

## COMMENT ON AVERAGE KEKULÉ-STRUCTURE COUNTS FOR RANDOM CONJUGATED COPOLYMERS\*

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In a recent sequence of papers [1–3], Gutman and co-workers have repeatedly addressed the formal problem of computing the average of the number of Kekulé structures over particular classes of particular copolymer structures imparted with a particular probability measure. The two *monomer structures* are catafused anthracenoid (*A*) and phenanthrenoid (*B*) hexagon graphs, as in figs. 1(a) and (b), respectively. The *L*th class is that of graphs with  $L - 2$  monomers each as in fig. 1(a) or (b), together with two end hexagons as in fig. 1(c). The *probability measure* assigns

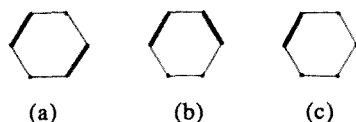


Fig. 1. In (a), (b) and (c) are shown *A*, *B* and "end" monomer units, wherein the boldface edges indicate edges to undergo fusion with adjacent monomer units.

a probability  $p^m(1-p)^n$  to each (ordered) sequence of *A*'s and *B*'s with *m* *A*'s and *n* *B*'s. In general, several catahex chains (with different "left" or "right" bends for each *B*) correspond to each sequence. Also,  $0 \leq p \leq 1$ , and *p* evidently is the probability that a (internal) monomer unit is of type *A*, while  $1 - p$  is the probability that it is of type *B*. In the first paper [1], the solution to the stated problem was (at least) conjectured and in the last [3] rigorously proved.

It may be of some interest that the type of problem so framed is also solved rigorously in a more general context via an approach of an earlier paper [4]. There, *transfer matrices*  $T_A$  and  $T_B$  for *A* and *B* monomers are used to count the Kekulé structures for a chain with a sequence  $C_1, C_2, \dots, C_{L-2}$  of monomers, as a trace

$$K(C_1, C_2, \dots, C_{L-2}) = \text{Tr}\{p T_{C_1} T_{C_2} \dots T_{C_{L-2}}\}, \quad (1)$$

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where  $\rho$  is a matrix characterizing the polymer ends. Indeed, (1) applies for quite general choices of the monomer units. Evidently, the average count desired by Gutman and co-workers is

$$\langle\langle K \rangle\rangle_{p,L} \equiv \sum_{C_1} \sum_{C_2} \dots \sum_{C_{L-2}} K(C_1, C_2, \dots, C_{L-2}) \prod_{i=1}^{L-2} p_{C_i}, \quad (2)$$

where  $p_A = p$  and  $p_B = 1 - p$ . Upon substitution of (1) into (2), one obtains

$$\langle\langle K \rangle\rangle_{p,L} = \text{Tr}\{\rho \mathcal{T}^{L-2}\}, \quad (3)$$

where we have followed ref. [4] in introducing an *ensemble* transfer matrix

$$\mathcal{T} \equiv p \mathbf{T}_A + (1 - p) \mathbf{T}_B. \quad (4)$$

Now,  $\langle\langle K \rangle\rangle_{p,L}$  may be developed in terms of the eigensolutions to  $\mathcal{T}$ , thus

$$\langle\langle K \rangle\rangle_{p,L} = \sum_{\lambda} A_{\lambda} \lambda^L, \quad (5)$$

where the sum is over distinct nonzero eigenvalues  $\lambda$  and  $A_{\lambda}$  is in general a polynomial in  $L$  with degree one less than the size of the maximum Jordan block associated to  $\lambda$ . For the typical case where a Jordan block is trivial (i.e. as when  $\mathcal{T}$  is diagonalizable)

$$A_{\lambda} = \text{Tr}(\rho O_{\lambda})/\lambda^2, \quad (6)$$

where  $O_{\lambda}$  is the projector onto the  $\lambda$ th eigenspace of  $\mathcal{T}$ . (Equations (5) and (6) follow directly from (4) via the spectral resolution of  $\mathcal{T}$ .) For large  $L$ , the maximum (magnitude) eigenvalue  $\Lambda$  (with  $A_{\Lambda} \neq 0$ ) dominates

$$\langle\langle K \rangle\rangle_{p,L} \approx A_{\Lambda} \Lambda^L. \quad (7)$$

Here, the correction factor clearly differs from 1 by terms which decrease exponentially with  $L$  (e.g.  $1 + O(\lambda/\Lambda)^L$ ). In fact, all these formulas apply for quite general "random" copolymer chains.

For the choice of monomers considered by Gutman et al.,

$$\rho = \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \quad \mathbf{T}_A = \begin{pmatrix} 1 & 0 \\ 1 & 1 \end{pmatrix}, \quad \mathbf{T}_B = \begin{pmatrix} 1 & 1 \\ 1 & 0 \end{pmatrix}, \quad (8)$$

as also is identified in [4]. This (rigorously) leads to the same results as already given elsewhere [1-4].

Results may be given for other copolymers. In a conversation in the spring of 1989, Gutman suggested the pair of monomer units in fig. 2. In fact, one may

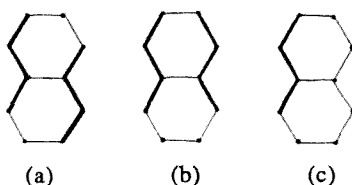


Fig. 2. In (a), (b) and (c) are shown a second (width  $w = 2$ ) choice for  $A$ ,  $B$  and "end" monomer units, wherein boldface again indicates edges where fusion occurs.

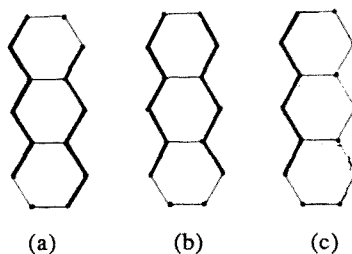


Fig. 3. In (a), (b) and (c) are shown a third (width  $w = 3$ ) choice for  $A$ ,  $B$  and "end" monomer units, wherein boldface again indicates fusion.

conceive of a whole sequence of monomer units of increasing width  $w$ : the first and second members are those of figs. 1 and 2, while the third case is given in fig. 3. The relevant matrices may be rather readily obtained from ref. [5], which considered the  $B$ -type monomer. The  $A$ -type case may be derived from this by reversing row labels. For the type of polymer ends as indicated in figs. 1(c), 2(c), 3(c), the relevant matrices are just  $w + 1$  by  $w + 1$ , with elements given by

$$(\rho)_{ij} = 1, \quad i, j = 1 \text{ to } w + 1;$$

$$(\mathbf{T}_A)_{ij} = \begin{cases} 1, & i - j \geq 0, \\ 0, & i - j < 0; \end{cases} \quad (9)$$

$$(\mathbf{T}_B)_{ij} = \begin{cases} 1, & i + j \leq w + 2, \\ 0, & i + j > w + 2. \end{cases}$$

For the larger matrices, here the eigenproblem is conveniently implemented on a computer. Generally, the eigenvalues here should be nondegenerate, as in the  $p \rightarrow 1$  limit [5].

A few qualifications, especially as relate to chemical relevance, seem to be in order. First, if the ends of the polymer chains change, then the structure of the

present transfer matrices may change (or more properly, one changes from one block to another of a more complete transfer matrix) and thence also the whole set of eigenvalues change as well as the numerical results. This is related to a type of "long-range order" implicit in Kekulé structures, as has previously been discussed several times, together with a variety of interesting chemical consequences (see refs. [4], [5] or [6], as well as other references therein). Second, for the random-polymer case it has also been suggested [4] that finer grained classes (or equivalently, a different probability measure) should be more relevant. These classes fix the numbers of *A*- and *B*-type monomers. Then, the ensemble matrix  $\mathcal{T}$  still plays a crucial role, but although the coefficients of  $T_A$  and  $T_B$  add to 1, they play the part of (thermodynamic) *activities* rather than concentrations (or probabilities). It emerges that phase transitions occur as these activities vary for some copolymers.

Many further details may be found in ref. [4]. There is some lack of rigor and approximation too, in dealing with the finer grained ensemble. Still, the developments there are seen to directly allow rigorous solution of a more general problem than that of Gutman et al.

## References

- [1] I. Gutman and S.J. Cyvin, Chem. Phys. Lett. 147(1988)121.
- [2] I. Gutman, Graph Theory Notes 15(1989)26.
- [3] I. Gutman, J.W. Kennedy and L.V. Quintas, J. Math. Chem., this issue.
- [4] D.J. Klein, T.P. Živković and N. Trinajstić, J. Math. Chem. 1(1987)309.
- [5] G.E. Hite, A. Metropoulos, D.J. Klein, T.G. Schmalz and W.A. Seitz, Theor. Chim. Acta 69(1986)369.
- [6] D.J. Klein, T.P. Živković and R. Valenti, Phys. Rev. B43(1991)723.