_{1'}^x F_{2'}^x \right\rangle_\tau \quad (27)$$

and similarly for y and z. Eq. (27) leads to the equivalence of the x and y matrix elements in Eq. (23) yielding:

$$E_{fl.}^{(3)} \approx \frac{\alpha_1^2}{r_{12}^3} \frac{\delta_1(2\delta_1 + \delta_s)}{2(\delta_1 + \delta_s)^2} \left[\left\langle F_{1'}^z F_{2'}^z \right\rangle_\tau - \left\langle F_{1'}^x F_{2'}^x \right\rangle_\tau \right] (1 - 3 \cos^2 \theta) \quad (28)$$

When the two molecules are the same distance from the surface ($\theta = 90^\circ$), the points 1' and 2' coincide with m the midpoint of r₁₂ and we already have $\left\langle F_{1'}^z F_{2'}^z \right\rangle_\tau$ and $\left\langle F_{1'}^x F_{2'}^x \right\rangle_\tau$ going over into $\left\langle \left(F_m^z \right)^2 \right\rangle_\tau$ and $\left\langle \left(F_m^x \right)^2 \right\rangle_\tau$, the same matrix elements appearing in $E_{fl.}^{(2)}$ (Eq. 21)). On the other hand when θ differs from 90° so that 1' and 2' are above and below m, writing

$$\left\langle F_{1'}^z F_{2'}^z \right\rangle_\tau \sim \left\langle \left| F_m^z \right|^2 \right\rangle_\tau \quad (29)$$

might be expected to provide a reasonable approximation. Actually somewhat later we shall give another quite different derivation of $E_{fl}^{(3)}$ which will show among other assumptions made above, the validity of Eq. (29).

It is, by this time, apparent that Eqs. (28) and (29) would permit the replacement of the matrix elements in $E_{fl}^{(3)}$ in terms of $E_{fl}^{(2)}$ (which might eventually be viewed as an empirical quantity) provided a simple relation can be found among the various components of $\langle |\vec{F}|^2 \rangle_\tau$. Fortunately such a relation does indeed exist. The same proportionality constant between $\langle (F^x)^2 \rangle_\tau$ and $\langle (F^z)^2 \rangle_\tau$ is obtained upon an examination of two very different models of a solid and the result is perhaps perfectly general. First, it has been shown¹⁵ that in the non-degenerate or degenerate free-electron gas model of a metal,

$$\langle (F^x)^2 \rangle_\tau = \langle (F^y)^2 \rangle_\tau = \frac{1}{2} \langle (F^z)^2 \rangle_\tau \quad (30)$$

Secondly, if we consider an insulator or a metal (Margenau-Pollard¹⁶ model) as made up of fluctuating-dipole sections (in the sense of "dispersion" forces) then $\langle (F^x)^2 \rangle_{\infty}$ etc. can be calculated from

$$\langle |\vec{F}_m|^2 \rangle_{\infty} \approx \int \langle |\vec{F}_{m\omega}|^2 \rangle_{\infty} d\omega \quad (31)$$

where $d\omega$ refers to an infinitesimal volume element in the solid and $\langle |\vec{F}_{m\omega}|^2 \rangle_{\infty}$ is the expectation value of the square of the field produced at $\underline{m}$ by the section $\underline{d\omega}$. Using

$$\vec{F}_{m\omega} = - \frac{T}{\omega^2} \cdot \vec{M}_{\omega} \quad (32)$$

where $\underline{T}_{\underline{m}\underline{n}}$ and $\underline{x}_{\underline{m}\underline{n}}$ are analogous to $\underline{T}_{12}$ and $\underline{r}_{12}$ of Eq. (11) and for the components

$$\left\langle (F_{\underline{m}\underline{n}}^x)^2 \right\rangle_{\infty} = \frac{\left\langle (\mu_{\underline{\omega}}^x)^2 \right\rangle_{\infty}}{r_{\underline{m}\underline{n}}^6} \left[1 + 3(\ell_{\underline{\omega}\underline{m}}^x)^2 \right] \quad (33)$$

and similarly for $\underline{y}$ and $\underline{z}$, $\ell_{\underline{\omega}\underline{m}}^x \rightarrow$ being the $\underline{x}$ -component of the unit vector in the direction from $\underline{\omega}$ to $\underline{m}$. Eq. (31) can be integrated separately for each component; e.g.

$$\left\langle (F_{\underline{m}}^x)^2 \right\rangle_{\infty} \approx \left\langle (\mu_{\underline{x}}^x)^2 \right\rangle_{\infty} \int_{R_{\underline{m}}}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{1 + 3x^2/r^2}{r^6} dx dy dz; \quad (34)$$

$\left\langle (\mu_{\underline{x}}^x)^2 \right\rangle_{\infty}$ is related to the polarizability of the solid per unit volume (Eqs. (5), (6)). Eqs. (33), (34) again lead to exactly the same result as Eq. (30) after performing the elementary integrations. Thus we take Eq. (30) as a sufficiently general result.

Finally, combining Eqs. (21), (22), (28), (29) and (30), we have an approximate relation between $E_{fl.}^{(3)}$ and $E_{fl.}^{(2)}$ analogous to the relation between the e.s. energies in Eqs. (19) and (20):

$$E_{fl.}^{(3)} \approx \frac{\alpha_1}{r_{12}^3} \Delta_0 | E_{fl.}^{(2)}(R_m) | \frac{1 - 3 \cos^2 \theta}{4}, \quad (35)$$

where

$$\Delta_0 = \frac{2\delta_1 + \delta_s}{(\delta_1 + \delta_s)}$$

and $E_{fl.}^{(2)}(R_m)$ usually^{3,4,14,16} is of the form

$$E_{fl.}^{(2)} = -\frac{K_f}{R_m^3} \quad (36)$$

with K_p a constant (to be determined empirically when $E_{e.s.}^{(2)} \sim 0$, or from the theories discussed in Section B.) and R_m the distance from m to the surface.

The derivation presented above has the advantage of being general and independent of the nature of the solid. Everything that would specifically involve the solid has been taken care of by $E_{fl.}^{(2)}$ which of course may be viewed if necessary as an experimental quantity. However a crucial assumption has been made in Eq. (27) depending on the uniformity of electron and nuclear distribution at all times, an assumption which seems reasonable intuitively but cannot be fully justified. We shall give another derivation of $E_{fl.}^{(3)}$ however which is quite independent of the first one, yet leads essentially to the same results as Eq. (35).

The matrix elements of the electric fields appearing in Eq. (22) can be evaluated directly if a specific model is adopted for the solid. This evaluation would be possible, for instance, for the free electron model of a metal;¹⁵ however this model is not suitable because Van der Waals interactions are very strongly influenced by electron correlation.^{2,14,21} The "oscillating-dipoles" model which we have already discussed is a valid one for insulators and even for metals.¹⁶ To evaluate $E_{fl.}^{(3)}$ for this model we again consider the solid to consist of small elementary portions $d\omega$ and write as in Eq. (31):

$$\left\langle \vec{F}_1 \cdot \vec{F}_2 \right\rangle_\tau = 3 \left\langle \vec{F}_1 \cdot \hat{\vec{L}}_{12} \hat{\vec{L}}_{12} \cdot \vec{F}_2 \right\rangle_\tau \approx$$

$$\int \left[\left\langle \vec{F}_{1\omega} \cdot \vec{F}_{2\omega} \right\rangle_\tau - 3 \left\langle \vec{F}_{1\omega} \cdot \hat{\vec{L}}_{12} \hat{\vec{L}}_{12} \cdot \vec{F}_{2\omega} \right\rangle_\tau \right] d\omega \quad (37)$$

where $F_{1\omega}$ and $F_{2\omega}$ are the fields due to the section $d\omega$ at the points 1 and 2. Substituting Eq. (32) and after some manipulation the integral in Eq. (37) becomes

$$3 \left\langle (\mu_{\omega}^x)^2 \right\rangle_{\infty} \int \frac{(3 \cos \theta_1 \cos \theta_2 \cos \theta_{\omega} + 1) d\omega}{r_{1\omega}^3 r_{2\omega}^3} \quad (38)$$

in terms of the angles and distances defining the triangle 12ω as shown in Fig. 2. Of course the integrand is just the expression that appears in the "triple dipole" energy⁸ and our task now is the integration of this energy over the entire solid for given positions of 1 and 2, as in the similar evaluation of $E^{(2)}$ by integrating (instead of summing) London forces between 1, say, and a section of the solid.^{3,4} We shall integrate Eq. (38) for two orientations of the molecules only, i.e. $\theta = 0^\circ$ and $\theta = 90^\circ$.

When $\theta = 0^\circ$, i.e. 1 and 2 are on the same normal to the surface, the integral A in Eq. (38) is exactly integrable in cylindrical coordinates with origin at m (Fig. 2). Writing θ_1 , θ_2 , θ_{ω} and $r_{1\omega}$, $r_{2\omega}$ in these coordinates one gets:

$$A = A_1 + 3 A_c \quad (39)$$

$$\text{where } A_1 = \int \frac{dV}{r_{1\omega}^3 r_{2\omega}^3} = 2\pi \int_{R_m}^{\infty} \int_0^{\infty} \frac{\rho d\rho dz}{[b^4 - 4a^2 z^2]^{3/2}},$$

$$A_c = \int \frac{\cos \theta_1 \cos \theta_2 \cos \theta_{\omega} dV}{r_{1\omega}^3 r_{2\omega}^3} = -2\pi \int_{R_m}^{\infty} \int_0^{\infty} \frac{(z^2 - a^2)(z^2 - a^2 + \rho^2) \rho d\rho dz}{[b^4 - 4a^2 z^2]^{5/2}},$$

$$\text{and } b^2 = z^2 + \rho^2 + a^2.$$

The result is

$$A(\theta = 0^\circ) = -\frac{\pi}{6R_m^3} \quad (40)$$

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Fig. 2. Derivation of $\underline{E}^{(3)}$ by integration.

On the other hand, when $\theta = 90^\circ$, i.e. when 1 and 2 are in the same monolayer, the integration is somewhat more involved due to the appearance of $\cos \phi$ in the denominators of

$$A_1 = \int \frac{dv}{b^6 (1 - k^2 \cos^2 \phi)^{3/2}},$$

$$A_c = \int \frac{a^2 (1 - 2a^2/b^2) (1 - \rho^2 \cos^2 \phi/a^2) dv}{b^8 (1 - k^2 \cos^2 \phi)^{5/2}} \quad (41)$$

$$k^2 = 4a^2 \rho^2 / b^4$$

Nevertheless by expanding these denominators in binomial series and keeping 3-4 terms, A is obtained to about one percent accuracy:

$$A(\theta = 90^\circ) \approx \frac{0.34\pi}{R_m^3} f(a, R_m),$$

$$f(a, R_m) = \left\{ \frac{2R_m^2 - a^2}{3(R_m^2 + a^2)} + 0.320 \frac{a^2 R_m^4}{(R_m^2 + a^2)^3} - 0.422 \frac{R_m^4}{(R_m^2 + a^2)^2} \right. \\ \left. + \frac{a^2}{5R_m^2} - \frac{a^4}{7R_m^4} + \frac{a^6}{9R_m^6} - \dots \right\} \quad (42)$$

where the arctan resulting from the final z integration has also been expanded in a power series of (a/R_m) .

The connection between these and the result of the former derivation, Eq. (35), becomes apparent when we substitute the troublesome quantity, $\left\langle (\mu_\omega^x)^2 \right\rangle_{00}$, related to the polarizability of the metal, in Eq. (38) from $\underline{E}^{(2)}$ based on the same model¹⁶ (See Eq. (34)). One obtains

$$E_{fl.}^{(3)}(\theta = 0^\circ) = -\frac{\alpha_1}{2r_{12}^3} \Delta_0 \left(\frac{K_f}{R_m^3} \right), \quad (43a)$$

and

$$E_{fl.}^{(3)}(\theta = 90^\circ) \approx \frac{\alpha_1}{r_{12}^3} \Delta_0 \left(\frac{K_f}{R_m^3} \right) f(a, R_m) \quad (43b)$$

Eq. (43a) is exactly the same as Eq. (35) provided a R_m^{-3} law is assumed for $E_{fl.}^{(2)}(R_m)$, and this result lends additional support to the assumption of Eq. (29) that had been made in the previous derivation. On the other hand, Eq. (43b) would also be the same as Eq. (35), if $f(a, R_m)$ of the former were to equal the factor of $1/4$ in the latter. An examination of the Eq. (42) reveals that $f(a, R_m)$ is a very slowly varying function of both a and R_m , and its value remains within about $\pm 15\%$ of 0.25 over the relevant ranges of these variables.

The previous derivation of Eq. (35) had been quite independent of the nature of the solid, and, for instance, the F 's are not restricted to dipole fields as in the second derivation. Yet, when the proper (e.g. empirical when $\langle F \rangle_{\infty} \approx 0$) $E^{(2)}$'s are used in both, the two derivations lead essentially to the same result (at least for the interesting cases, $\theta = 0^\circ$ and $\theta = 90^\circ$ examined). This is not surprising, however, since any differences that would have arisen between the results of the two derivations as a consequence of the specific model used in the second, are largely cancelled in the elimination of $\langle (\mu_\omega^x)^2 \rangle_{\infty}$ which is common to both $E_{fl.}^{(2)}$ and $E_{fl.}^{(3)}$.

$E_{e.s.}^{(3)}$ and $E_{fl.}^{(3)}$ in Eqs. (19) and (35) have the same dependence on θ and r_{12} and can be combined together giving the total surface intermolecular potential $E_{12s}^{(3)}$

$$E_{12s}^{(3)} \approx \frac{\alpha_1^2}{r_{12}^3} (1 - 3 \cos^2 \theta) \left\{ \langle F_m^2 \rangle_{\infty} + \frac{1}{4} \Delta_0 |E_{fl.}^{(2)}(R_m)| \right\} \quad (44)$$

The "electrostatic" or average field $\langle F^Z \rangle_{\infty}$ is independent of the $\underline{x}, \underline{y}$ coordinates on the surface and we have also made the approximation

$$\langle F_1^Z \rangle_{\infty} \langle F_2^Z \rangle_{\infty} \sim \langle F_m^Z \rangle_{\infty}^2 \quad (45)$$

and used the average field at $\underline{m}$. The total $E_{12s}^{(3)}$ cannot be related to the total $E_{1s}^{(2)}$, because the relative importance of the e.s. terms are quite different in each case. Nevertheless Eq. (44) can be put into a very useful form after substituting for $\langle F_m^Z \rangle_{\infty}$ from Eq. (20):

$$E_{12s}^{(3)} \approx \frac{\alpha}{r_{12}^3} (1 - 3 \cos^2 \theta) |E_{1s}^{(2)}(R_m)| \left(\frac{\Delta_0 + \gamma_m \Delta_1}{4} \right) \quad (46)$$

where

$$\Delta_1 \equiv \left(\frac{6\delta_1 + 7\delta_s}{\delta_1 + \delta_s} \right),$$

and we have defined the parameter

$$\gamma_m \equiv \frac{E_{e.s.}^{(2)}(R_m)}{E_{1s}^{(2)}(R_m)} = \frac{E_{e.s.}^{(2)}}{E_{e.s.}^{(2)} + E_{fl.}^{(2)}} \quad (47)$$

i.e. the "electrostatic" fraction of the total van der Waals attraction of a molecule at $\underline{m}$ to the surface. γ_m is not a constant

but depends on R_m , because $E_{fl}^{(2)}$ varies in general^{3,4} as R_m^{-3} , whereas $E_{e.s.}^{(2)}$ falls off exponentially.¹³ However if we are interested in the behaviour of molecules strictly in a monolayer, then we find a simple proportionality between $E^{(3)}$ and $E^{(2)}$. In general the range of R_m that is important for $E^{(3)}$ is not very large so that we might replace γ_m by an average $\bar{\gamma}$ either over the whole range or at least up to a certain R_m^0 and then assume $\gamma_m = 0$ for $R_m > R_m^0$.

If a Lennard-Jones (12-6) potential had been assumed between two molecules (e.g. in inert gases), when the molecules are adsorbed on a surface the new intermolecular potential is modified and now becomes

$$\epsilon'(r_{12}) = \epsilon_0 \left[\left(\frac{r_0}{r_{12}} \right)^{12} - 2 \left(\frac{r_0}{r_{12}} \right)^6 \right] + \frac{S(R_m)}{r_{12}^3} (1 - 3 \cos^2 \theta) \quad (48)$$

provided the original r_{12}^{-12} repulsion has not been altered appreciably by the surface. ϵ_0 and r_0 are unchanged and are the gas phase parameters.¹⁷ $S(R_m)$ includes both the e.s. and fl. contributions (Eq. (46)). When more than two molecules are considered on the surface, the total potential energy of interaction between the molecules themselves will be obtained by summing ϵ'_{12} over all pairs. In other words, the intermolecular energy is still "pairwise additive" to the same extent as the gas phase Lennard-Jones potential. Bade¹¹ has found that for a system of molecules the third order energy is "triple-wise additive." With a system of molecules and the surface the only additional triplets that we haven't included

in $\underline{E}^{(3)}$ is the "triple-dipole" energy⁸ of three adsorbed molecules and this of course is the same as in the gas phase. Then, "pairwise-additivity" of $\underline{\epsilon}'(r_{12})$, Eq. (48), to the same extent as the Lennard-Jones (12-6) $\underline{\epsilon}(r_{12})$ follows. An estimate of the contribution of higher order perturbations to $\underline{\epsilon}'(r_{12})$ can also be obtained from the work of Bade¹¹ with reference to the model we have used in the second derivation of $\underline{E}^{(3)}$. Replacing summation over the solid by integration as in Eq. (37) the effect of higher order perturbations on $\underline{\epsilon}'_{12}$ can be shown to be negligible. This is to be expected since the higher terms involve higher inverse powers of the distances.

The full use of Eqs. (46), (47) and (48) in conjunction with experimental data and relative magnitudes of $\underline{E}_{fl.}^{(3)}$ and $\underline{E}_{e.s.}^{(3)}$ will be discussed in the next section.

D) Applications and Magnitudes

$\underline{E}^{(3)}$ as given by Eq. (46) can be obtained most directly when the electrostatic effects are quite unimportant as on most insulators.³ One only has to substitute for $\underline{E}_{1s}^{(2)}$. Especially in a "monolayer" the repulsion between two atoms can be estimated simply by using $1.5 \underline{U}_0$ for $\underline{E}_{1s}^{(2)}$, (Eq. (9)), if we assume the atoms to be restricted to their minimum energy distances ($\underline{R}_0$) from the surface and behave like a two dimensional gas; then one does not need an estimate of this distance $\underline{R}_m = \underline{R}_0$ but only $\underline{U}_0$, the energy of adsorption at zero coverage.

The most straightforward application of Eq. (46) is in connection with the virial coefficients treatment of physical adsorption.⁵ There, $\underline{E}_{1s}^{(2)}$ can be obtained without the complications of non-zero coverage from $\underline{B}_{1s}$, the "second surface virial coefficient" involving a single molecule and the surface.⁵ When $\bar{\gamma}$ is not negligible, the total $\underline{E}^{(2)}$ might be approximated by a general $\underline{R}_m^{-n}$ law and its parameters obtained from a best fit to $\underline{B}_{1s}$ data. Similarly $\underline{E}_{12s}^{(3)}$ is related to $\underline{C}_{12s}$, the two-molecule-surface virial coefficient.^{5b} A combination of $\underline{B}_{1s}$ and $\underline{C}_{12s}$ would enable one to get an estimate of an average $\bar{\gamma}$. Notice that although in general it is difficult to estimate a reliable value for δ_s , the surface "mean excitation energy", its appearance in $\underline{\Delta}_0$ and $\underline{\Delta}_1$ of Eq. (46) is not critical. Because $\underline{\Delta}_0$ varies only from unity to two, and $\underline{\Delta}_1$ from six to seven as (δ_s/δ_1) ranges from infinity to zero. In general $\underline{\Delta}_0$ will lie close to 1.5 and $\underline{\Delta}_1$ to 6.5.

A few applications with actual data will serve to demonstrate the use of some of these ideas and at the same time show the relative magnitudes of $\underline{E}_{fl}^{(3)}$ and $\underline{E}_{e.s.}^{(3)}$.

Ehrlich and Hudda⁷ have estimated the heat of desorption of Xe on tungsten to be about 8 kcal/mole and $\underline{E}_{e.s.}^{(2)} \sim 1.6$ kcal/mole.

If we neglect any effects of non-zero coverage and assume that

$(8 - 1.6) = 6.4$ kcal/mole represents the energy minimum $\underline{U}_0$ of a Lennard-Jones (9-3) potential, then $\underline{E}_{fl.}^{(2)}(\underline{R}_0) \sim 9.6$ kcal/mole.

— The same value is obtained from Kirkwood-Müller formula^{2,4} at $\underline{R}_m = 3.1 \text{ \AA}^0$, so that this estimate is reasonable. Taking δ_s very

roughly as twice the ionization potential $\underline{I}$ of tungsten atom (see

Section B about δ_1 's), $\underline{\Delta}_0 \sim 1.59$. With these values one gets

$\underline{E}_{fl.}^{(3)} \sim 0.163$ kcal/mole and $\underline{E}_{e.s.}^{(3)} \sim 0.133$ kcal/mole, at $\underline{r}_{12} = \underline{r}_0$ and

when $\theta = 90^\circ$ and the two molecules are at their equilibrium distance

from the surface. Comparing these figures with the gas phase Lennard-

Jones (12-6) potential minimum, $\underline{\epsilon}_0$, between two Xe atoms, we observe

that $\underline{E}_{fl.}^{(3)}$ amounts to $\sim 37\%$ and $\underline{E}_{e.s.}^{(3)} \sim 30\%$ of $\underline{\epsilon}_0$. The resulting inter-

molecular potential is the curve (b) in Fig. 3. On the other hand if

we consider the case of the two molecules on top of another as in

multilayer formation we get $\underline{E}_{fl.}^{(3)} \sim -0.18 \underline{\epsilon}_0$, i.e. an attraction when

the first molecule is at $\underline{R}_1 \sim 3.5 \text{ \AA}^0$ and $\underline{r}_{12} = \underline{r}_0$.

Freeman²⁷ has studied the adsorption of single atoms of Kr on alumina and A on carbon black. Neglecting the e.s. effects for this

²⁷M. P. Freeman, J. Phys. Chem., 62, 723 (1958).

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Fig. 3. Potential energy of interaction between two Xe atoms.

Curve a - Lennard-Jones (12-6) potential in the gas phase.

Curve b - Lennard-Jones (12-6) plus the third order repulsion between two Xe atoms in a monolayer on tungsten. Both atoms are the same distance, R_0 , from the surface.

system and using $E_{1s}^{(2)} = 1.5 U_0 = 4.58 \text{ kcal/mole}^{27}$ and $\delta_s \sim 8.2 \text{ ev}$, estimated by comparing the Kirkwood-Müller and London formulas,² one obtains $E_{12s}^{(3)}(R_0) \sim 23.1\%$ of ϵ_0 at $r_{12} = r_0$ and $\theta = 90^\circ$ and about $-10\% \epsilon_0$ attraction when $\theta = 0^\circ$.

Of course very often it is also possible to estimate $E^{(3)}$ using a calculated value of $E_{fl.}^{(2)}$, e.g. from Kirkwood-Müller's formula. For instance, the attraction of Kr to tungsten, $E_{fl.}^{(2)}$, is found to be $\sim 6.9 \text{ kcal/mole}$ at a distance of $R_0 \sim 3 \text{ \AA}$ by this formula. This leads to $0.32 \epsilon_0$ repulsion in the monolayer at $r_{12} = r_0$. (The Lennard-Jones parameters, ϵ_0 , r_0 in the above calculations as well as I 's have been taken from Reference 20, p. 339).

Finally the estimation of $\bar{\gamma}$ from data can be demonstrated on the system: A and carbon black. At the distance of minimum energy, R_0 , one has

$$E_{fl.}^{(2)} \sim \frac{1.5 U_0 (1 - \gamma)}{1 + (\gamma/2)} \quad (49)$$

if it is assumed that a Lennard-Jones (9-3) potential has been fitted only to $E_{fl.}^{(2)}$ excluding $E_{e.s.}^{(2)}$. We take $\delta_s \sim 2 I = 22.4 \text{ ev}$ and from Freeman²⁷ $1.5 U_0 = 5.8 \text{ kcal/mole}$. Then for a total repulsion, $E_{12s}^{(3)}$ between two A atoms in a "monolayer" that would amount to about 70% of ϵ_0 at $r_{12} = r_0$, as in the Xe - W case, one would get $\bar{\gamma} \sim 38\%$. This number compares favorably with $\bar{\gamma} \sim 30\%$ that one gets from Eq. (49) after calculating $E_{fl.}^{(2)}$ from Kirkwood-Müller's formula at $R_0 = 2.94 \text{ \AA}$.²⁷

The results presented above might be summarized by stating that the third-order perturbation introduces, aside from the "electrostatic" effect, a repulsion between the molecules in a monolayer which amounts

to about 20 - 40% of their gas phase potential minimum, ϵ_0 (at $r_{12} = r_0$). The same third-order "fluctuation" energy gives rise to an attraction, if two molecules lie on top of one another, which might be about 10 - 20% of ϵ_0 . This additional attraction is among the factors contributing to the formation of multilayers ("molecular adsorption").

It is well known that with a relatively dense adsorbate resembling a liquid only a small amount of additional attraction above and beyond the heat of liquefaction of the adsorbate is needed to provide for the formation of multilayers.³ Although the greater portion of this energy is provided by the ordinary van der Waals field of the surface,^{28,29}

²⁸T. L. Hill, Advances in Catalysis, 4, 236 (1952)

²⁹G. D. Halsey, Ibid, 4, 265 (1952).

i.e. by $E_{fl}^{(2)}$, (e.g. effects decreasing exponentially from the surface, might be negligible in the additional layers) $E_{fl}^{(3)}$ as discussed above is also a contributing factor; in the Xe - W example with only two molecules on the surface $E_{12s}^{(3)}$ amounts to roughly ten percent of the $E_{fl}^{(2)}$ acting on the top molecule at $R_2 \sim 8 \text{ \AA}$.

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