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Statistical mechanics with topological constraints: I

S. F. EDWARDS
Department of Theoretical Physics, University of Manchester
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Abstract. The entropy of very long flexible molecules in the presence of topological constraints is studied, and a formula deduced which needs the probability that a random walk will have a particular topological specification. Examples are solved, including a plane random walk sweeping out a given angle around a point in the plane which is generalized to three dimensions including the passage of a random walk past many lines in space, and the probability that a random walk will penetrate through or become multiply entangled with a closed ring.

1. Introduction

There exist several substances such as rubber, glass and polymerized materials, whose molecules possess topological relationships to one another, and these relationships are either permanent, or survive long enough to be considered permanent in the calculation of thermodynamic properties. Such relationships raise two problems: firstly, they require some modification of the formulae of statistical mechanics which normally have the absence of such constraints implicitly built into them, and, secondly, the topological constraints themselves need to be translated into explicit and useful mathematical forms. The full problem of calculating, say, the equation of state of a glass, which will contain elastic constants depending on the way the various silica chains are linked up, is a very difficult problem or rather series of problems for different conditions. In this paper, therefore, the very simplest problems having the topological specification as their key ingredient will be studied.

Let us consider for example an ensemble of N perfectly flexible long molecules with fixed end points lying in the plane of the paper. Let us consider a rod at right angles to the plane, meeting it at $\mathbf{R}$. This will divide, once and for all, the ensemble into chains specified by whether they lie 'above' or 'below' $\mathbf{R}$ or encircle it once from above, or once from below, and so on. This specification will lead to a free energy (obtained explicitly below) which is a function of R. For small R it will be shown that

$$\frac{\partial^2 F}{\partial R_i \partial R_j} = \alpha_{ij} \kappa T$$

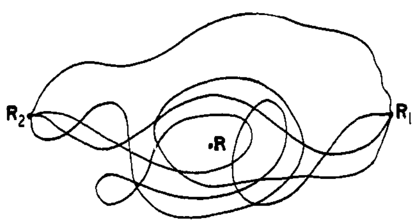

Figure 1.

where α will be obtained, and thus Hooke's law is established for this system and the elastic constants calculated.

Similar problems can be studied in three dimensions, for example a long polymer molecule whose ends are fixed and which encounters a ring. If the molecule is completely flexible and so delineates a random walk in space, what are the relative probabilities of the three paths shown? Clearly an analogous idealized elasticity problem can be constructed in this case from the probabilities which are obtained in § 4, but the constraints in three dimensions need reference to self-effects, i.e. to knot; this is considered in a second paper (to be published).

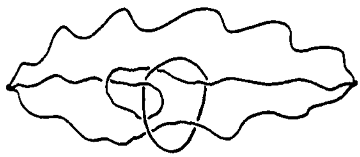

Figure 2.

2. The entropy of a constrained system

Taking the system of figure 1, in two dimensions a single chain with no constraints other than its end points will have $g(\mathbf{R}_1, \mathbf{R}_2, L, l)$ different configurations, where

$$g(\mathbf{R}_1, \mathbf{R}_2, L, l) = g_0(\pi L l)^{-1} \exp\left\{-\frac{(\mathbf{R}_1-\mathbf{R}_2)^2}{Ll}\right\} \tag{2.1}$$

g_0 being the total number of configurations without any constraints, L the total length and l the length of the freely hinged individual molecules. Now let us consider the obstacle $\mathbf{R}$ put in place when an ensemble of N molecules is present. The different configurations of the string can be categorized in this way. Let us take $\mathbf{R}$ as origin and take $\mathbf{r}(s)$ as the intrinsic equation of the molecule, and let us define $\dot{\theta} = (x\dot{y}-y\dot{x})/(x^2+y^2)$. By integration θ will be the normal polar coordinate modulo 2π, but it is these 2π's that categorize the configuration. Thus, if $\widehat{R_1RR_2}$ is Θ ($\Theta < \pi$),

$$\int \dot{\theta}\, ds = \Theta + 2\pi n \qquad (n \geqslant 0) \qquad \text{'above'}$$

or (2.2)

$$\int \dot{\theta}\, ds = \Theta - 2\pi(n+1) \qquad (n \geqslant 0) \qquad \text{'below'}.$$

One can define the probability that a random walk in L/l steps commencing at $\mathbf{R}_1$ and ending at R_2 will generate these angles by p_n^+ and p_n^-, so that

$$\sum_n (p_n^+ + p_n^-) = (\pi L l)^{-1} \exp\left\{-\frac{(\mathbf{R}_1-\mathbf{R}_2)^2}{Ll}\right\} \tag{2.3}$$

and

$$g = g_0 \sum_n (p_n^+ + p_n^-). \tag{2.4}$$

These will be evaluated in the next section, but let us suppose they have been obtained. Then at the instant of time when $\mathbf{R}$ is inserted it is supposed that the system is completely random and so there will be Np_n^+ molecules trapped in the condition specified by $+$, n and so on. The number of configurations remaining to this molecule is $g_0 p_n^+$ so its entropy is $\kappa \log(g_0 p_n^+)$. The total entropy of the system is then

$$\begin{aligned} S &= \kappa N \sum \{p_n^+ \log(p_n^+ g_0) + p_n^- \log(p_n^- g_0)\} \\ &= \kappa N \log g_0 + \kappa N \sum_n (p_n^+ \log p_n^+ + p_n^- \log p_n^-). \end{aligned} \tag{2.5}$$

Now, if these p_n^+ are put into a system of coordinates of arbitrary origin, they are

$$p_n^+(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}, L, l).$$

Let $\mathbf{R}$ be now moved to a new position $\mathbf{R}'$; the partition of N amongst the $+$, $-$, n is unchanged, but the number of configurations permitted to a particular chain lying in one of the topological classes will be changed to $p_n^+(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}', L, l)$. Hence the entropy becomes

$$S = \kappa N \log g_0 + \kappa N \sum_n [p_n^+(\mathbf{R}) \log\{p_n^+(\mathbf{R}')\} + p_n^-(\mathbf{R}) \log\{p_n^-(\mathbf{R}')\}]. \tag{2.6}$$

If quite generally one uses p_{T} for the initial probabilities in some topology T, and p_{T}' for the current probability and ΔS for the change in entropy due to the change

$$\Delta S = \kappa N \sum_{\mathrm{T}} p_{\mathrm{T}} \log\left(\frac{p_{\mathrm{T}}'}{p_{\mathrm{T}}}\right) \tag{2.7}$$

in terms of the free energy

$$\Delta F = -N\kappa T \sum_{\mathrm{T}} p_{\mathrm{T}} \log\left(\frac{p_{\mathrm{T}}'}{p_{\mathrm{T}}}\right). \tag{2.8}$$

It should be noted that

$$\begin{aligned} \left.\frac{\partial F}{\partial \mathbf{R}'}\right|_{\mathbf{R}'=\mathbf{R}} &= -N\kappa T \sum_{\mathrm{T}} \left.\frac{\partial p_{\mathrm{T}}'}{\partial \mathbf{R}'}\right|_{\mathbf{R}'=\mathbf{R}} \\ &= -N\kappa T \frac{\partial}{\partial \mathbf{R}'} \sum_{\mathrm{T}} p_{\mathrm{T}}' \\ &= 0 \end{aligned} \tag{2.9}$$

and

$$\begin{aligned} \left.\frac{\partial^2 F}{\partial \mathbf{R}' \partial \mathbf{R}'}\right|_{\mathbf{R}=\mathbf{R}'} &= -N\kappa T \frac{\partial}{\partial \mathbf{R}'} \frac{\partial}{\partial \mathbf{R}'} \sum_{\mathrm{T}} p_{\mathrm{T}}' + N\kappa T \sum_{\mathrm{T}} \frac{1}{p_{\mathrm{T}}} \frac{\partial p_{\mathrm{T}}}{\partial \mathbf{R}} \frac{\partial p_{\mathrm{T}}}{\partial \mathbf{R}} \\ &= N\kappa T \sum_{\mathrm{T}} \frac{1}{p_{\mathrm{T}}} \frac{\partial p_{\mathrm{T}}}{\partial \mathbf{R}} \frac{\partial p_{\mathrm{T}}}{\partial \mathbf{R}} \end{aligned} \tag{2.10}$$

forms which conform to one's general expectation. There may be constraints much more general than that described by a single coordinate $\mathbf{R}$, so the general formula for infinitesimal changes is

$$\Delta^2 F = N\kappa T \sum_{\mathrm{T}} \frac{(\Delta p_{\mathrm{T}})(\Delta p_{\mathrm{T}})}{p_{\mathrm{T}}}. \tag{2.11}$$

Now the p_n^+, p_n^- will be calculated explicitly to show how it goes.

3. The point constraint in a plane

It is convenient to use the Weiner representation of the random walk in which the probability is represented by

$$p(\mathbf{R}_1, \mathbf{R}_2, L, l) = \mathcal{N} \int \exp\left\{-\frac{1}{l}\int_0^L \dot{\mathbf{r}}^2(s)\, ds\right\} \delta r \tag{3.1}$$

where the integral is taken over all paths $\mathbf{r}(s)$ such that $\mathbf{r}(0) = \mathbf{R}_1$, $\mathbf{r}(L) = \mathbf{R}_2$, and the normalization $\mathcal{N}$ is so arranged that $\int p(\mathbf{R}_1, \mathbf{R}_2, L, l)\, d^2R_2 = 1$. Now let us consider applying the constraint that

$$\int_0^L \frac{x\dot{y} - yx}{x^2+y^2}\, ds = \vartheta \tag{3.2}$$

$$p_\vartheta = \mathcal{N} \int \delta\left(\vartheta - \int_0^L \frac{x\dot{y} - y\dot{x}}{x^2+y^2}\right) \exp\left\{-\frac{1}{l}\int_0^L \dot{\mathbf{r}}^2(s)\, ds\right\} \delta r \tag{3.3}$$

which has the correct form for

$$\int_{-\infty}^{\infty} p_0\, d\vartheta = p. \tag{3.4}$$

It is convenient to introduce

$$\mathbf{A}(r) = \frac{1}{x^2+y^2}(y, -x) \tag{3.5}$$

and the representation

$$\delta(a) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \exp(i\lambda a)\, d\lambda.$$

Then

$$p_\vartheta = \frac{\mathcal{N}}{2\pi}\int_{-\infty}^{\infty} d\lambda \exp(i\lambda\vartheta) \int \delta r \exp\left\{-\frac{1}{l}\int_0^L (\dot{\mathbf{r}}^2 + il\lambda\mathbf{A}\,.\,\dot{\mathbf{r}})\, ds\right\}. \tag{3.6}$$

At this point a well-known identification of these integrals used in quantum mechanics by Feynman will be employed. If $L(r, \dot{r})$ is a Lagrangian and $H(p, r)$ the corresponding Hamiltonian, then if

$$p = \mathcal{N}\int \delta\mathbf{r} \exp\left(-\frac{i}{\hbar}\int_0^t L\, d\tau\right) \tag{3.7}$$

the integral taken between limits $\mathbf{r}' = \mathbf{r}(0)$, $\mathbf{r} = \mathbf{r}(t)$, p satisfies the differential equation

$$\left\{i\hbar\frac{\partial}{\partial t} + H\left(i\hbar\frac{\partial}{\partial \mathbf{r}}, r\right)\right\} p(\mathbf{r}, \mathbf{r}'; t, t') = \delta(t-t')\delta(\mathbf{r}-\mathbf{r}') \tag{3.8}$$

(the Schrodinger equation). Translated into our present problem, the simple random walk Weiner integral becomes Fick's equation

$$\left(\frac{\partial}{\partial L} - \frac{l}{4}\nabla^2\right)p = \delta(L)\delta(\mathbf{r}-\mathbf{r}'). \tag{3.9}$$

When the new term is added, the 'Lagrangian'

$$\frac{\dot{\mathbf{r}}^2}{l} + i\lambda l\mathbf{A}\,.\,\dot{\mathbf{r}} \tag{3.10}$$

has the form appropriate to a charged particle moving in a field of 'vector potential' **A**.

Now when

$$L = \tfrac{1}{2}m\dot{\mathbf{r}}^2 + \frac{l}{c}\dot{\mathbf{r}}\,.\,\mathbf{A} \tag{3.11}$$

$$H = \frac{\{\mathbf{p}-(l/c)\mathbf{A}\}^2}{2m}. \tag{3.12}$$

Performing the translation, one finds

$$\left[\frac{\partial}{\partial L} - \frac{l}{4}\left\{\frac{\partial}{\partial \mathbf{r}} - i\lambda\mathbf{A}(\mathbf{r})\right\}^2\right]p(\mathbf{r}, \mathbf{r}', L) = \delta(\mathbf{r}-\mathbf{r}')\delta(L). \tag{3.13}$$

This result can of course be obtained directly from the Weiner integral also. Multiplying this out, in polar coordinates about **R**,

$$\left[\frac{\partial}{\partial L} - \frac{l}{4}\left\{\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\left(\frac{\partial}{\partial\phi} + i\lambda\right)^2\right\}\right]p = \frac{\delta(r-r')}{(rr')^{1/2}}\delta(\phi-\phi')\delta(L) \tag{3.14}$$

or if

$$p = \sum p_m \exp\{im(\phi-\phi')\} \tag{3.15}$$

$$\left[\frac{\partial}{\partial L} - \frac{l}{4}\left\{\frac{\partial^2}{\partial r^2} + \frac{1}{\gamma}\frac{\partial}{\partial r} - \frac{(\lambda+m)^2}{r^2}\right\}\right]p_m = \frac{\delta(r-r')}{(rr')^{1/2}}\delta(L). \tag{3.16}$$

Putting $R_1 = r$, $R_2 = r'$, the solution to this equation is given in terms of Bessel functions:

$$p_m = (\pi Ll)^{-1} \exp\left(-\frac{R_1{}^2+R_2{}^2}{Ll}\right) \mathrm{I}_{|\lambda+m|}\left(\frac{2R_1R_2}{Ll}\right) \tag{3.17}$$

where

$$\left\{\frac{\partial^2}{\partial a^2}+\frac{1}{a}\frac{\partial}{\partial a}-1-\frac{(\lambda+m)^2}{a^2}\right\}\mathrm{I}_{|\lambda+m|}(a) = 0.$$

Thus

$$p_\vartheta = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\lambda \sum_m \exp(\imath m\phi+\imath\lambda\vartheta)\mathrm{I}_{|\lambda+m|}\left(\frac{2R_1R_2}{Ll}\right)\exp\left(-\frac{R_1{}^2+R_2{}^2}{Ll}\right). \tag{3.18}$$

By writing $\lambda+m \to \lambda$ and employing the identity

$$\sum_{m=-\infty}^{\infty} \exp\{\imath m(\phi-\vartheta)\} = 2\pi \sum_{n=-\infty}^{\infty} \delta(\phi-\vartheta+2\pi n) \tag{3.19}$$

one finds that ϑ must take the values $\phi+2\pi n$ as is obvious from the diagram, and in terms of the previous notation

$$p_n{}^{\pm} = \int d\lambda \exp[\imath\lambda\{\phi\pm 2\pi(n+\tfrac{1}{2})-\pi\}]\mathrm{I}_{|\lambda|}\left\{\exp\left(-\frac{R_1{}^2+R_2{}^2}{Ll}\right)\right\}. \tag{3.20}$$

This result has been obtained by a different method by Ito and McKean (1965). It is of interest to take the integral a stage further by using the representation of I by a contour integral

$$\mathrm{I}_{|\lambda|}(a) = \int_{\mathrm{C}} dw \exp(a\cosh w-|\lambda|w) \tag{3.22}$$

where C consists of the imaginary axis from $-i\pi$ to $+i\pi$ and the lines $i\pi+$real positive, $-i\pi+$real positive, i.e.

$$\mathrm{I}_{|\lambda|}(a) = \frac{1}{2\pi}\int_{-\pi}^{\pi} \exp(a\cos y+i|\lambda|y)\,dy + \frac{1}{2\pi}\int_0^{\infty} \exp(-a\cosh x-|\lambda|x)\{\exp(\imath|\lambda|\pi)-\exp(-\imath|\lambda|\pi)\}\,dx. \tag{3.22}$$

The first integral can be performed over λ and contains $\delta\{\mathscr{I}w-\phi-2\pi(n+\frac{1}{2})-\pi\}$, where $i\pi > \mathscr{I}w > -i\pi$. Thus it contributes only to $n = 0$ and gives

$$p_0{}^{\pm} = \frac{p}{2}\mp(\pi Ll)^{-1}\exp\left\{-\frac{(R_1-R_2)^2}{Ll}\right\}\int_0^{\infty}\exp\left\{-\frac{2R_1R_2}{Ll}(\cosh x-1)\right\} \times\left\{\frac{\phi\pm 2\pi}{x^2+(\phi\pm 2\pi)^2}-\frac{\phi}{x^2+\phi^2}\right\}dx \tag{3.23}$$

$$(n\neq 0)\qquad p_n{}^{\pm} = (\pi Ll)^{-1}\exp\left\{-\frac{(R_1-R_2)^2}{Ll}\right\}\frac{1}{\pi}\int_0^{\infty}\exp\{-2R_1R_2{}'L^{-1}(\cosh x-1)\} \times\left[\frac{\phi\pm(2n+1)\pi+\pi}{x^2+\{\phi\pm(2n+1)\pi+\pi\}^2}-\frac{\phi\pm(2n+1)\pi-\pi}{x^2+\{\phi\pm(2n+1)\pi-\pi\}^2}\right] \tag{3.24}$$

$$p_0{}^{+}+p_0{}^{-}+\sum_{n\neq 0} p_n{}^{\pm} = p. \tag{3.25}$$

Asymptotic forms can be obtained

$$R_1 R_2 \gg Ll$$

$$p_n^+ = \frac{\exp\{-(R_1-R_2)^2/lL\}}{\pi Ll}\left(\frac{2RR'}{Ll}\right)^{-1/2}\frac{\sqrt{\pi}}{\{\phi+2\pi(n+1)\}(\phi+2\pi n)}$$

$$\phi \to \pi, \qquad L \to 0$$

$$p_n^+ = \frac{\exp\{-(R_1-R_2)^2/Ll\}}{\pi Ll}\left(\frac{2RR'}{Ll}\right)^{-1/2}\sqrt{\pi}\left[\left\{\frac{1}{\phi+(2n+1)\pi}\right\}^2 - \frac{1}{(\phi+2n\pi)^2}\right]. \quad (3.26)$$

Having the $p_n^{\pm}$ explicitly now permits the calculation of the elastic constants of the system, but the calculation has not been taken further, since it is a very idealized system.

4. Some generalizations

The results of § 3 can be put this way. To enquire about the topological effect of field curves upon a random flight one needs to work out the magnetic field of a uniform current flowing along the fixed curves (disregarding of course the physical constants like e, c) and then solve the diffusion equation modified by the addition of $i\lambda_j$ times this field in the role of a vector potential, where j labels the different curves. From the solution of this diffusion equation the probabilities can be deduced. To give some examples let us consider a set of lines in space (the two-dimensional case worked through in detail above is the case of the line being perpendicular to the plane and meeting it at R). The angle swept out by the curve $\mathbf{r}(s)$ around the line $\boldsymbol{\xi}(\eta) = \mathscr{A}+\eta\mathscr{B}$ (η in $(-\infty, \infty)$) is

$$\int\int \frac{(d\mathbf{r}\times d\boldsymbol{\xi})\cdot(\mathbf{r}-\boldsymbol{\xi})}{|\mathbf{r}-\boldsymbol{\xi}|^3} = \int \dot{\mathbf{r}}\cdot\mathbf{A}(\mathbf{r})\,ds \quad (4.1)$$

where

$$\mathbf{A} = \text{curl}\int\frac{\mathscr{B}\,d\eta}{|\mathbf{r}-\boldsymbol{\xi}|} \quad (4.2)$$

($\mathbf{A}$ has the form of the Biot and Savart magnetic *field*, though it appears in (4.3) and (4.4) below as a vector *potential*). Thus, if a value ϑ_j is ascribed to the jth line, one has the Weiner integral with $\Pi_j\delta(\vartheta_j - \int\dot{\mathbf{r}}\cdot\mathbf{A}_j)$, i.e. an exponent

$$\frac{3}{2l}\int \dot{\mathbf{r}}^2\,ds + i\sum_j \lambda_j\int\dot{\mathbf{r}}\cdot\mathbf{A}_j\,ds \quad (4.3)$$

so that, if $\mathbf{A} = \Sigma_j\lambda_j\mathbf{A}_j$, one must solve

$$\left\{\frac{\partial}{\partial L} - \frac{l}{6}\left(\frac{\partial}{\partial\mathbf{r}} - \mathbf{A}\right)^2\right\}p(\mathbf{r},\mathbf{r}';L) = \delta(L)\delta(\mathbf{r}-\mathbf{r}'). \quad (4.4)$$

This is no longer soluble analytically, but one can still go directly to asymptotic forms and develop appropriate approximations should this problem develop any useful applications.

Another interesting case is that of a closed curve, where again a well-defined topological invariant can be produced. In figure 2 the curve misses altogether, goes round once, and goes straight respectively. By using Stokes theorem one has that

$$\int\oint\frac{(\dot{\mathbf{r}}\times\boldsymbol{\xi})\cdot(\mathbf{r}-\boldsymbol{\xi})}{|\mathbf{r}-\boldsymbol{\xi}|^3}\,d\tau\,ds = \psi + 4\pi n \quad (4.5)$$

where $\boldsymbol{\xi}(\tau)$ is the closed curve and ψ is the value for one of the paths, say the one which misses altogether. Again, defining $\mathbf{A}$ by

$$\mathbf{A} = \text{curl}\oint\frac{d\boldsymbol{\xi}}{|\mathbf{r}-\boldsymbol{\xi}|} \quad (4.6)$$

the development proceeds as before. For a circular ring the analysis can be taken further by the use of toroidal coordinates

$$\begin{aligned} x &= c \sinh u \cos \phi \,(\cosh u - \cos \theta)^{-1} \\ y &= c \sinh n \sin \phi \,(\cosh u - \cos \theta)^{-1} \\ z &= c \sin \theta \,(\cosh u - \cos \theta)^{-1}. \end{aligned} \tag{4.7}$$

It is the angle θ which will be swept out by different paths in amounts differing by $4\pi n$. The field **A** can be expressed in terms of complete elliptical integrals of the first and second kind, and a formula analogous to (3.24) deduced. Again it does not seem worth while to write out all the details, but asymptotic forms can be deduced.

Well-defined topologies are only possible relative to closed curves, or curves extending to infinity, but the cases of physical interest do effectively have this property.

5. Conclusions

The examples given above illustrate the formulae of § 2, and in two dimensions exhaust the problem, except inasmuch as the ordering of entanglements around different points is ignored. But in three dimensions, although the procedure outlined solves the problems in the form posed, there are other entanglement possibilities. For example the two cases of figure 3 both have the same **A** relative to the line, but the first is entangled with the line by virtue of being entangled with itself. The analysis so far has ignored this possibility, which is clearly related to the entanglement of two random path molecules. This is closely related to the ordering problem in two dimensions. This problem is solved in a subsequent paper.

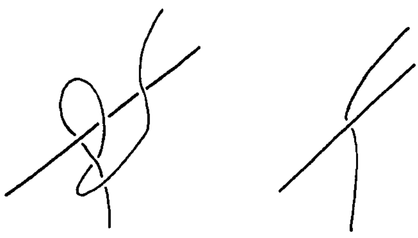

Figure 3.

Acknowledgments

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