Applications of path integrals in ideal polymer chains

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Introduction

Path integrals have a natural application to polymer problems as the path is exactly the polymer. As a result, the mathematics of summing up all possible paths can be more intuitively understood. The ideal polymer chain is a path of fixed length containing N monomers of length l. This is simpler than free particle path integral problems, where all possible paths of any length must be considered.
The most successful application of these techniques has been in solving problems of knots, links and macromolecule entanglement. [2]

Random walk model

The simplest approach to polymer problems is the random walk model. Each monomer is able to rotate freely in space relative to the previous monomer, with no preference for any orientation. Therefore the vector **R** end to end distance can be calculated via a 3D random walk. The distribution function for this distance is expressed by the path integral:

$$\Psi(\mathbf{R}, N) = \int_{0,0}^{\mathbf{R},N} exp\left(-\int_0^N L d\nu\right) \mathcal{D}\mathbf{R}(\nu) \tag{1}$$

$$L = \frac{3}{2l^2}\left(\frac{d\mathbf{R}}{d\nu}^2\right) \tag{2}$$

The variable ν describes the spatial configuration of the polymer. [4]

The polymer configuration with the highest probability amplitude will be the one that minimizes the exponent (the *action*). By using calculus of variation, from this integral one can obtain the Euler-Lagrange equation and solve for **R**(N).

Despite being a crude approach, this probability distribution correctly predicts the variance and average polymer length $\sqrt{N}L$ in line with other statistical methods in the thermodynamic limit N goes to infinity.

Obstructions and Excluded Volume

The position of a polymer will be affected by spatial obstructions, such as dust, walls and the polymer itself. The random walk model can be amended to include these obstructions, by replacing L with L + f(R) in (1) according to the nature of the obstruction.

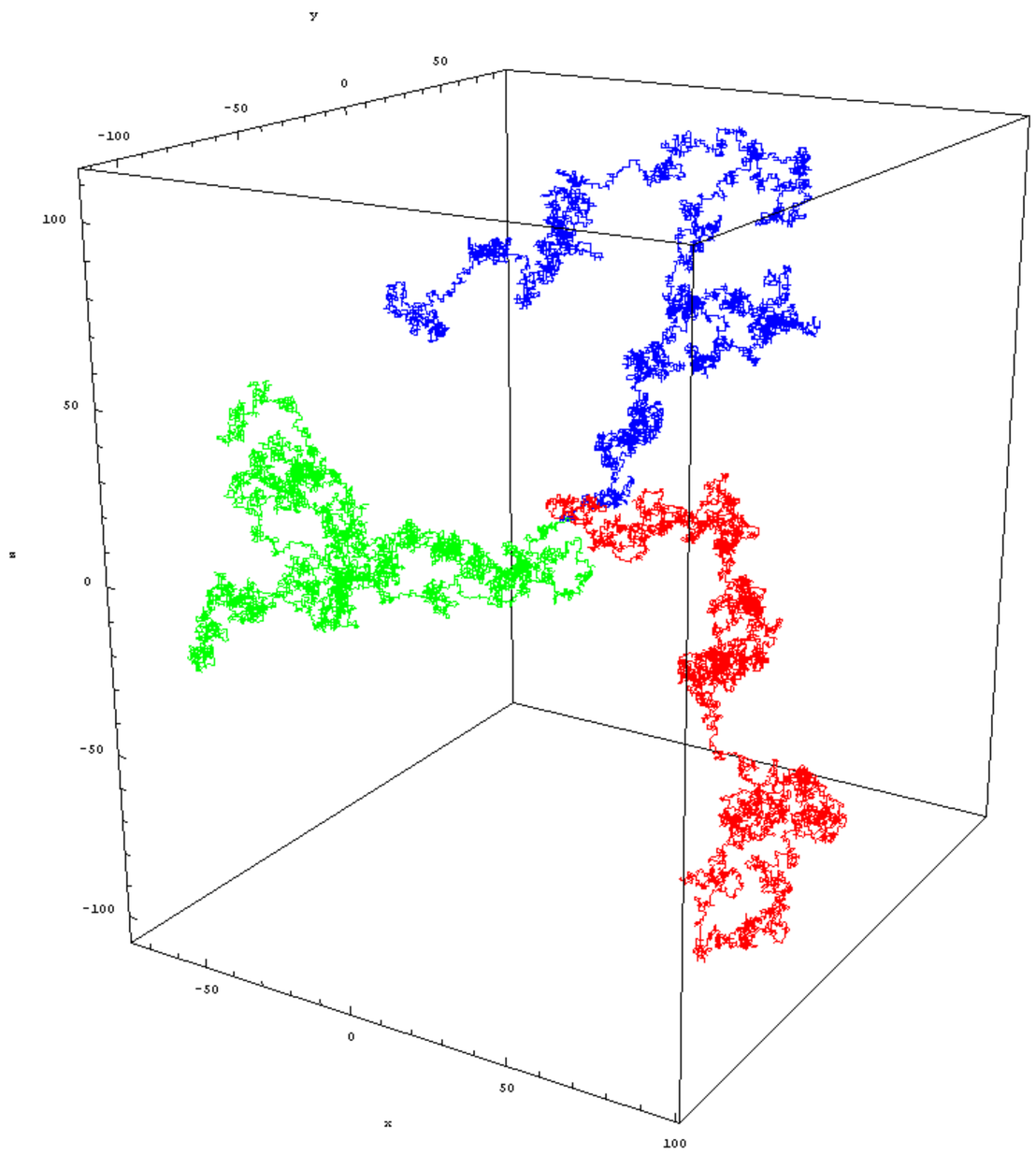
For random dust particles, f(R) is a value with range 0 to 1 denoting the fraction of space that cannot contain a monomer.

For a containing wall, $\frac{f(R)}{l^2} \to \infty$ for all forbidden regions.

For interactions within the polymer itself, each monomer is modelled as a hard sphere of radius $a < l/2$. The volume described by this sphere is then forbidden for all other monomers. The problem of calculating the sum of these non-interacting configurations is the excluded volume problem, and is unsolved. [4]

"These molecules are themselves like an incarnation of the concepts of path integration" - Wiegel

3D random walk of three particles



[5]

Wiener Integrals

Equation (1) is a Wiener integral, which also arises in the path integral formulation of the Brownian motion propagator and harmonic potentials.[3]

Path integrals are inherently probabilistic, and can be used to solve many statistical problems.

Modern research

Polymers are unique for their high tensile strength, elasticity and relevance in biological systems. A large research area is studying polymer degradation in plastics, with the aim of building materials that degrade predictably. By better understanding their behaviour on the micro scale, we investigate how to tailor these unique properties and maximize the full potential of polymeric materials. [1] Alongside computer modelling, path integrals will play a key role in this investigation.

References

[1] Stephen Z.D. Cheng. *Phase Transitions in Polymers*. 2008.

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[3] D. C. Khandekar. *Path Integral Methods and Their Applications*.

[4] Frederik W. Wiegel. *Introduction to path-integral methods in physics and polymer science*. 1986.

[5] User: Zweistein. commons.wikimedia.org, 2006.