ments, all with synchrotron-radiation-like intensities but in a small lab-sized electron-energy-loss machine.

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[1] P. M. Platzman and P. A. Wolff, *Waves and Interactions in Solid State Plasmas* (Academic, New York, 1973).

[2] G. S. Brown and A. E. Meixner, to be published.

[3] Graphite sample kindly prepared from monochromator-grade pyrolytic graphite by J. Wilson, Bell Laboratories, Murray Hill, N. J.

[4] 200-Å film from The Arizona Carbon Foil Co., Tuscon, Ariz.

[5] D. L. Greenway, G. Harber, F. Bussani, and E. Tosatti, Phys. Rev. 178, 1340 (1969).

[6] S. Hagstrom and S. E. Karlsson, Ark. Fys. 26, 451 (1964).

[7] S. G. Slusky *et al.*, Phys. Rev. Lett. 36, 326 (1976); C. H. Chen and J. Silcox, Phys. Rev. B 16, 4246 (1977).

[8] P. A. Lee and G. Beni, Phys. Rev. B 15, 2862 (1977).

[9] P. H. Citrin, P. Eisenberger, and B. M. Kincaid, Phys. Rev. Lett. 36, 1346 (1976); B. M. Kincaid, P. H. Citrin, and P. Eisenberger, to be published.

[10] Carbon phase shift kindly supplied by P. A. Lee.

[11] C. Colliex and B. Jouffrey, Philos. Mag. 25, 491 (1972); J. J. Ritsko *et al.*, Phys. Rev. Lett. 37, 1068 (1976).

[12] R. P. Feynman, *Quantum Electrodynamics* (Benjamin, New York, 1962).

[13] Synchrotron Radiation Research, Stanford Synchrotron Radiation Project Report No. SSRP 76/100, August 1976 (unpublished).

[14] R. A. Mack, Cambridge Electron Accelerator Report No. CEAL-1027, February 1966 (unpublished).

[15] G. S. Brown, private communication.

Concentration-Dependent Collapse of a Large Polymer

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The observed condensation of DNA in salt solution in the presence of a second polymer of lower molecular weight is treated by straightforward statistical mechanics. We neglect the details of DNA structure and represent it by a simple polymer of large molecular weight interacting via single-contact repulsive forces with a large number of smaller polymers. In this approximation, the derivative of free energy with respect to the size of the large polymer shows a singularity at a critical concentration of smaller polymers.

In recent years a large body of experimental work has accumulated on the collapse of DNA in water-salt solutions in the presence of a second polymer of lower molecular weight. This phenomenon, called Ψ condensation, has been reviewed by Lerman,[1] and it has significant biological relevance since DNA of bacteriophage *T*4 at certain concentrations of internal proteins can collapse in a similar manner.[2]

In a typical experiment, DNA of a virus with molecular weight of about 10^8 is dissolved in a salt-water solution of approximately 0.5 molar salt and 10^{-12} molar DNA. If now one adds to this solution a second polymer [typically polyethylene oxide (PEO)] of a molecular weight of about 7000, the hydrodynamic properties of the system DNA-salt-water-PEO undergo drastic change (transition) at a critical concentration of PEO, in this case about 0.3 molar. The change in the hydrodynamic properties such as viscosity or sedimentation coefficient indicate a drastic and sudden change in the mean volume occupied by DNA molecules.[3,4] Spectroscopic and x-ray data also support this interpretation.[5,6] Thus experiments point to the interpretation that a concentration-dependent collapse of DNA (large polymer) is brought about as a result of dissolution of the second polymer of lower molecular weight at a critical concentration of the latter. The process is reversible and has the nature of a phase transition.

Lerman has attempted to explain this phenomenon by simple thermodynamic arguments and has concluded that dominant forces causing the collapse are repulsive forces operating between the large and small polymers. The transition is relatively sharp in DNA solutions because of its considerable size, but polymer fractionation experiments in which a polydisperse polymer solution progressively precipitates in fractions of decreasing molecular weight must be related to this phenomenon.

In what follows we attempt to show the existence of a phase transition in a model system by straightforward statistical mechanics. Experimental evidence indicates that the role of salt in a DNA-polymer solution is to overcome the electrostatic repulsive force within the DNA chain by counterion binding. At the outset, consideration of electrostatic forces will unduly complicate the problem. We have considered the condensation of a large nonpolar polymer in interaction with a large number of smaller nonpolar polymers. We show that in such a system, the derivative of free energy with respect to average size of the large polymer depends on the concentration of the second polymer. Moreover, the free energy and its derivations have a singularity at the critical concentration of the second polymer.

We consider a single large polymer with N_1 statistical bonds in a solution of volume V. Within the same volume, n smaller polymers each with N_2 statistical bonds are immersed. By considering the solvent as a continuum, the potential energy $U_{\mathrm{SP}}(\{\vec{\mathrm{R}}\})$ for any single polymer can formally be written as

$$U_{\mathrm{SP}}(\{\vec{\mathrm{R}}\}) = U_{\mathrm{LJ}}(\{\vec{\mathrm{R}}\}) + U_{\mathrm{s.r.}}(\{\vec{\mathrm{R}}\}), \tag{1}$$

$$U_{\mathrm{LJ}}(\{\vec{\mathrm{R}}\}) = \sum_{0 \le i < j \le N} u(R_{ij}), \tag{2}$$

$$U_{\mathrm{s.r.}}(\{\vec{\mathrm{R}}\}) = \sum_{i=1}^{N+1} v(R_{i,i-1}). \tag{3}$$

Here $\{\vec{\mathrm{R}}\}$ is the $3N$-dimensional position vector of the polymer with N elements. The potential energy is split into two parts: U_{LJ} the contribution due to Lennard-Jones (dipole, electrostatic, etc.) forces between any two elements and $U_{\mathrm{s.r.}}$ the contribution due to (short-ranged) bonding forces operative between any two adjacent elements along a chain. The form of $U_{\mathrm{s.r.}}$ is such that a chain will be formed. The configurational partition function Z for a single polymer can now be written as[7,8]

$$Z = \int \cdots \int \exp\left[-\frac{1}{k_{\mathrm{B}}T} \sum_{0 \le i < j \le N} u(R_{ij})\right] \Gamma d\{\vec{\mathrm{R}}\}, \tag{4}$$

$$\Gamma = \prod_{l=1}^{N} \tau_l(R_{l,l-1}), \tag{5}$$

$$\tau_i(R_{i,i-1}) = \exp\left[-\frac{v(R_{i,i-1})}{k_{\mathrm{B}}T}\right] = \left(\frac{3}{2\pi b^2\sigma^2}\right)^{3/2} \exp\left(-\frac{R_{i,i-1}^{\;2}}{2b^2\sigma^2}\right). \tag{6}$$

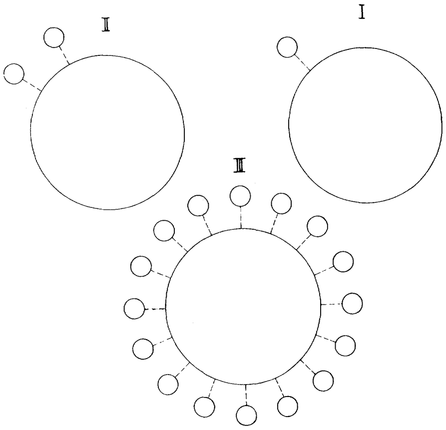

FIG. 1. Diagramatic representation of the interaction between a large polymer and small polymers.

In this model $\tau_i(R_{i,i-1})$ is taken to be a Gaussian function in $R_{i,i-1}$ with a mean square $\langle R_{i,i-1}^{\;2}\rangle = b^2\sigma^2$. Thus the mean bond length is b but it may be varied through a multiplying factor σ. $u(R_{ij})$ is as usual the nonbond interaction potential. The mean extension of the polymer in space such as the mean-square radius of gyration can be varied in this model through the choice of parameter σ which is sometimes called the expansion factor. Thermodynamic quantities, such as mean potential energy, thus depend on the value of σ.

The system under investigation in this work contains one large polymer of N_1 segments and n polymers of N_2 segments each. The total potential energy of the system will now be the sum of n separate energies given by Eq. (1) for each of the n small polymers of N_2 bonds plus a single energy of the form of Eq. (1) with N_1 bonds and an interaction energy between separate polymers. The experimental conditions indicate that the dominant interactions giving rise to collapse are those between small polymers and the large one. The reason for this is that the elements of the large polymer (DNA) are distributed over a much larger volume than those of the smaller polymers, which despite their higher concentration are generally confined to small regions around the center of mass of each polymer. A quantitative analysis will not be made here of the relative contributions of these separate terms. Since we are studying the behavior of the large chain, the interactions between small polymers will be neglected; thus the interpolymer potential energy U_{int} is given by

$$U_{\mathrm{int}} = \sum_{k=1}^{n} \sum_{j=1}^{N_2} \sum_{l=1}^{N_1} u(R_{lj}^{\;k}), \tag{7}$$

where $u(R_{Ij}{}^{k})$ is the interaction between element number I of the large polymer and element number j of the kth small polymer (the elements of the large polymer are designated by capital letters and those of small polymers by lower-case letters). The total configurational partition function of the system can now be written as

$$Z_{\text{tot}}=\int\cdots\int \exp\left[-\frac{1}{k_{\text{B}}T}\sum_{0\le I<J\le N_1} u(R_{IJ})\right]\Gamma_1\prod_{k=1}^{n}\left[\exp\left(-\frac{1}{k_{\text{B}}T}\sum\sum_{0\le i<j\le N_2} u(R_{ij}{}^{k})\right)\right.$$
$$\left.\times\,\Gamma_2{}^{k}\exp\left(-\frac{1}{k_{\text{B}}T}\sum_{j=1}^{N_2}\sum_{I=1}^{N_1} u(R_{Ij}{}^{k})\right)d\{\vec{\text{R}}^{k}\}\right]d\{\vec{\text{R}}\},\tag{8}$$

where Γ_1 and $\Gamma_2{}^{k}$ are the short-range contributions [Eq. (5)] for the large polymer and the kth small polymer, respectively, and

$$\vec{\text{R}}_{Ij}{}^{k}=\vec{\text{R}}_{I}-\vec{\text{R}}_{j}{}^{k},\quad R_{ij}{}^{k}=\vec{\text{R}}_{i}{}^{k}-\vec{\text{R}}_{j}{}^{k}.\tag{9}$$

We now introduce the approximation that the large polymer interacts with any small polymer through a single segment-segment contact. This is justified in view of the size of the small polymers. More precisely this is expressed in terms of the Ursell-Mayer cluster expansion[9] as

$$\exp\left[-\frac{1}{k_{\text{B}}T}\sum_{j=1}^{N_2}\sum_{I=1}^{N_1}u(R_{Ij}{}^{k})\right]=\prod_{j=1}^{N_2}\prod_{I=1}^{N_1}(1+f_{Ij}{}^{k})\simeq 1+\sum_{j=1}^{N_2}\sum_{I=1}^{N_1}f_{Ij}{}^{k},\tag{10}$$

where $f_{Ij}{}^{k}$ is as usual defined by

$$\exp\left[-\frac{1}{k_{\text{B}}T}u(R_{Ij}{}^{k})\right]\equiv 1+f_{Ij}{}^{k}.\tag{11}$$

By substitution of Eq. (10) into Eq. (8) and carrying out the combinatorial problem, one arrives at the following simplified form of the total partition function:

$$Z_{\text{tot}}=Z_1Z_2{}^{n}\left[1+\frac{n!}{1!(n-1)!}\frac{N_2N_1!}{(N_1-1)!}\left(\frac{B}{V}\right)+\frac{n!}{2!(n-2)!}\frac{N_2{}^{2}N_1!}{(N_1-2)!}\left(\frac{B}{V}\right)^{2}+\cdots\right.$$
$$\left.+\frac{n!}{(n-N_1)!N_1!}\frac{N_2{}^{N_1}N_1!}{(N_1-N_1)!}\left(\frac{B}{V}\right)^{N_1}\right].\tag{12}$$

Each term in the brackets in Eq. (12) corresponds to a fixed number of small polymers interacting via single contacts with the large polymer. Thus the first term is the contribution of no contacts, the second is that of all possible one-contact situations shown in diagram I of Fig. 1, the third term is the contribution of all possible diagrams of the type II of Fig. 1, and the final term in the brackets is the contribution of a diagram where all N_1 segments of the large polymer are interacting each with a small polymer via single contact. In Eq. (12), Z_1 is the single-polymer partition function for the large polymer according to Eq. (4) and Z_2 is the single-polymer partition function for one small polymer. B in Eq. (12) is given by

$$\frac{B}{V}=\frac{1}{Z_2}\int\cdots\int\exp\left[-\frac{1}{k_{\text{B}}T}\sum_{0\le i<j\le N_2}u(R_{ij}{}^{\gamma})\right]\Gamma_2{}^{\gamma}f_{\text{A}\beta}{}^{\gamma}\,d^3R_{\text{A}\beta}{}^{\gamma}\,d\{\vec{\text{R}}^{\gamma}\}_{\text{A}j\ne\text{A}\beta}.\tag{13}$$

This equation relates to a diagram where the Ath element of the large polymer is coupled to the βth element of the small polymer γ. One has introduced the coordinate transformation $\vec{\text{R}}_{\beta}{}^{\gamma}\to\vec{\text{R}}_{\text{A}\beta}{}^{\gamma}$ in order to decouple the integrals. Since $n \gg N_1$, one may make the approximation

$$\frac{n!}{(n-2)!}\approx n^2,\quad \frac{n!}{(n-3)!}\approx n^3.\tag{14}$$

If all terms involving factorials of n are so approximated, by introducing the concentration of the small polymer, C, as

$$C=nN_2/V,\tag{15}$$

one arrives at the simplified total partition function

$$Z_{\text{tot}}=Z_1Z_2{}^{n}(1+CB)^{N_1}.\tag{16}$$

We now derive the equation of state for the large polymer. One notes that the chains in the system may be expanded or contracted by varying the parameter of Eq. (6). Insofar as the large and small polymers differ in their chemical nature, the expansion coefficient σ will be different for these two types of polymers. We denote the expansion coefficient for the large polymer by σ_1, and that for small polymers by σ_2. We introduce the new variables into the definitions of Z_{tot} [Eq (8)] with

$$d^3R_i = \sigma_1{}^3 d^3R_i{}', \quad i = 1, \ldots, N_1; \tag{17}$$

$$d^3R_i{}^k = \sigma_2{}^3 d^3R_i{}'^k, \quad i = 1, \ldots, N_2, \quad k = 1, \ldots, n. \tag{18}$$

The dependence of Z_{tot} on σ_1 and σ_2 is given as follows:

$$Z_{\text{tot}} = \sigma_1{}^{3N_1} \sigma_2{}^{3nN_2} Z_1 Z_2{}^n (1 + CB)^{N_1}. \tag{19}$$

We intend to calculate the derivative of the free energy with respect to expansion of the large polymer; the free energy F is given by

$$F = -k_{\text{B}} T \ln Z_{\text{tot}}. \tag{20}$$

Computation of the derivative $\partial F/\partial\sigma_1$ follows from Eqs. (8), (11)–(13), and (20) in a straightforward manner. The result is

$$\left(\frac{\partial F}{\partial \sigma_1}\right)_{T, N_1, N_2, n} = -k_{\text{B}} T \left[\frac{\partial \ln Z_1}{\partial \sigma_1} - \frac{C\Pi}{1 + CB}\right]. \tag{21}$$

Here one has used the equation

$$\frac{\partial f_{\text{A}\beta}{}^\gamma}{\partial \sigma_1} = -\frac{1}{k_{\text{B}} T} \frac{\partial u(R_{\text{A}\beta}{}^\gamma)}{\partial R_{\text{A}\beta}{}^\gamma} \frac{R_{\text{A}}}{\sigma_1} \cos\theta (1 + f_{\text{A}\beta}{}^\gamma), \tag{22}$$

where θ is the angle between vectors $\vec{\text{R}}_{\text{A}}$ and $\vec{\text{R}}_{\text{A}\beta}{}^\gamma$. The constant Π is given by

$$\Pi = \frac{1}{\sigma_1 k_{\text{B}} T} \sum_{\alpha=1}^{N_1} P^{(2)}(R_{0\alpha}) R_{0\alpha} I d^3R_{0\alpha}, \tag{23}$$

$$I = \frac{1}{Z_2} \int \cdots \int \exp\left[-\frac{1}{k_{\text{B}} T} \sum_{j=1}^{N_2} \sum_{I=1}^{N_1} u(R_{Ij}{}^\gamma)\right] \Gamma_2 \frac{\partial u(R_{\text{A}\beta}{}^\gamma)}{\partial R_{\text{A}\beta}{}^\gamma} (1 + f_{\text{A}\beta}{}^\gamma) \cos\theta \, d^3R_{\text{A}\beta}{}^\gamma, \tag{24}$$

$$P^{(2)}(R_{0\alpha}) = \frac{1}{Z_1} \int \cdots \int \exp\left[-\frac{1}{k_{\text{B}} T} \sum_{0 \le i < j \le N_1} u(R_{ij})\right] \Gamma_1 d\{\vec{\text{R}}\}_{j \ne 0, \alpha}. \tag{25}$$

We are now in a position to discuss the singularities of the partition function and free energy. One notes from definition of B in Eq. (13) that this constant has a negative value when the potential of interaction between large and small polymers is repulsive. The partition function Eq. (16) will be zero for negative B, at a certain concentration c_T given by $|B| = 1/c_T$. The c_T thus defines a transition concentration when B is negative. We may now rewrite Eq. (16) as follows:

$$Z_{\text{tot}} = Z_1 Z_2{}^n [1 - C/C_T]^{N_1}, \quad C < C_T, \; B < 0. \tag{26}$$

Accordingly the free energy and its derivatives are singular when $C \approx C_T$. In particular we consider Eq. (21). If one sets $\partial F/\partial\sigma_1$ equal to zero, the resulting equation will define the stable form of the large polymer as a function of C. Using $|B| = C_T$ one gets

$$\partial \ln Z_1/\partial\sigma_1 = C\Pi/(1 - C/C_T). \tag{27}$$

To interpret this equation one may use a known form of $\partial \ln Z_1/\partial\sigma_1$ given by many authors[10,11]:

$$\partial \ln Z_1/\partial\sigma_1 \approx -\sigma_1 + \sigma_1{}^{-1} + \sigma_1{}^{-4} + \cdots. \tag{28}$$

Equations (27) and (28) indicate that as $C \to C_T$, $\sigma_1 \to 0$. Thus for repulsive forces, the large polymer will collapse as experiments indicate. The value of σ after collapse will be determined by the excluded-volume forces within the large polymer.

A number of known experimental facts have not yet been analyzed in this Letter; among them are the molecular-weight dependence of the transition concentration c_T and an estimate of the value of c_T which can be arrived at by using a model potential.

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[1] L. S. Lerman, in *Physico-Chemical Properties of the Nucleic Acids*, edited by J. Duchesne (Academic, New York, 1973), pp. 61–76.

[2] U. K. Lammli, Proc. Nat. Acad. Sci. U. S. A. 72, 4288 (1975).

[3] N. M. Akimenko, E. B. Dijakowa, Yu. M. Evdokimov, E. V. Frisman, and Ya. M. Varshavsky, FEBS Lett. 38, 61 (1973).

[4] Yu. M. Evdokimov, A. L. Platonov, A. S. Tikhomenko, and Ya M. Varshavsky FEBS Lett. 23, 180 (1972).

[5] L. S. Lerman, Proc. Nat. Acad. Sci. U. S. A. 68, 1886 (1971).

[6] C. F. Jordan, L. S. Lerman, and J. H. Venable, Nature (London) New Biol. 236, 67 (1972).

[7] H. Yamakawa, *Modern Theory of Polymer Solutions* (Harper and Row, New York, 1971), Chap. 3.

[8] N. K. Ailawadi and J. Naghizadeh, J. Chem. Phys. 66, 5809 (1977).

[9] See J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (Wiley, New York, 1976).

[10] P. Flory, *Principles of Polymer Chemistry* (Cornell Univ. Press, Ithaca, 1953).

[11] P. G. de Gennes, J. Phys. (Paris), Lett. 36, L55 (1975).