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Scale-invariant power law and fractality for molecular weights

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Abstract

The fractal ideas of Mandelbrot are extended to the systematics of molecular weights of chemical compounds. A scale-invariant power law for molecular weights is introduced and exemplified for a randomly selected set of molecules and their dependence on effective molecular number. It is also shown that the isotopic composition of chemical compounds is characterized by a fractal pattern, which extends over the range of more than two orders of magnitude. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Concepts of atomic and molecular weights are fundamental to chemistry. The atomic weight of a naturally occurring chemical element is the average of isotopic weights, weighted to take into account relative abundances of isotopes [1,2]. Consequently, the molecular weight of a chemical compound can be considered as a weighted average of the isotopic weights of all isotopic configurations (combinations of nuclides) corresponding to the chemical formula of the compound.

Here we extend the fractal ideas of Mandelbrot [3] to a description of the molecular weights of chemical compounds. The concept of fractal geometry, closely linked to scale invariance, provides a framework for the analysis of natural phenomena in various scientific domains [3–6]. Fractal structures have been discussed in such diverse fields as critical phenomena, particle trajectories, waves, biological organisms, landscapes, coastlines, mountains, rivers, rocks, metals, composite materials, polymers, gels, etc., on a wide range of scales from microscopic to astronomic [3–6].

In some cases the fractal properties of natural objects are hidden and can only be perceived if data are studied as a function of time or mapped in some special way [7], as for example, reactions in heterogeneous chemistry [8], chromatin texture in benign and malignant breast cells [9], fractal properties of fetal breathing dynamics [7], basal metabolic rate in biological organisms [10], etc.

There have been many specific applications of the fractal-geometry concept to chemistry (see, for example, [11–24]). For example, fractals have found a wide range of applications in the studies of colloidal aggregation phenomena [11–14], in proposing a new class of benzenoid hydrocarbons named fractal benzenoids [16,17], in the structure of branched macromolecules and sol–gel transitions [18], in the description of the reaction dimension [21] and applications of that concept in pharmacology and catalysis [6,22], etc. In many of

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these cases fractality is related to the corresponding power laws.

In this Letter we address the following question: To what extent is it possible to extend the concept of fractality to the molecular level, and in particular, can one trace the fingerprints of fractality in the systematic behaviour of molecular weights?

2. Power law for molecular weights

The distribution of stable nuclides in the A,Z-chart and of their natural abundances hints at fractality and at a scale-invariant power law for atomic weights [25]:

$$A_{\mathrm{r}} = \alpha_{\mathrm{c}} Z^{\beta_{\mathrm{c}}}. \tag{1}$$

We find that Eq. (1) provides a good fit of the data on atomic weights [1] with the power law exponent $\beta_{\mathrm{c}} = 1.120$.

The atomic power law (1) provides a good phenomenological description of atomic weights. On the other hand, the power law captures something about the internal structure of the object. We have shown that the well-known theoretical formula obtained by minimizing nuclear mass in the droplet model formula, $A - 0.006A^{5/3} = 2Z$ [26], approximately corresponds to the atomic power law (1). This is seen from the fit of both formulae to the systematics of stable chemical elements: the χ^2 value in the log–log plot for a fit to the droplet model formula is $\chi^2 = 0.007$, while the fit to the atomic power law (1) gives $\chi^2 = 0.004$. One might further argue whether the somewhat smaller χ^2 value for the power law formula is of some significance, being related to an underlying fractality of the corresponding quantum mechanical dynamics.

Let us now consider a molecule:

$$(\mathrm{E}_1)_{n_1}(\mathrm{E}_2)_{n_2}\cdots(\mathrm{E}_s)_{n_s} \tag{2}$$

consisting of n_i atoms of chemical element E_i with atomic number Z_i ($i = 1,2,\ldots,s$), and $\sum_i n_i = n$. Using the atomic power law (1), we can express the molecular weight of the molecule (2) as

$$M_{\mathrm{r}} = \alpha_{\mathrm{c}} \sum_i n_i Z_i^{\beta_{\mathrm{c}}}. \tag{3}$$

Let us now introduce the molecular power law

$$M_{\mathrm{r}} = \alpha Z_{\mathrm{eff}}^{\beta}, \tag{4}$$

where Z_{eff} denotes a parameter characterizing the molecule (2), which has to be determined.

On the basis of comparison of Eq. (3) and the power law (4) the effective molecular number Z_{eff} is defined by

$$Z_{\mathrm{eff}} = \left(\sum_i n_i Z_i^{\beta_{\mathrm{c}}}\right)^{1/\beta_{\mathrm{c}}}, \tag{5}$$

where $\beta = \beta_{\mathrm{c}}$ is used. Let us take $\beta_{\mathrm{c}} = 1.120$ from the fit of Eq. (1) to the data on atomic weights. (We note that because of the power law functions in Eqs. (3) and (4) similar results are obtained by considering a more general relation $\beta = k\beta_{\mathrm{c}}$, with k being an arbitrary coefficient of proportionality.)

We note that for the value $\beta_{\mathrm{c}} = 1$, Eq. (5) reduces to the sum of atomic numbers of all atoms contained in the molecule, $Z_{\mathrm{tot}} = \sum_i n_i Z_i$.

For some molecules the values of Z_{eff} and Z_{tot} differ sizeably, by up to $\approx$50%. For example, for the molecule $\mathrm{H_5BW_{12}O_{40}\cdot 30H_2O}$ we obtain $Z_{\mathrm{eff}} = 995$, $Z_{\mathrm{tot}} = 1518$.

Let us now consider the log–log plot for molecular weights M_{r} and their dependence on Z_{eff} for a random set of molecules (190 chemical com-

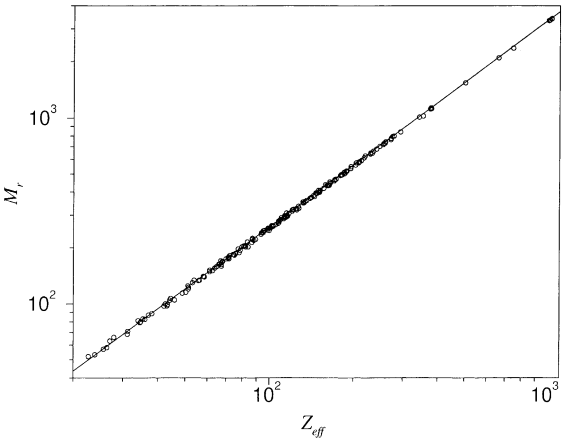

Fig. 1. Log–log plot of data points for molecular weights of 190 randomly selected inorganic compounds [27] as a function of the effective molecular number Z_{eff} (open circles). The straight line is a fit of the power law (Eqs. (4) and (5)) to data ($\sum_i n_i Z_i > 20$).

pounds chosen randomly from [1]). For each chemical compound the corresponding data point is displayed (open circles in Fig. 1).

In the next step, a fit of the power law (4) to these data points is performed (solid line in Fig. 1). Very good fit was obtained with

$$\alpha = 1.55 \pm 0.03, \qquad \beta = 1.113 \pm 0.002, \tag{6}$$

indicating applicability of the power law (4) to molecular weights.

To gain a better insight into the quality of the power law (4) in fitting molecular data in the M_r vs. Z_{eff} diagram, we have considered, for comparison, a diagram displaying M_r and their dependence on the total proton number Z_{tot} (Fig. 2). The scatter of data points in the M_r vs. Z_{tot} diagram in Fig. 2 is much larger (the χ^2 value is 18 times larger) than in the M_r vs. Z_{eff} diagram in Fig. 1. (Here, $\chi^2 = (1/n)\sum_i [\ln M_r(i) - (\ln\alpha + \beta \ln Z_{eff}(i))]^2$).

In order to test the consistency of the fitted values (6) let us consider an alternative fitting procedure. Instead of using the fitted value of β_c to calculate Z_{eff} for the construction of data points in the M_r vs. Z_{eff} diagram, let us start with a set of uniformly distributed initial values of β_c. For each initial value of β_c we calculate the corresponding Z_{eff} value using Eq. (5), and the corresponding M_r vs. Z_{eff} diagram is constructed. Then, the fit of the power law (4) is performed to the data points in each of these diagrams. For each initial value of β_c the fitted value of β and the corresponding χ^2 value were determined. Fig. 3a displays χ^2 and Fig. 3b the power law exponent β and their dependence on initial values of β_c. As seen, the best fit is obtained for $\beta_c \approx 1.1$ (Fig. 3a), in accordance with the value (6).

The molecular power law (4) holds only for a finite scaling window. More stringently, the semi-empirical droplet model of nuclei is not a very good fit for light nuclei. Thus, one can expect that, in the regime of molecules consisting of very light nuclei only, the power law is less appropriate. This

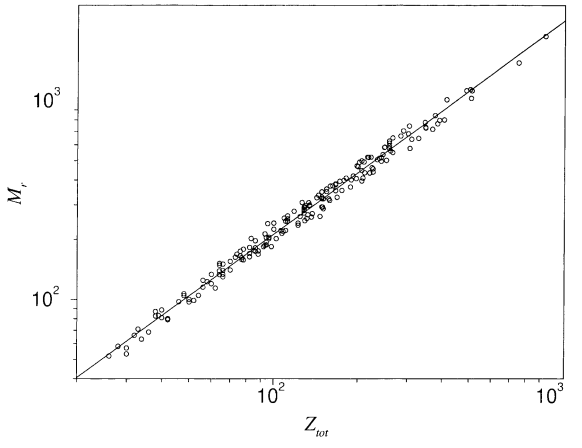

Fig. 2. Log–log plot of data points as a function of the total proton number Z_{tot} (open circles).

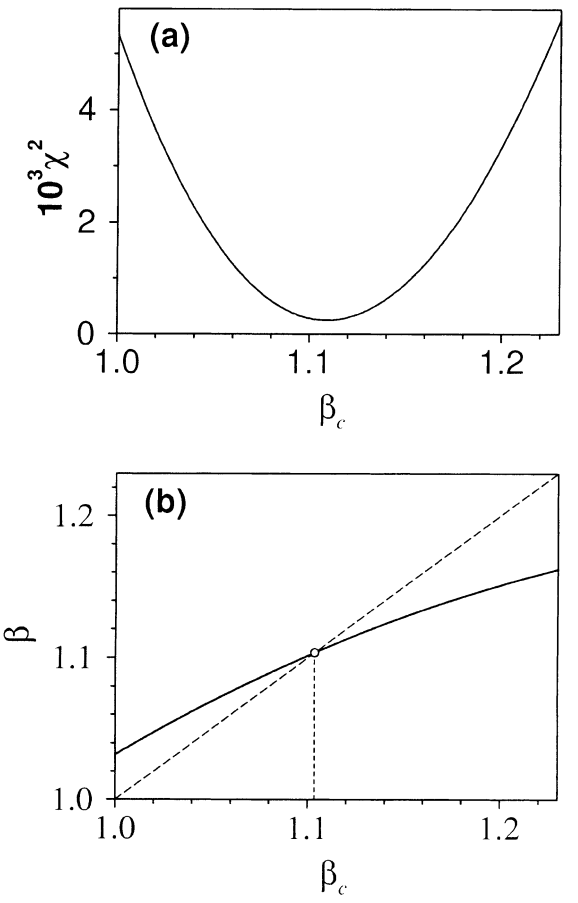

Fig. 3. Test of fit of the power law (4) for the M_r vs. Z_{eff} diagrams constructed for Z_{eff} values corresponding to a set of uniformly distributed initial values of β_c. For each initial value of β_c the corresponding Z_{eff} value was calculated using Eq. (5). (a) χ^2 value as a function of the initial value β_c. (b) Fitted values of β as a function of the initial values of β_c.

is seen by a more careful analysis to find the regime where the atomic power law (1) holds, comparing deviations of atomic weights from the atomic power law formula. In the log–log plot the χ^2 value for deviation of the atomic power law (1) from data for all stable elements is $\chi^2 = 0.004$ while, excluding the five lightest elements from the fit, a sizeably lower χ^2 value of 0.0005 was obtained, i.e., a sizeably better fit.

3. Fractality of the molecular isotopic abundance set

The appearance of the power law is often related to a kind of underlying fractality [3–7]. Thus, the empirical power law (4) may indicate the presence of fractal features associated with the molecular weights. We have detected evidence of fractality by investigating the isotopic composition of each chemical compound. The isotopic composition of the chemical compound (2) is obtained by taking into account that each chemical element E_i, contained in the molecule, is composed of t_i different stable isotopes. Thus the number of different isotopic configurations associated with the molecule (2) is

$$N = \prod_i \binom{t_i + n_i - 1}{n_i}, \tag{7}$$

where ( ) denotes the binomial coefficient.

Already for small molecules the total number of isotopic configurations is sizeable. For example, for Sb_2Se_3 ($n_1 = 2,\ t_1 = 2;\ n_2 = 3,\ t_2 = 6$) Eq. (7) gives $N = 168$ isotopic configurations. For a more complex molecule $Nd(C_{11}H_{12}H_2O)_6(ClO_4)_3$ the total number of different isotopic configurations is $N = 1\,302\,788\,200$.

The isotopic abundance of each isotopic configuration in a chemical compound is calculated by multiplying isotopic abundances of the constituent nuclides. For example, the isotopic abundance of the isotopic configuration $^{121}Sb^{123}Sb^{78}Se^{80}Se^{80}Se$ of the chemical compound Sb_2Se_3 is $0.573 \times 0.427 \times 0.235 \times 0.496 \times 0.496 = 0.014$.

To each chemical compound (2) we assign a set of the corresponding isotopic abundances (isotopic abundance set). Let us display these values along the coordinate axis. We find that this set of abundances is fractal for each chemical compound. Its fractal dimension is calculated by using the box counting method [4,5]. As an illustration, in Fig. 4 we display the $\log N_i$ vs. $\log(1/\epsilon_i)$ diagram for the molecule Sb_2Se_3. This set is approximately fractal over a range of more than two orders of magnitude, which is more than for most of the reported fractal objects in nature [28]. The calculated fractal dimension is $d_f \approx 0.4$, clearly revealing fractality. (In the case of a uniformly or randomly distributed set of points on the coordinate axis, the calculated dimension should be 1, showing the absence of fractality.)

Displaying isotopic abundance sets of different compounds, a combined set is obtained with an overall fractal dimension. This situation could be formally compared with, for example, the determination of the fractal dimension of families of asteroids, where the fractal dimension of the size distribution was calculated for some asteroid families and on the basis of the cumulative size distributions an overall fractal dimension was obtained [29].

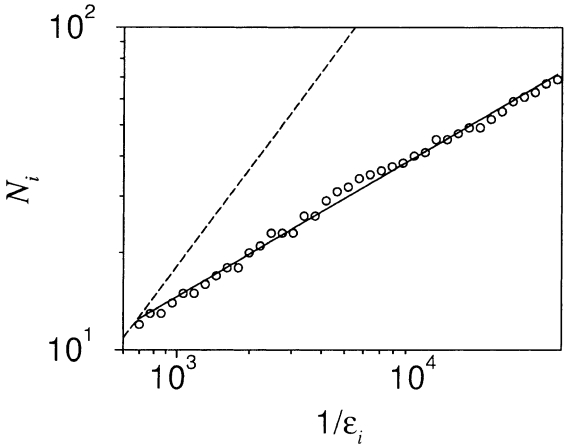

Fig. 4. Log–log plot for the number of nonempty boxes N_i vs. $1/\varepsilon_i$ (ε_i is the size of a grid box) overlaying the set of points displaying isotopic composition of the chemical compound Sb_2Se_3 along the coordinate axis. The straight line is fitted through the points calculated at several values of the box size ε_i and corresponds to the fractal dimension of 0.4. For comparison, the line corresponding to a dimension of 1 is presented (dashed line).

4. Conclusion

In this Letter we have introduced the power law for molecular weights and displayed the fractality of isotopic abundances of chemical compounds.

It is well known that a power law is often connected with an underlying fractality of the system [4,5]. Examples of such relations are the power law dependence of basal metabolic rate on the mass of mammals and the fractal structure of organs [11], power law distribution of drainage-basin area and fractal dimension of a river network [30], power law for X-ray scattering by rat lens nucleus which may be evidence of fractal structures in the lens [31], etc.

Power laws have been found also in cases without being related to an underlying fractality. For example, a power law dependence on molecular weights was found experimentally for interactions between polyethylene oxide layers adsorbed on glass surfaces [32], for stretching ridges in a crumpled elastic sheet [33], etc.

It was recently pointed out that the scaling range of experimentally declared fractality is extremely limited, spanning mainly between 0.5 and 2.0 decades (factors of 10), while the exact fractals exhibit fractality over all scales [28]. On this basis it might be questionable if the limited-range power law objects in nature are fractal. On the other hand, regardless of that the result of resolution analysis is often a very useful power law, which condenses the description of a complex fractal geometry and allows one to correlate in a simple way properties of a system to its structure [28].

Relating natural objects to truncated fractals instead of exact fractals may shed more light on this question. For example, basin boundaries of some dynamical systems can be both statistically scale-invariant fractals and restricted to a certain range of scales [34,35].

One may ask whether the molecular power law can be traced back to the power law of nuclei. One thing is certain, namely that, because of small electron energies, the molecular power law is determined by the nuclear composition. However, we also point out that the molecular power law can nevertheless be of chemical significance because of its close resemblance to the laws governing critical properties of assemblies of molecules [12,13].

We are also opening an interesting question as to whether the power law for isotopic abundances can also be derived from the dynamics of the droplet model, or from some other model. In the present formulation, the molecular power law is dominated by the most abundant isotopes, while the influence of less abundant isotopes is accounted for as a gross effect.

Another point with regard to the fractality of natural objects is related to the question of identifying dynamics which gives rise to fractality. In this connection regarding the molecular power law, we note that the role of fractal geometry in quantum physics and quark dynamics was recently reviewed [36]. It was pointed out that the fractal geometry, which shows up in particular observables, is generated by the dynamics of the quantum system, the first example of fractal geometry in quantum systems being invoked in describing the self-similarity of paths occurring in the Feynman path integral method. It was also shown that velocity-dependent interactions, which appear in the theory of nuclear matter, lead to a noninteger dimension and that the fractal dimension appears for the free fermion propagator which is relevant for the geometry of quark propagation in quantum chromodynamics [36]. This may be relevant to the appearance of scale invariance at the atomic level.

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