groups at the ambient side of the monolayer. A pictorial structure of an isolated adsorbate molecule that incorporates features consistent with our data is given in Figure 3. Recent measurements on a monolayer consisting of a diacid with a $(CD_2)_6$ segment at the center of the chain demonstrate that the fold must consist of at least six methylene groups.[28] These experiments, additional ones involving more complex folded molecular structures, and further characterization of the ordering in such structures will be reported in detail in future publications.

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Principle of Maximum Hardness

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From his considerable experience with the concepts of chemical hardness and softness, in 1987 Ralph Pearson concluded that "there seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible."[1] Subsequent studies of particular problems support this principle and imply that its validity may require conditions of constant temperature and chemical potential.[2] Following is a formal proof of the principle, as so modified.

Absolute hardness η and absolute softness S, of the equilibrium state of an electronic system at temperature T, are defined by

$$2\eta = \left(\frac{\partial\mu}{\partial N}\right)_{v(\mathrm{r}),T} \quad \text{and} \quad S = \frac{1}{2\eta} = \left(\frac{\partial N}{\partial\mu}\right)_{v(\mathrm{r}),T} \tag{1}$$

where μ is the electronic chemical potential (constant through the system),[3] N is the number of electrons, and $v(\mathrm{r})$ is the potential acting on an electron at r due to the nuclear attraction plus such other external forces as may be present. These definitions are the finite-temperature extensions of the ground-state definitions of these quantities.[4-6] The chemical potential is the Lagrange multiplier for the normalization constraint in the finite-temperature density-functional theory.[6,7] It also is the negative of the absolute electronegativity.[3] In terms of the Helmholtz free energy, $\mu = (\partial A/\partial N)_{v(\mathrm{r}),T}$. Note that $v(\mathrm{r})$ constant implies total volume constant.

Imagine a grand canonical ensemble consisting of a large number of perfect replicas of a particular electronic system of interest, in equilibrium with a bath at temperature T and chemical potential μ, with the bath also controlling $v(\mathrm{r})$. The members of the ensemble may exchange energy and electrons with each other. Equilibrium averages being denoted with brackets, N will fluctuate about $\langle N\rangle$. The equilibrium softness is given by[5]

$$\langle S\rangle = \left[\frac{\partial\langle N\rangle}{\partial\mu}\right]_{v(\mathrm{r}),T} = \beta\langle(N - \langle N\rangle)^2\rangle \tag{2}$$

where $\beta = 1/kT$. Or,

$$\langle S\rangle = \beta\sum_{N,i} P^0_{N,i}(N - \langle N\rangle)^2 \tag{3}$$

where

$$P^0_{N,i} = (1/\Xi)\exp[-\beta(E_{Ni} - N\mu)] \tag{4}$$

and

$$\Xi = \sum_{N,i}\exp[-\beta(E_{Ni} - N\mu)] \tag{5}$$

Ξ is the grand partition function. The probabilities $P^0_{N,i}$ define the equilibrium distribution. They are functions of the parameters that characterize the ensemble: β, μ, and $v(\mathrm{r})$; dependence on $v(\mathrm{r})$ comes through the fact that the E_{Ni} depend on $v(\mathrm{r})$.

Now consider the countless other, nonequilibrium ensembles of the same system of interest, at temperature T but characterized by probabilities $P_{N,i}$ different from the canonical probabilities $P^0_{N,i}$. An average in any such ensemble may be denoted with overbars, as for example $\bar{S} = \beta\sum_{N,i}P_{N,i}(N - \langle N\rangle)^2$. Consider only those of these nonequilibrium ensembles that can be generated as equilibrium ensembles by changing the bath parameters μ and $v(\mathrm{r})$, by small amounts. For any one of these, it will be shown that

$$\bar{S} - \langle S\rangle = \beta\sum_{N,i}(N - \langle N\rangle)^2(P_{N,i} - P^0_{N,i}) \geq 0 \tag{6}$$

Consequently, among all these states, the equilibrium state may be characterized as having minimum softness.

Proof of eq 6 follows from the fluctuation–dissipation theorem of statistical mechanics.[8] For simplicity employing classical statistical mechanics, let the equilibrium probability distribution function for the system of interest, with grand potential $\Omega(\mathbf{r}^N,\mathbf{p}^N) = H(\mathrm{r}^N,\mathbf{p}^N) - \mu N$, be $f(\mathrm{r}^N,\mathbf{p}^N)$ (corresponding to $P^0_{N,i}$) and let the corresponding arbitrary nearby distribution be $F(\mathrm{r}^N,\mathbf{p}^N)$ (corresponding to $P_{N,i}$). Then the physical perturbation $\Delta\Omega(\mathrm{r}^N,\mathbf{p}^N)$ generating F at time $t = 0$ must satisfy

$$F(\mathrm{r}^N,\mathbf{p}^N) = \frac{\exp(-\beta\Delta\Omega)}{\langle\exp(-\beta\Delta\Omega)\rangle}f(\mathrm{r}^N,\mathbf{p}^N) \tag{7}$$

$$= \langle A\rangle^{-1}A(\mathrm{r}^N,\mathbf{p}^N)\,f(\mathrm{r}^N,\mathbf{p}^N) \tag{8}$$

where

$$CA(\mathrm{r}^N,\mathbf{p}^N) = \exp(-\beta\Delta\Omega) \quad \text{and} \quad \Delta\Omega = -\left(\frac{1}{\beta}\right)\ln\,[CA(\mathrm{r}^N,\mathbf{p}^N)] \tag{9}$$

$f(\mathrm{r}^N,\mathbf{p}^N)$ and $\langle A\rangle$ are independent of time, and C is a positive constant serving the purpose of a field component of the perturbation which couples with A; other quantities depend on time. Equation 8 shows that the conditions are satisfied for Exercise 8.3, p 242, of ref 8. Accordingly, it follows that

$$\langle A\rangle[\bar{A}(t) - \langle A\rangle] = \langle(A(0) - \langle A\rangle)(A(t) - \langle A\rangle)\rangle \tag{10}$$

and

$$\bar{A}(0) - \langle A\rangle = \langle A\rangle^{-1}\langle(A(0) - \langle A\rangle)^2\rangle \tag{11}$$

Here $\bar{A}(t)$ is the average of $A(t)$ for the nonequilibrium distribution F. Now take A to be the observable that is the softness,

$$A = \beta(N - \langle N\rangle)^2 \tag{12}$$

Since this $\langle A\rangle$ is positive, eq 11 implies

$$\bar{S}(0) - \langle S\rangle \geq 0 \tag{13}$$

which is the inequality of eq 6.

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(1) Pearson, R. G. *J. Chem. Educ.* **1987**, *64*, 561–567.

(2) (a) Zhou, Z.; Parr, R. G.; Garst, J. F. *Tetrahedron Lett.* **1988**, *29*, 4843–4846. (b) Zhou, Z.; Parr, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 7371–7379. (c) Zhou, Z.; Parr, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 5720–5724.

(3) Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* **1978**, *68*, 3801–3807.

(4) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512–7516.

(5) Yang, W.; Parr, R. G. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 6723–6726.

(6) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford: New York, 1989.

(7) Mermin, N. D. *Phys. Rev.* **1965**, *137*, A1441–A1443.

(8) Chandler, D. *Introduction to Modern Statistical Mechanics*; Oxford: New York, 1987; Chapter 8.

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The derivation is finished if the class of neighboring states defined by eqs 9 and 12, that is, by

$$C\beta(N - \langle N\rangle)^2 = \exp(-\beta\Delta\Omega) \qquad (14)$$

can be shown to include all possible physically acceptable nearby nonequilibrium distributions that can evolve into the given original equilibrium distribution. Presumably it does, as eq 14 is a minimal requirement to produce $\langle A\rangle = \langle S\rangle$, and such assumptions are standard in traditional linear response theory. Note that constant T and μ are required because the averaging after the perturbation is removed is done with the $P^0_{N,i}$ or $f(r^N,p^N)$.

Is there certainly a rule of nature that chemical systems at constant temperature and chemical potential evolve toward minimum softness or maximum hardness? A major concern with the proof just given should be whether statistical mechanics indeed applies to electrons in individual molecules in the sense employed. Evidence is accumulating that it does, at least to some reasonable accuracy,[6] but one should not, at this time, imply certainty. Nevertheless, with some confidence one may assert, with Pearson, the maximum hardness principle. If one also asserts, with Sanderson,[9] the electronegativity (chemical potential)[3] equalization principle, then one has reached two basic, broadly applicable electronic-structure principles.

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(9) Sanderson, R. T. *Science* **1981**, *114*, 670-672.

HSAB Principle

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It is generally accepted that a variety of acid-base reactions can be described by the HSAB principle:[1] "Hard likes hard and soft likes soft". It is not, however, easy to theoretically establish this principle. Here two proofs are offered of this principle with a restriction added: Among potential partners of a given electronegativity, hard likes hard and soft likes soft.

For the ground state of an N-electron system at 0 K, or for the equilibrium state at the temperature T, according to density-functional theory[2] hardness and softness are given by[3,4]

$$2\eta = \left(\frac{\partial\mu}{\partial N}\right)_{v(\mathrm{r}),T} \text{ and } S = \frac{1}{2\eta} = \left(\frac{\partial N}{\partial\mu}\right)_{v(\mathrm{r}),T} \qquad (1)$$

where μ and $v(\mathrm{r})$ are the chemical and external potentials, respectively. When two species combine to give a third, their chemical potentials are equalized. Chemical potential is the negative of electronegativity. The maximum hardness principle or minimum softness principle states that, at constant μ, $v(\mathrm{r})$, and T, systems evolve toward minimum total softness.[5,6]

First Proof.[11] When acid A and base B interact to give AB, two things happen, which can be taken as happening in succession. First there is a charge transfer producing a common chemical potential, and then there is a reshuffling of the charge distributions. In the first step there is an energy gain proportional to the square of the original chemical potential difference and inversely proportional to the resistance to charge transfer which is the hardness sum. The specific old formula,[3]

$$\Delta E = -\frac{(\mu_B - \mu_A)^2}{4(\eta_A + \eta_B)} = -\frac{(\Delta\mu)^2}{2}\,\frac{S_AS_B}{S_A + S_B} \qquad (2)$$

need not be precisely valid; the essential point is the indicated dependence on softnesses. The greater $S_AS_B/(S_A + S_B)$ is, the more stabilizing is the charge transfer. For a given S_A, the larger S_B is, the better.

In the next, reshuffling step, which is at constant μ and T, the minimum-softness principle applies. The total softness is, at least roughly, $S_A + S_B$ by application of eq 1 to nonoverlapping A plus B with a total number of electrons $N_A + N_B$.[7] The preference in this step is for S_A and S_B to be as small as possible. So, for a given S_A, the smaller S_B is, the better. Thus there are two opposing tendencies, and the optimum situation will be a compromise.

Suppose S_A is fixed, let $S_B = \alpha S_A$, and consider the question of what will be the best value of S_B or α. The supremum value of $\alpha/(1 + \alpha)$, 1, corresponds to maximum initial energy gain and maximum softness, while the infimum value, 0, has these roles reversed. If nothing is known about the relative importance of the two conditions, a most natural compromise would be to take the average value, viz., $\alpha/(1 + \alpha) = {}^1/_2$. This is the HSAB principle: $\alpha = 1$. In this analysis S_A and S_B are softnesses either before or after the chemical potential equalization step; fortunately these quantities are known to be insensitive to the number of electrons.[8] The final chemical bond formation may be assumed not to much affect the partitioning $S_A + S_B$ and not to much affect the components S_A and S_B.

To quantify the argument: For a given $\Delta\mu$ and S_A, the problem is to find the most favorable S_B, or the most favorable α. From eq 2 one would want $\alpha/(1 + \alpha)$ to be as large as possible, which favors a large α value. But to minimize $S = S_A + S_B = S_A(1 + \alpha)$ one would want α to be as small as possible. Simultaneous satisfaction of the two conditions being impossible, what one must assess is the relative importance of the two conditions. Let λ be the weight of the first relative to the second. Then α is determined from

$$\frac{\mathrm{d}}{\mathrm{d}\alpha}\left[(1 + \alpha) - \lambda\left(\frac{\alpha}{1 + \alpha}\right)\right] = 0 \qquad (3)$$

This gives $\alpha = \sqrt{\lambda} - 1$. For a fixed value of λ (λ may be hoped to be a more or less universal constant), the result is that, from among a series of B's with the same chemical potential (electronegativity), a given A will prefer one, and similarly with other A's. The HSAB principle follows precisely if one takes $\lambda = 4$, for then $\alpha = 1$ and $S_B = S_A$. An argument that λ should be close to 4 is not easy to construct.

Note that $A'B + AB' \rightarrow AB + A'B'$ is predicted to be a hardness-raising or softness-lowering process if $S_A = S_B$, $S_{A'} = S_{B'}$. The maximum hardness (minimum softness) principle is demanded by the HSAB principle.

Second Proof.[12] To obtain a second proof, rewrite eq 2 in the form

$$\Delta E = \Delta\Omega_A + \Delta\Omega_B \qquad (4)$$

where

$$\Delta\Omega_A = -\frac{(\mu_B - \mu_A)^2}{4}\,\frac{\eta_A}{(\eta_A + \eta_B)^2} \quad \text{and} \quad \Delta\Omega_B = -\frac{(\mu_B - \mu_A)^2}{4}\,\frac{\eta_B}{(\eta_A + \eta_B)^2} \qquad (5)$$

Assume that for a given $\mu_B - \mu_A$ and η_B, $\Delta\Omega_A$ is minimized with respect to η_A. There follows

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(1) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533-3539.

(2) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford: New York, 1989.

(3) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512-7516.

(4) Yang, W.; Parr, R. G. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 6723-6726.

(5) Pearson, R. G. *J. Chem. Educ.* **1987**, *64*, 561-567.

(6) Parr, R. G.; Chattaraj, P. K. *J. Am. Chem. Soc.*, preceding communication in this issue.

(7) Nalewajski, R. F.; Korchowiec, J.; Zhou, Z. *Int. J. Quantum Chem.* **1988**, *22*, 349-366.

(8) Fuentealba, P.; Parr, R. G. *J. Chem. Phys.* In press.