Letters

On the calculation of a limit for infinite systems from data on finite systems

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Abstract. We propose a mathematical model for the calculation of physical or chemical properties of infinite polymers, based on data for structurally closely related finite molecules. The modelling is phenomenological but permits a physical interpretation of the parameters involved in the equations.

Key words: Polymers – Benzenoids – Resonance – Conjugation

1 Introduction

Recently, Randić et al. [1] presented a comparative study of several families of large, structurally related benzenoid hydrocarbons with increasing numbers of fused benzene rings. They tried to determine how large a finite molecule must be in order to model infinite polymeric structures and how terminal groups influence local properties in the central part of the molecule as it approaches the limit of an infinite system. Their main concern was how to extract highly accurate limiting values for certain molecular properties from limited data on smaller members of the same family.

To obtain the limiting values several fitting functions were employed to model the properties in question, e.g. the ratios R_1/nK and R_2/nK where R_1 and R_2 are the counts of six- and ten-membered conjugated circuits in a molecule, respectively, K is the number of Kekulé valence structures in the molecule and n is the number of carbon atoms. They studied how to fit R_1/nK and R_2/nK, for smaller members of the family, to certain functions in order to extract the limiting values of those quantities when the number of fused rings goes to infinity. The most successful function was that given as a polynomial expansion in inverse powers of N (the number of fused benzene rings) which for R_1/nK is given by

$$R_1/nK = c_0 + \frac{c_1}{N} + \frac{c_2}{N^2} + \frac{c_3}{N^3} + \cdots . \tag{1}$$

For a third-degree polynomial fit: $c_0 = 0.15647218$, $c_1 = 0.00245947$, $c_2 = -0.00079578$ and $c_3 = 0.00019747$.

The limiting value of R_1/nK, obtained when $N \to \infty$ is 0.15647218, which can be compared to the exact value of 0.15647203. It was found that better accuracy could be obtained by including higher powers of $1/N$ in Eq. (1). In fact, a quintic polynomial in $1/N$ reproduces the exact value before numerical oscillations affect the fitting to higher-degree polynomials. Several other procedures were also tried, i.e. a geometric series and an orthogonal curve fitting [1].

In this article we present another phenomenological model which accurately reproduces the limiting value of R_1/nK and whose parameters can be interpreted in terms of contributions of the different parts of the molecule. The fittings were done by the Marquardt-Levenberg method [2, 3]. Furthermore, a mathematical interpretation of that model and of Eq. (1) in terms of Padé approximants is presented.

2 Expansion of R_1/nK in inverse powers of an effective N

In this section we modify Eq. (1) to obtain a better convergence with fewer terms. Consider a new or "effective" number of fused benzene rings $\overline{N}$ given by

$$\overline{N} = N - a , \tag{2}$$

here a is the shift parameter to improve the convergence properties of Eq. (1). It is obtained by forcing the second-order term in the expansion of R_1/nK in powers of $1/\overline{N}$ to vanish.

By rearranging Eq. (1) in terms of $\overline{N}$, expanding in inverse powers of $\overline{N}$ and retaining terms up to $\overline{N}^{-3}$ we obtain

$$R_1/nK = c_0 + \frac{c_1}{\overline{N}} + \frac{(c_1 a - c_2)}{\overline{N}^2}$$
$$+ \frac{a^2 c_1 - 2a c_2 + c_3}{\overline{N}^3} + \cdots . \tag{3}$$

The shift parameter a can now be obtained by forcing the coefficient in $\overline{N}^{-2}$ to zero, i.e.

$$a = \frac{c_2}{c_1} \quad . \tag{4}$$

Thus, a good representation of R_1/nK must be

$$R_1/nK = c_0 + \frac{c_1}{N - \frac{c_2}{c_1}} + \frac{c_3 - c_2^2/c_1}{\left(N - \frac{c_2}{c_1}\right)^3} \tag{5}$$

or, numerically, using Eq. (1)

$$R_1/nK = 0.15647218 + \frac{0.00245947}{N + 0.323558} - \frac{6.00106 \ 10^{-5}}{(N + 0.323558)^3} \quad . \tag{6}$$

A direct fitting of the first 12 data points given in Table 2 of [1] to Eq. (5) produces

$$R_1/nK = 0.1564741 + \frac{0.0024388}{N + 0.3119694} \quad , \tag{7}$$

with two terms, and

$$R_1/nK = 0.1564742 + \frac{0.0024381}{N + 0.3119694} + \frac{1.2381843 \times 10^{-6}}{(N + 0.3119694)^3} \tag{8}$$

with three terms.

It is seen that both Eq. (7), and Eq. (8) give excellent results for the limiting value when N goes to infinity as well as giving a finite value when N goes to zero. Also, it can be shown that Eq. (8) gives an excellent reproduction of the data for finite N.

One could ask why such a rearrangement of terms in Eq. (1) into Eq. (5), or the direct fitting to Eq. (5), gives such excellent results. The reason has to do with the fact that Eq. (5) effectively represents a resummation of Eq. (1) and as such must be related to a Padé approximant of a certain order. The excellent numerical accuracy that can be obtained by representing a few terms of a series by a low-order Padé approximant is well known [4]. To prove this let us construct a [1/1] Padé approximant for Eq. (1). This is given in [4] as

$$[1/1] = \frac{a_0 + a_1 N}{b_0 + b_1/N} \quad . \tag{9}$$

The coefficients a_0, a_1, b_0 and b_1 are given in terms of c_0, c_1 and c_2 by $a_0 = c_0$, $a_1 = c_1 - c_0 c_2/c_1$, $b_0 = 1$ and $b_1 = -c_2/c_1$. Thus, Eq. (9) becomes

$$[1/1] = \frac{c_0 + (c_1 - c_0 c_2/c_1)(1/N)}{1 - (c_2/c_1)(1/N)} \quad , \tag{10}$$

or, numerically, using Eq. (1)

$$[1/1] = \frac{0.15647218 + 0.0530872/N}{1 + 0.323558/N} \quad . \tag{11}$$

It is easy to show that on keeping the first two terms, Eq. (5) is the same as Eq. (10). These results suggest that it is better to fit the data directly to Padé approximants instead of transforming the series in $1/N$ first. A direct

fitting of the 12 data points for R_1/nK in [1] to a [1/1] Padé approximant yields the following result

$$[1/1] = \frac{0.1564741 + 0.0512539/N}{1 + 0.3119690/N} \quad . \tag{12}$$

3 A physical interpretation

It is interesting to mention that Smittenberg and Mulder [5] used an empirical function similar to Eq. (5) to represent physical properties (refraction index, density, etc.) of hydrocarbons belonging to a homologous series, i.e.

$$x = x_\infty = \frac{k}{n + z} \quad , \tag{13}$$

where x represents the physical constant of a hydrocarbon containing n carbon atoms, x_∞ is the limit of the physical constant at an infinite number of carbon atoms, and k and z are empirical constants, characteristic for the series. Later, Fortuin [6] derived a physical interpretation of k and z. In this study we adapt Fortuin's argument and apply it to derive a physical interpretation of the constants in Eq. (5). It will be evident from what follows that the interpretation is based on the conversion of the data to Padé approximant functional forms.

R_1/nK is the quotient of two molecular values, let us call them p and q, and they depend linearly on N, the number of repeating units in a finite molecule. Then

$$R_1/nK = \frac{p}{q} = \frac{Np_1 + p_0 + p'}{Nq_1 + q_0 + q'}$$
$$= \frac{p_1/q_1 + \frac{p_0/q_1}{N} + \frac{p'/q_1}{N}}{1 + \frac{q_0/q_1}{N} + \frac{q'/q_1}{N}} \quad , \tag{14}$$

where p_0 and q_0 denote the contributions by end groups, p_1 and q_1 the contributions by the repeating unit, and p' and q' are the nonlinear contributions which become negligible as higher terms of the series are considered.

From Eq. (14) we obtain

$$R_1/nK = \frac{p_1}{q_1} + \frac{p_1}{q_1} \frac{\frac{p_0 + p'}{p_1} - \frac{q_0 + q'}{q_1}}{\frac{q_0 + q'}{q_1} + N} \quad . \tag{15}$$

Now, let us make

$$\frac{p_1}{q_1} = R_1^\infty, \frac{p_0 + p'}{p_1} = \alpha' \quad \text{and} \quad \frac{q_0 + q'}{q_1} = \beta' \tag{16}$$

and substitute in Eq. (15) to obtain

$$R_1 = R_1^\infty + \frac{(\alpha' - \beta')R_1^\infty}{\beta' + N} \quad , \tag{17}$$

where α' and β' represent the ratio of the contribution by the end groups to the contribution of the repeating unit. Equation (17) has the same form as Eq. (5).

Neglecting the nonlinear contributions p' and q', we obtain from Eq. (17)

$$N = \beta \frac{R_1^0 - R_1}{R_1 - R_1^\infty} \quad , \tag{18}$$

where

$$R_1^0 = \frac{p_0}{q_0} \quad . \tag{19}$$

Thus, R_1^0 is related to the end groups and R_1^∞ to the repeating unit. Equation (18) shows that β can be considered as the number of repeating units per molecule of a polymer having a R_1 of $(R_1^0 + R_1^\infty)/2$. Using Eqs. (7) and (19) we obtain $R_1^0 = 0.1642916$, $R_1^\infty = 0.1564741$ and $\beta = 0.3119694$.

4 Conclusions

In this work we have presented a formula which permits the molecular properties of an infinite polymer to be obtained from a few known values for finite systems composed of the same repeating unit. Benzenoid polymers were studied using data recently published by Randić et al. [1]. They showed that for large systems an expansion in powers of $1/N$, where N is the number of the repeating unit, parallels the mixed power-geometric expansion, which is the natural expansion in the calculation of the conjugated-circuit resonance energy per electron. However, in the study of other properties such as melting point, viscosity, etc., we do not know the analytical dependence. Thus, an expansion in inverse powers of an effective number of repeating units, such as the one introduced in this article, could prove useful for the determination of properties of infinite systems, starting from a few known values for finite systems.

Our approach, based on Padé approximants, also clarifies some previous findings in the literature. Indeed, the molecular interpretation given by Fortuin of the formula introduced by Smittenberg and Mulder, Eq. (13) in the present paper, can now be understood simply as a resummation of an expansion of a molecular property of a large system in inverse powers of the number of repeating units of the system.

We think that our results are important for the study of other properties of polymers because even though we are dealing with phenomenological modelling, a physical interpretation of the terms involved in the equations can be given. In the case of experimentally determined values of physical constants, the use of the so-called statistical Padé approximants [7] should prove to be more suitable to represent the dependence of physical quantities of large polymers on inverse powers of the number of repeating units.

References

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