Statistical model of a flexible inextensible polymer chain: the effect of kinetic energy

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Because of the holonomic constraints, the kinetic energy contribution in the partition function of an inextensible polymer chain is difficult to find, and it has been systematically ignored. We present the first thermodynamic calculation incorporating the kinetic energy of an inextensible polymer chain with the bending energy [1]. To explore the effect of the translation-rotation degrees of freedom, we propose and solve statistical model of a fully flexible chain of $N+1$ linked beads which, in the limit of smooth bending, is equivalent to the well-known worm-like chain model. The partition function with the kinetic and bending energies and correlations between orientations of any pair of links and velocities of any pair of beads are found. This solution is precise in the limits of small and large rigidity-to-temerature ratio b/T . The last exact solution is essential as even very "harmless" approximation results in loss of the important effects when the chain is very rigid. For very high b/T, the orientations of different links become fully correlated. Nevertheless, the chain does not go over into a hard rod even in the limit $b/T \to \infty$: while the velocity correlation length diverges, the correlations themselves remain weak and tend to the value $\propto T/(N+1)$. The N dependence of the partition function is essentially determined by the kinetic energy contribution as predicted in [2]. We demonstrate that to obtain the correct energy and entropy in a constrained system, the T derivative of the partition function has to be applied before integration over the constraint-setting variable.

References

[1] V.M. Pergamenshchik and A.B. Vozniak, Phys. Rev. E **95**, 012501 (2017).

[2] V.M. Pergamenshchik, J. Stat. Mech. P05016 (2012).