J Math Chem (2014) 52:1–5
DOI 10.1007/s10910-013-0263-3

BRIEF COMMUNICATION

Note on the asymptotic isomer count of large fullerenes

Jerzy Cioslowski

Received: 17 July 2013 / Accepted: 7 September 2013 / Published online: 22 September 2013

Abstract The leading term in the large-N asymptotics of the isomer count of fullerenes with N carbon atoms is extracted from the published enumerations for $N \leq 400$ with the help of methods of series analysis. The uncovered simple N^9 scaling is distinct from isomer counts of most classes of chemical structures that conform to mixed exponential/power-law asymptotics. The second leading asymptotic term is found to be proportional to $N^{25/3}$. A conjecture concerning isomer counts of the IPR fullerenes is also formulated.

Keywords Fullerenes · Isomer count · Series analysis

1 Introduction

Recent advances in graph-theoretical algorithms have opened new vistas for enumeration of chemical isomers. In particular, significant progress has been achieved in the case of fullerenes C_N, of which all structures with $N \leq 400$ have now been generated [1,2]. The availability of these data has prompted speculations concerning the behavior of the fullerene isomer counts at the $N \to \infty$ limit, both the N^9 [3] and $N^{19/2}$ [4] asymptotics being inferred from crude log–log plots and supported by heuristic arguments. For the reason spelled out in the following, this simple power-law scaling appears unlikely at the first glance.

J. Cioslowski (✉)
Institute of Physics, University of Szczecin, Wielkopolska 15, 70-451 Szczecin, Poland
e-mail: jerzy@wmf.univ.szczecin.pl

J. Cioslowski
Max-Planck-Institut für Physik komplexer Systeme, Nöthnitzer Str. 38,
D-01187 Dresden, Germany

Complete information about isomer counts for a class of chemical species is encoded in the generating function $F(t)$ given by the for formal series

$$F(t) = \sum_{k=1}^{\infty} M(k)\, t^k, \tag{1}$$

where $M(k)$ is the number of isomers comprising k units (such as atoms, bonds, rings, etc.). Since, in general, $M(k+1) \geq M(k)$ for all $k > 0$, the series (1) possesses a finite radius of convergence. Consequently, $F(t)$ possesses at least one singular point, at which it behaves like $(t_c - t)^{\zeta_c}$, where $0 < t_c \leq 1$. The smallest critical point t_c and the corresponding critical exponent ζ_c determine the leading term in the large-k asymptotics of $M(k)$, which reads

$$M(k) = A\, t_c^{-k}\, k^{-(\zeta_c+1)} + \cdots , \tag{2}$$

where A is a constant. Typically, $t_c < 1$ (e.g. ca. 0.35518 for alkanes [5], ca. 0.20915 for polyenes [5], and $\frac{1}{5}$ for catafusenes [5–7]), giving rise to the mixed exponential/power-law asymptotics (2). On the other hand, the alleged power-law scaling of the fullerene isomer counts would imply $t_c = 1$.

In order to investigate this matter, in this note we invoke the mathematical formalism of series analysis that is commonly used in lattice statistics [8]. Such a formalism has been previously employed in successful extraction of the asymptotic isomer counts of several classes of chemical structures [5].

2 Series analysis

Let $M(k)$ be the number of isomers of the C_{2k} fullerene. Let $U_0 = 1$, $W_0 = 0$, and $\{U_k,\ k = 1, \ldots m\}$, $\{V_k,\ k = 0, \ldots m\}$, $\{W_k,\ k = 1, \ldots m\}$ be the solution of the system of equations

$$\sum_{j=0}^{m} \left[U_j\,(k-j)^2 + V_j\,(k-j) + W_j \right] C_{k-j} = 0, \quad k = 1, \ldots, 3m-2, \tag{3}$$

where

$$C_k = \begin{cases} M(k+n) & \text{for} \quad k \geq 0 \\ 0 & \text{for} \quad k < 0 \end{cases}. \tag{4}$$

Let

$$Q(z) = z \sum_{k=0}^{m} U_k\, z^k \tag{5}$$

and

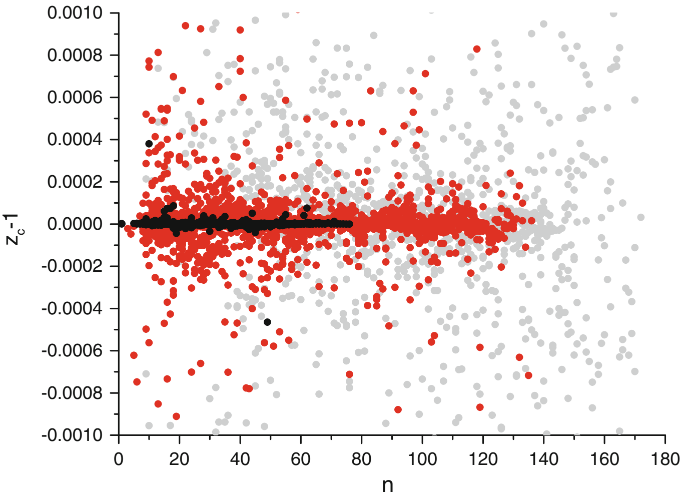

Fig. 1 The deviations of the estimates z_c from 1 versus n for $1 \leq m \leq 20$ (*gray*), $21 \leq m \leq 40$ (*red*), and $41 \leq m \leq 66$ (*black*) (Color figure online)

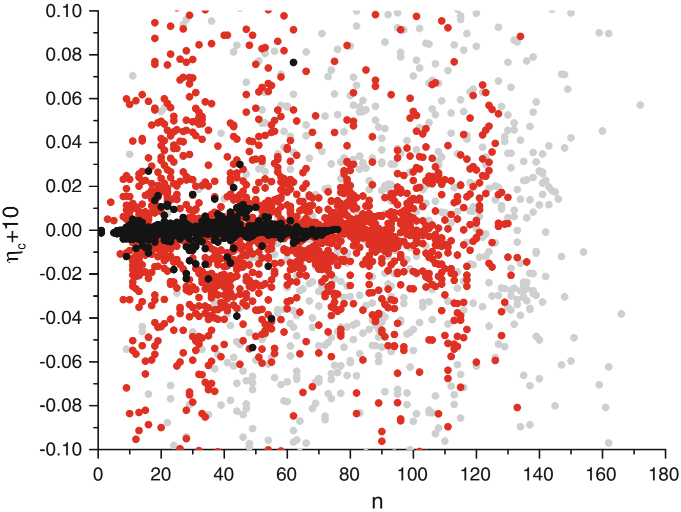

Fig. 2 The deviations of the estimates η_c from -10 versus n for $1 \leq m \leq 20$ (*gray*), $21 \leq m \leq 40$ (*red*), and $41 \leq m \leq 66$ (*black*) (Color figure online)

$$R(z) = \sum_{k=0}^{m} (U_k + V_k)\, z^k. \tag{6}$$

The smallest positive root z_c of $Q(x)$ and the quantity $\eta_c = 1 - R(z_c)/Q'(z_c)$ yield unbiased estimates for t_c and ζ_c, respectively [5,8]. In general, the accuracy of these estimates increases with both n and m.

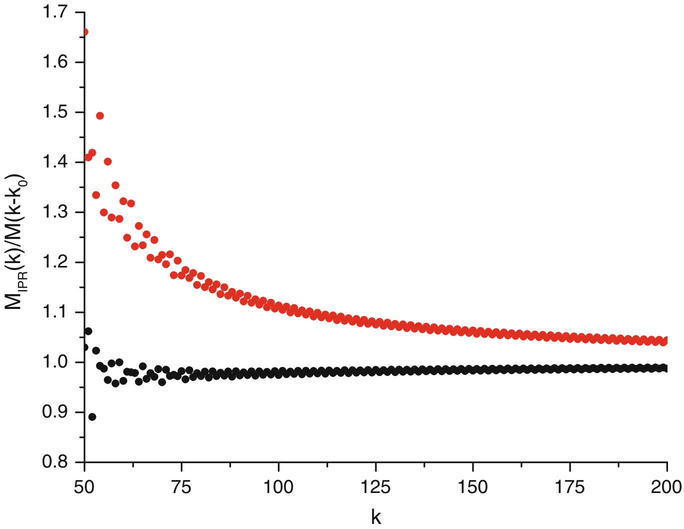

Fig. 3 The ratios $M_{IPR}(k)/M(k-k_0)$ for $k_0 = 24$ (*red*) and $k_0 = 25$ (*black*) (Color figure online)

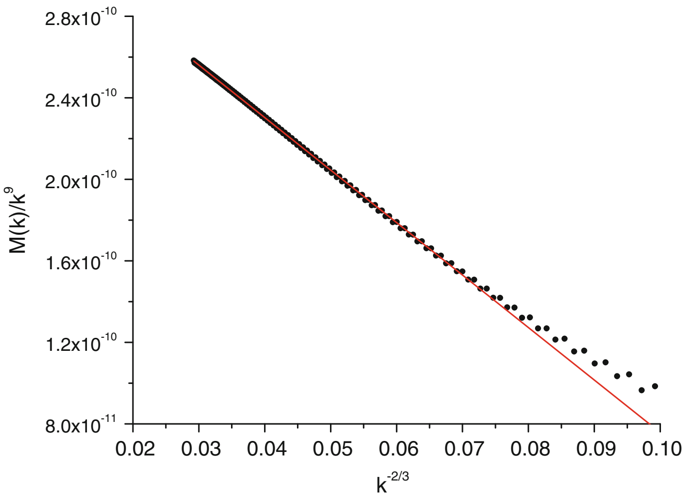

Fig. 4 The reduced isomer count $M(k)/k^9$ versus $k^{-2/3}$

3 Results and conclusions

Application of the aforedescribed formalism to the isomer counts reported in Ref. [1] produces estimates that clearly converge to $t_c = 1$ (Fig. 1) and $\zeta_c = -10$ (Fig. 2). Thus, the leading term proportional to N^9 in the large-N asymptotics of the isomer count of fullerenes with N carbon atoms is now firmly established (although not rigorously proven).

The present result imposes the same asymptotics for the isomer count $M_{IPR}(k)$ of the IPR fullerenes with $2k$ carbon atoms as $0 < M_{IPR}(k) < M(k)$ and $\lim_{k\to\infty} M_{IPR}(k)/M(k) \to 1$. Curiously, inspection of the published data [1] allows one to formulate the following conjecture (see Fig. 3):

For all $k > 53$, $M(k-24) < M_{IPR}(k) < M(k-25)$, i.e. for all $N > 106$, the number of the IPR fullerene isomers with N carbon atoms is bracketed by the total numbers of isomers of the C_{N-50} and C_{N-48} fullerenes.

The second leading term in the large-k asymptotics of $M(k)$ is also of interest. As revealed by the plot of $M(k)/k^9$ versus $k^{-2/3}$ (Fig. 4), this term scales simply as $k^{25/3}$ and is negative. The combination of the N^9 and $N^{25/3}$ asymptotics explains the apparent $N^{19/2}$ scaling deduced from a crude log–log plot [4].

Acknowledgments The author acknowledges funding from MPI PKS Dresden.

References

1. G. Brinkmann, J. Goedgebeur, B.D. McKay, J. Chem. Inf. Model. **52**, 2910 (2012)
2. G. Brinkmann, A.W.M. Dress, J. Algorithms **23**, 345 (1997)
3. P. Schwerdtfeger, L. Wirz, J. Avery, J. Comput. Chem. **34**, 1508 (2013)
4. D.J. Klein, T. Doslić, Personal communication, Dubrovnik (2013)
5. J. Cioslowski, Theor. Chim. Acta **76**, 47 (1989)
6. I. Gutman, Z. Naturforsch. **41a**, 1089 (1986)
7. F. Harary, R.C. Read, Proc. Edinb. Math. Soc. Ser. II **17**, 1 (1970)
8. A.J. Guttmann, G.S. Joyce, J. Phys. A Gen. Phys. **5**, L81 (1972)