where $u_s(\mathbf{r}_1)$ is the gas–solid energy and $u(r_{ij})$ the mutual interaction energy of the gas molecules with one another. The volume elements are $d\mathbf{r}_1$ and $d\mathbf{r}_2$ if molecules 1 and 2 are located at $\mathbf{r}_1$ and $\mathbf{r}_2$ respectively.

Gregg and Sing[2] have discussed the shape of the adsorption isotherm by means of a analysis of the point of inflection in the BET equation.[3] By applying the same ideas to Eq. (1) it is easy to deduce that the pressure P_i corresponding to the point of inflection of the adsorption isotherm is given by

$$P_i = -kT\, C_{AAS}/3\, D_{AAAS} \qquad (5)$$

while the corresponding number of adsorbed molecules, $N_a(i)$ is, in a first approximation, given by

$$N_a(i) = -C_{AAS}\, B_{AS}/3\, D_{AAAS} \quad . \qquad (6)$$

These equations allow some considerations to be made in relation to physisorption isotherms of types II and III according to the classical classification.[4] Since type III isotherms are those that do not show a point of inflection, according to Eq. (5) they would correspond to the case in which P_i is negative, which is true only if C_{AAS} and D_{AAAS} have the same sign. This has been confirmed in our laboratory for some systems whose experimental data we have published previously.[5,6] Physically this argument is related to the existence of characteristic temperatures observed in adsorption systems.[7]

It can then be said that the existence of a type III isotherm implies the same form of energy contribution between structure AAS and AAAS, while that of type II implies the opposite.

Since P_i is not a function of B_{AS}, it can be seen that the shape of the isotherm is independent of the AS configuration. However, Eq. (6) shows that, when the pressure is P_i, the number of adsorbed molecules is a function of the three virial coefficients. On the other hand, even though $N_a(i)$ does not belong to the monolayer, it may correspond, at least in the majority of type II isotherms, to a first approximation of the value.[2]

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ERRATA

Erratum: Representations of molecular force fields. V. On the equilibrium structure of methane [J. Chem. Phys. 68, 1213 (1978)]

L. S. Bartell

Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109

Kozo Kuchitsu

Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

Expressions for the stretch–bend–bend cubic constants should be amended to read:

$$\tilde{f}_{122} = r_e(-F' + F + F_3)/6$$

and

$$\tilde{f}_{144} = r_e(-5F' - 3F + F_3)/6 \quad .$$

Associated numerical values of the methane cubic constants are changed from those reported by less than 0.2 mdyn/Å^2. The corrections $(\langle r \rangle - \langle r_s \rangle)$ of Table II should be increased by 0.0004 to 0.0005 Å for the different isotopic species and different parameterizations (KB or MUB-2).