

FIGURE 5. Susceptibility of an antiferromagnetic case in the quenched system.

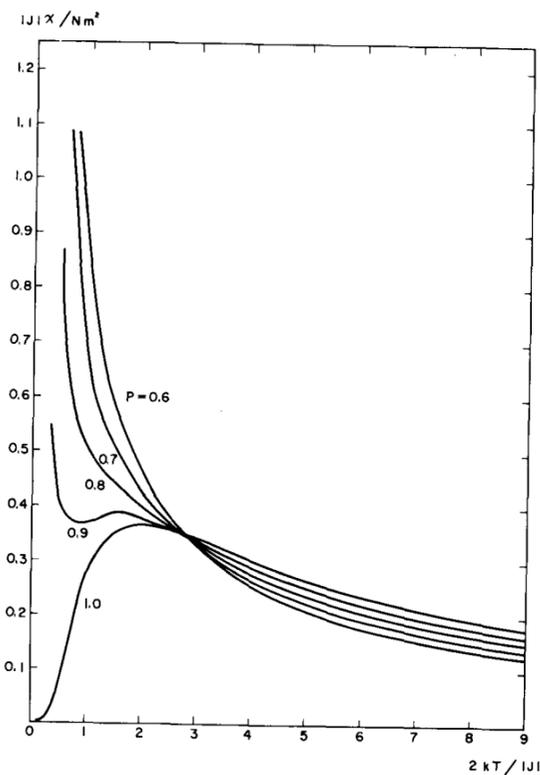


FIGURE 6. Susceptibility of an antiferromagnetic case in Syozi's model.

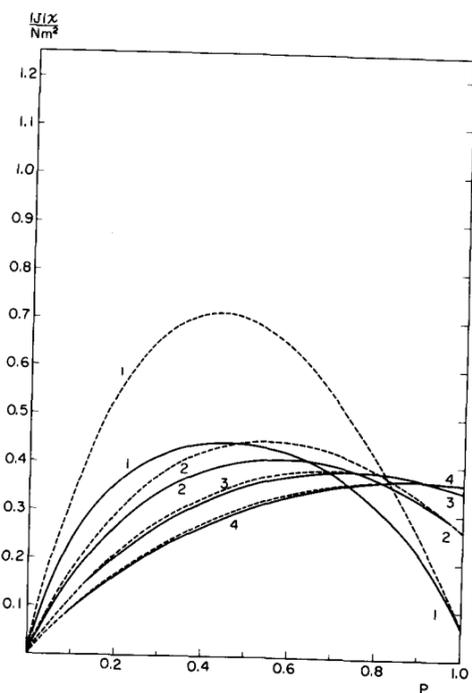


FIGURE 7. Concentration dependence of the antiferromagnetic susceptibility.
Solid line: the annealed system. Dashed line: the quenched system.
1: $T=|J|/4k$, 2: $T=2|J|/4k$,
3: $T=3|J|/4k$, 4: $T=4|J|/4k$.

concentration p , and the paramagnetic configuration gives the dominant contribution compared with the antiferromagnetic configuration. On the other hand, in the annealed system, the energy of the paramagnetic configuration is high compared with the antiferromagnetic configuration, and hence it dies and the susceptibility tends to zero.

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IBM 7090 in UNICON (University contribution of Japan IBM).

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The Statistical Mechanics of a Single Polymer Chain

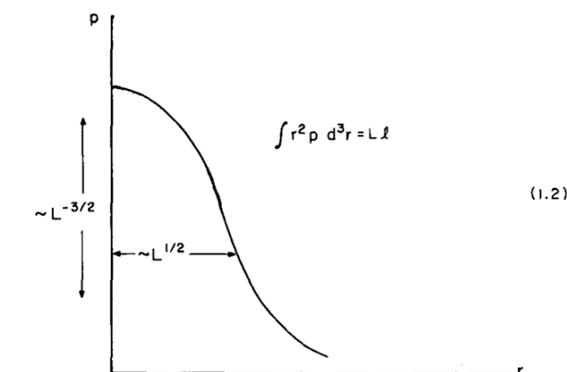
S. F. Edwards

University of Manchester, Manchester, Great Britain

It is clear from the papers presented at this conference that near critical points thermodynamic functions and correlation functions take on forms which reflect only a very small amount of the detailed structure of the systems considered, and are rather manifestations of the three dimensionality of space and the short range of interactions. The configurational statistics of polymers shares this feature and is therefore interesting as an indication of how the critical behavior may be generated mathematically; in fact the problem is one way of approximating to the Ising lattice as was mentioned by Professor Domb [1]. In this talk I shall develop the theory applied to polymers themselves however, and comment on their critical behavior, since whether the analysis will really be useful for bulk systems remains to be seen. A polymer without interaction will have the well-known distribution

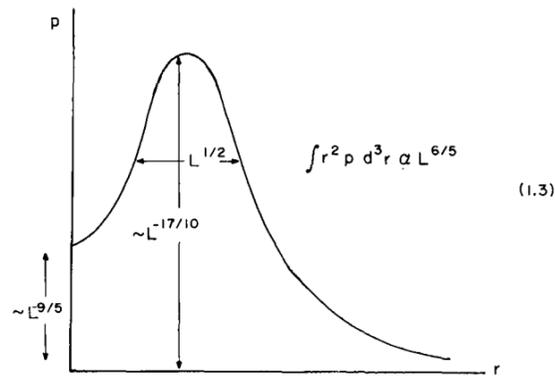
$$p(\mathbf{r}, L) = \left(\frac{2\pi L l}{3}\right)^{-3/2} \exp\left(-\frac{3r^2}{2Ll}\right) \quad (1.1)$$

for the probability that the end points are at $\mathbf{0}, \mathbf{r}$ when the length is L . This has the form



For the case of excluded volume i.e., a repulsion between elements of the polymer, p has no simple analytic form, but salient features are shown in

the diagram (schematic)



Expressions will also be obtained for the number of configurations allowed to the polymer.

2. Mathematical Formulation of the Problem

Firstly the problem is to be stated mathematically and brought down to its simplest form. Suppose the polymer consists of n identical molecules freely hinged in a chain, and there is a potential U between molecules. If the length of one molecule is l , and the coordinate of the end of the m th molecule is \mathbf{R}_m , then the probability of finding a particular configuration $P(\mathbf{R}_1, \dots, \mathbf{R}_n)$ is given by

$$P(\mathbf{R}_1, \dots, \mathbf{R}_n) = \mathcal{N} \prod_i p(\mathbf{R}_i, \mathbf{R}_{i+1}) \exp \left[\frac{1}{kT} \sum_{m=1}^n U(\mathbf{R}_m - \mathbf{R}_i) \right] \quad (2.1)$$

where \mathcal{N} is the normalization

$$\int P \Pi d^3R = 1 \quad (2.2)$$

and p is the constraint

$$p(\mathbf{R}_i, \mathbf{R}_{i+1}) = \delta(|\mathbf{R}_i - \mathbf{R}_{i+1}| - l). \quad (2.3)$$

(Note since normalizations are constantly occurring they will all be denoted by \mathcal{N} .) Of course, one can put structure into the molecules making U an integral over the molecule and one can put in bond flexibilities, but the basic problem is already in

(1.1) including the case of hard exclusions in which

$$U = \infty \quad |\mathbf{R}_m - \mathbf{R}_e| < a \quad (2.4)$$

= 0 otherwise.

A lattice polymer, can also be included if the definition (1.3) is suitably modified, but it is again a complication not a simplification. The probability that starting at the origin, the polymer's n th link will end at \mathbf{r} , is given by

$$p(\mathbf{r}, L) = \int P(\mathbf{R}_1, \dots, \mathbf{R}_n) \delta(\mathbf{r} - \mathbf{R}_n) \Pi d^3R_i \quad (2.5)$$

where L , the length, is nl . A method of evaluating p for a slightly simpler problem, that of the infinite polymers, has been given by the author (reference [2], hereafter referred to as I) in a paper which develops a physical picture of what is going on and translates the physical picture into mathematics. A more formal but precise method of approach is given in an appendix to I, and in this paper, after reviewing the physical arguments, it is this formal development which will be given and extended to give a more complete theory of the single finite polymer.

Firstly it must be explained that the fact that there are n integrations in (1.1) is a nuisance; it is easier to consider a continuous function $\mathbf{R}(L')$ where $0 < L' < L$ and integrate over all functions $\mathbf{R}(L')$. The constraint $\prod_i p(\mathbf{R}_i, \mathbf{R}_{i+1})$ is the expression

originally considered by Weiner when he introduced functional integration and can be expressed as

$$\mathcal{N} \exp \left(-\frac{3l}{2} \int_0^L \left(\frac{\partial \mathbf{R}}{\partial L'} \right)^2 dL' \right) \quad (2.6)$$

so that, putting $V = UL^{-2}$

$$p(\mathbf{r}, L) = \mathcal{N} \int_{\mathbf{R}(0)=0}^{\mathbf{R}(L)=\mathbf{r}} d(\text{path } \mathbf{R}(L')) \exp \left(-\frac{3l}{2} \int_0^L \left(\frac{\partial \mathbf{R}}{\partial L'} \right)^2 dL' \right) \quad (2.7)$$

$$-\frac{1}{2kT} \int_0^L \int_0^L V(\mathbf{R}(L') - \mathbf{R}(L'')) \frac{dL'}{dL''} \quad (2.7)$$

At this point a parametric representation can be

employed. It is well known that

$$e^{-a^2/2} = \int_{-\infty}^{\infty} e^{iux - x^2/2} dx / \int_{-\infty}^{\infty} e^{-x^2/2} dx. \quad (2.8)$$

This can be generalized to

$$\exp \left(-\sum_{ij} a_i A_{ij} a_j / 2 \right) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp \left(i \sum_j a_j x_j - \sum_{i,k} x_i A_{ik}^{-1} x_k / 2 \right) / \int \int \int_{-\infty}^{\infty} e^{-\sum x_i A_i} \Pi dx, \quad (2.9)$$

where A^{-1} is the inverse matrix to A , and hence to the functional form

$$\exp \left(-\int a(\alpha) A(\alpha\beta) a(\beta) d\alpha d\beta \right) = \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} (\Pi dx) \exp \left[i \int a(\alpha) x(\alpha) d\alpha - \frac{1}{2} \int \int x(\alpha) A^{-1}(\alpha\beta) x(\beta) d\alpha d\beta \right] \times \left[\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp \left[-\int \int x(\alpha) A^{-1}(\alpha\beta) x(\beta) d\alpha d\beta \right] \Pi dx \right] \quad (2.10)$$

where A^{-1} is the inverse operator to A ,

$$\int A^{-1}(\alpha\beta) A(\beta\gamma) d\beta = \delta(\alpha - \gamma). \quad (2.11)$$

This theorem allows one to write

$$\exp \left(-\frac{1}{2kT} \int_0^L \int_0^L V(\mathbf{R}(L') - \mathbf{R}(L'')) dL' dL'' \right) = \mathcal{N} \int \delta\chi \exp \left[i \int_0^L \chi(\mathbf{R}(L')) dL' - \frac{kT}{2} \int \int d^3r d^3s \chi(\mathbf{r}) V^{-1}(\mathbf{r} - \mathbf{s}) \chi(\mathbf{s}) \right], \quad (2.12)$$

where

$$\int V^{-1}(rs) V(sr') d^3s = \delta(r - r'), \quad (2.13)$$

and $\int \delta\chi$ represents the integral over all functions. It is supposed that $\int \chi V^{-1} \chi$ is positive definite, corresponding to V being repulsive. If this is not the

case one has to split V into a part with positive Fourier coefficients and a part with negative Fourier coefficients and parameterize them separately. This will be equivalent to χ becoming complex and the functional integration being over its real and imaginary parts independently. Although physical forces always do have attractions and repulsions it is well known from the study of the Ursell-Mayer cluster expansion, that provided the system remains of low density the effects of interparticle potentials can be simulated by pseudo potentials which will give rise to the correct virial coefficient. Thus if the excluded volume is defined by

$$v = \int [1 - \exp(-U/kT)] d^3r \quad (2.14)$$

the effective pseudo potential is $v\delta(r)$, whose inverse is $v^{-1}\delta(r)$. It will be assumed now that v is positive, i.e., the mean effect of the forces is a repulsion. Then finally

$$p(\mathbf{r}, L) = \mathcal{N} \int_0^r \exp \left[-\frac{3l}{2} \int_0^L \left(\frac{\partial \mathbf{R}}{\partial L'} \right)^2 dL' - i \int_0^L \chi(\mathbf{R}(L')) dL' - \frac{l^2}{2v} \int \chi^2(S) d^3S \right] \delta\chi \delta R \quad (\delta R \text{ for the integral over all paths}). \quad (2.15)$$

The theorem states that the probability p is that of diffusion in the presence of a potential $i\chi$ (a Markov process), averaged over all potentials with a Gaussian weight. It is a well-known theorem elsewhere in physics. Since the evaluation of the functional integral over δR is equivalent to solving the diffusion equation, one can obtain the final form

$$p(\mathbf{r}, L) = \mathcal{N} \int \delta\chi G(\mathbf{r}, L, [\chi]) W([\chi]) \delta\chi \quad (2.16)$$

where

$$W([\chi]) = \exp \left(-\frac{l^2}{2v} \int \chi^2 d^3s \right), \quad (2.17)$$

$$\left(\frac{\partial}{\partial L} - \frac{l}{6} \nabla^2 + i\chi(\mathbf{r}) \right) G(\mathbf{r}, L, [\chi]) = \delta(\mathbf{r}) \delta(L) \quad (2.18)$$

and $\mathcal{N} = \mathcal{N}(L)$ is defined from $\int p d^3r = 1$.

3. The Solution

Two problems have presented themselves in (2.16). Firstly one has to get G from (2.18) and then do the integral over χ . It will be argued that the mathematical tools for these problems are already available, at least within reasonable stretching: the Green function can be got by the JWKB method, and the χ integration by the method of steepest descent. Physically one can argue that, since one knows that the polymer starts at the origin, on an average a "polymer density" will build up having its maximum at the origin. It is this field which will be uncovered by the steepest descent calculation, and it will be a field with a long range effect, slowly varying in space so that the JWKB method will be the correct method to assess its effect on the diffusion. That this mean field can be expected to be long range is seen at once from the noninteracting distribution (1.1). From (1.1) the probability that a very long noninteracting polymer goes through \mathbf{r} for some L is

$$\int \left(\frac{2\pi}{3} Ll\right)^{-3/2} \exp\left(-\frac{3r^2}{2Ll}\right) dL = \left(\frac{3}{2\pi l}\right) \frac{1}{r}$$

If there were a very strong self-repulsion, the polymer would shoot out in a straight line and the average would be taken over the orientation of this straight line, i.e., would give $(4\pi r^2)^{-1}$. These give upper and lower bounds on the form of the mean polymer density so that one expects the χ integration to be centered about a steepest descent function χ having a dependence lying between $\frac{1}{r}$ and $\frac{1}{r^2}$ and in fact it will turn out to go like $\frac{1}{r^{4/3}}$.

It is convenient to Fourier transform G with respect to L

$$\left(iE - \frac{1}{6}\nabla^2 + i\chi\right) G(E, \mathbf{r}, [\chi]) = \delta(\mathbf{r}) \quad (3.1)$$

and to seek a solution in the form

$$G = e^{\phi}/r. \quad (3.2)$$

Then

$$i(E + \chi) - \frac{1}{6}r^2\mathcal{L}(\phi) - \frac{1}{6}\frac{d^2\phi}{dr^2} - \frac{1}{6}\left(\frac{d\phi}{dr}\right)^2 = 0 \quad (3.3)$$

where $\mathcal{L}(\phi)$ contains the angular derivatives. It will turn out that the steepest descent function is spherically symmetric, so the angular terms will be ignored for the present and ϕ treated as if it were $\phi(r, E)$ and $\chi(\mathbf{r})$ also as if it were $\chi(r)$. The JWKB argument is now that the $(d\phi/dr)^2$ term dominates over the $d^2\phi/dr^2$ term (which can be confirmed subsequently) so that

$$\phi \cong \left(\frac{6i}{l}\right)^{1/2} \int_0^r (E + \chi(s))^{1/2} ds \quad (3.4)$$

and one is left with

$$\rho = \mathcal{N} \int \delta\chi dE \exp \left[\int_0^r \left(\frac{6}{l}\right)^{1/2} i^{1/2}(E + \chi)^{1/2} ds - iEL - \frac{l^2}{2v} \int \chi^2 d^3s \right]. \quad (3.5)$$

(One must watch for complications at the branch point $E + \chi = 0$; note also that one integral is ds , the other d^3s). To evaluate, one looks for the $\bar{E}, \bar{\chi}$ which make the exponent stationary: differentiating with respect to E

$$iL = \frac{1}{2} \left(\frac{6i}{l}\right)^{1/2} \int_0^r (\bar{E} + \bar{\chi})^{-1/2} ds \quad (3.6)$$

and functionally with respect to χ

$$\frac{l^2}{v} \chi(s) = \left(\frac{1}{4\pi s^2}\right) \frac{1}{2} \left(\frac{3i}{l}\right)^{1/2} (\bar{E} + \bar{\chi})^{-1/2} \begin{cases} s < r \\ s > r \end{cases} = 0 \}.$$

Therefore one may write also

$$iL = \frac{l^2}{v} \int_0^r \bar{\chi}(s) ds. \quad (3.8)$$

$$\bar{\chi} = \bar{\chi}(s, \bar{E}) \quad (3.9)$$

$$\bar{E} = \bar{E}(r, L). \quad (3.10)$$

Make these equations clearer by introducing

$$\zeta = \frac{5}{3} \left(\frac{L}{r^{5/3}}\right) \frac{\pi^{1/6}}{2} \left(\frac{v}{6l}\right)^{1/3} \quad (3.11)$$

$$\bar{\chi} = \left(\frac{1}{8\pi}\right)^{2/3} \left(\frac{6}{l}\right)^{1/2} \left(\frac{v}{l^2}\right)^{2/3} S^{-4/3} \vartheta$$

$$\bar{E} = \left(\frac{1}{8\pi}\right)^{2/3} \left(\frac{6}{l}\right)^{1/2} \left(\frac{v}{l^2}\right)^{2/3} r^{-4/3} \epsilon$$

$$s' = s/r$$

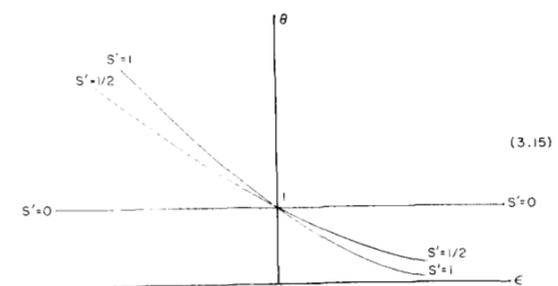
Then one has to determine ϑ, ϵ in terms of ζ where

$$\zeta = \frac{5}{3} \int_0^1 \frac{ds' s'^{2/3}}{(\vartheta + \epsilon s'^{4/3})^{1/2}} \quad (3.12)$$

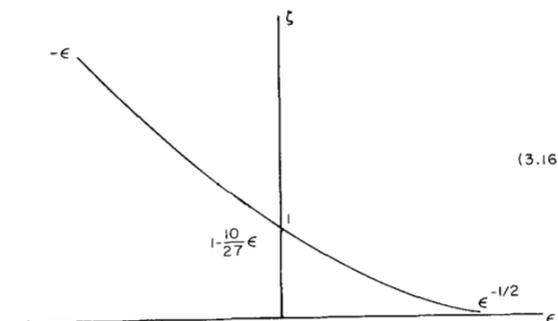
$$\vartheta = (\vartheta + \epsilon s'^{4/3})^{-1/2} \quad (3.13)$$

$$\zeta = \frac{5}{3} \int_0^1 ds' s'^{2/3} \vartheta(s'). \quad (3.14)$$

The ϵ, ϑ, s' relation is plotted below



Special cases are $\epsilon = 0, \vartheta = 1, (\zeta = 1)$; $\epsilon = -\infty, \vartheta = \epsilon^{-1/2} s'^{-2/3}$; $\epsilon = -\infty, \vartheta = -\epsilon s'^{4/3}$. This, physically sensible, solution has ϑ positive and leads to a relation like



One may now see that neglecting fluctuations for the moment

$$\rho(\mathbf{r}, L) = \mathcal{N}(L) \exp \left[\int_0^r \left(\frac{6i}{l}\right)^{1/2} (\bar{E} + \bar{\chi})^{1/2} ds - iEL - \frac{l^2}{2v} \int \bar{\chi}^2 d^3s \right] \quad (3.17)$$

$$\rho(\mathbf{r}, L) = \mathcal{N}(L) \exp[-r^{1/3} F(\zeta, \vartheta, \epsilon)] \quad (3.18)$$

$$= \mathcal{N}(L) \exp[-r^{1/3} F(Lr^{-5/3})] \quad (3.19)$$

$$= \mathcal{N}(L) \exp[-Z(r, L)]. \quad (3.20)$$

say.

The function e^{-Z} is sketched in the introduction. Its maximum comes at $\partial Z/\partial r = 0$, i.e.,

$$0 = \frac{\partial Z}{\partial \bar{E}} \frac{\partial \bar{E}}{\partial r} + \int \frac{\delta Z}{\delta \bar{\chi}(s)} \frac{\partial \bar{\chi}(s)}{\partial r} d^3s + \left[-\frac{4\pi l^2}{v} r^2 \bar{\chi}^2(r) + \left(\frac{6i}{l}\right)^{1/2} (\bar{E} + \bar{\chi})^{1/2} \right] \quad (3.21)$$

Since Z is stationary with respect to E and $\bar{\chi}$ this gives

$$\frac{4\pi l^2}{v} \bar{\chi}^2(r_m) r_m^2 = \left(\frac{6i}{l}\right)^{1/2} (\bar{E} + \bar{\chi}(r_m))^{1/2} \quad (3.22)$$

i.e.,

$$\bar{\chi}(r = r_m) = \left(\frac{6}{l}\right)^{1/3} \left(\frac{v}{4\pi l^2}\right)^{2/3} \frac{1}{r_m^{4/3}}. \quad (3.23)$$

Near the peak the

$$\zeta = \zeta_m \text{ i.e., } L = \left(\frac{l}{v}\right)^{1/3} r_m^{5/3} \times \text{constant}. \quad (3.24)$$

And the distribution looks like

$$\mathcal{N}(L) \exp\left(-f \left(L - gr^{5/3} \left(\frac{l}{v}\right)^{1/3}\right)^2 r^{-3} l^{-2} v\right) \quad (3.25)$$

where f and g are constants derived from (3.23), (3.13), and (3.14). For the right ζ is small, ϵ large so that $\zeta \propto \epsilon^{-1/2}$.

$$F \propto \frac{1}{\zeta}. \quad (3.26)$$

This implies a distribution $b\mathcal{N}\exp(-cr^2/2L)$ where b and c are constants. Towards the origin ρ becomes very small, and one is in the well-known trouble of trying to fit a tail of a function by working away from its maximum. This will be considered in detail in section 4.

The fluctuations i.e., the remaining quadratic integrals over $E - \bar{E}$ and $\chi - \bar{\chi}$ have not yet been

considered. Unlike steepest descent methods in a single variable, these are of great consequence and indeed are the substance of conventional field theory. To go straight ahead expanding ϕ to order χ^2 is inadequate as can be seen physically. Consider what one expects the addition of one more molecule to the polymer to involve. Say for the moment one confined oneself to steps on a close packed lattice. There would be at most eleven sites to go on to i.e., 12, less the one it is at. But it must have wandered around the neighborhood before it arrived at the present site, so one expects a further reduction bringing the number of available sites to $\mu < 11$. In addition the long range effect reduces it further to $\mu(1+f(n))$ (where $f(n)$ will turn out to be $(\log n)/5n$). If one were not using the steepest descent method by normal field theory one would argue, after Dyson, that by studying the perturbation series, that (using $\langle G \rangle$ for (2.16) unnormalized)

$$\left(iE - \frac{l}{6}k^2 + \Sigma(k, E)\right) \langle G(k, E) \rangle = 1 \quad (3.27)$$

where in the first approximation

$$\Sigma(k, E) = \int \frac{|V(\mathbf{k}-\mathbf{j})|^2}{iE - \frac{l}{6}j^2} d^3j \quad (3.28)$$

but it is difficult to get in general. If $\langle G \rangle$ is considered to have a pole i.e., $\left(iE - l' \frac{k^2}{6} + \Sigma_0\right) \langle G \rangle \cong 1$ and Σ is expanded around it

$$\Sigma = \Sigma_0 - \Sigma_1 k^2 + \Sigma_2 \left(iE - \frac{l'}{6}k^2\right) + \dots \quad (3.29)$$

$$\left(iE - \frac{(1+\Sigma_1)l}{(1+\Sigma_2)6}k^2 + \frac{\Sigma_0}{1+\Sigma_2}\right) \langle G \rangle = \frac{1}{1+\Sigma_2} \quad (3.30)$$

Here $\frac{1+\Sigma_1}{1+\Sigma_2}l = l'$ is a "renormalized" step length, and the $\Sigma_0/(1+\Sigma_2)$ factor represents the changed number of available sites as expected. (Since it gives a $e^{-2\alpha l}$ factor in $\langle G \rangle$ it will not appear in p). The conventional field theory fails completely to describe the long range effects and it is these which determine the $\bar{r}^2: L$ relation. As has been shown the present theory suggests that these long range effects are simulated by a potential centered at

the origin. The local effects should be adequately handled by the conventional methods and they really will involve the fine structure of V , and if one attempts to use the pseudo potential one gets divergences. To avoid these one must write

$$p(r, E, [\chi]) = \frac{1}{r} e^{\{A + \int B\chi - \bar{\chi}\} + \int C\chi - \bar{\chi}^2 + iEL + iEL - \bar{L} + D(E - \bar{E})} \quad (3.31)$$

where

$$(\nabla^2 + \nabla A \nabla)A(r) = -\bar{\chi}(r)$$

$$(\nabla^2 + 2\nabla A \nabla)B(r, r') = \delta(r - r')$$

$$(\nabla^2 + 2\nabla A \nabla)C(r, r_2, r_3) = \nabla B(r, r_2) \nabla B(r, r_3)$$

$$\frac{l^2}{v} V^{-1} \chi = \frac{1}{4\pi r^2} \nabla B.$$

and so on. The interference between $\bar{\chi}$ and the fluctuations is analogous to the Lamb shift and a proof is needed that this does not interfere with the functional forms discovered so far. Though this appears to be so by explicit calculation, I am trying to obtain a general proof on the lines of the Dyson treatment of electrodynamics.

4. The Inner Region

One can see why the inner region has been so far inaccessible. The solution has a peak near $L \sim r^{3/5}$ and almost all the probability lies in the peak. This means that though the chance of the polymer getting back close to the origin is small, it is much larger than that suggested by the solution (3.5). That solution suggests that in order to be still near $r \sim 0$ as $L \rightarrow \infty$ one must have stayed all the time near $r \sim 0$. Clearly what will happen is that one will go out into the high probability region and then walk back to the inner region. Since under the parametric integral sign one has a Markov process one may always break up G

$$G(\mathbf{r}, L, [\chi]) = \int G(\mathbf{r}-\mathbf{s}, L-M, [\chi]) G(\mathbf{s}, M, [\chi]) d^3s \quad (4.1)$$

Note there is no integral over M and the left-hand side should be independent of M . To modify (4.1) to be M independent one can average along the

whole length to give

$$p = \frac{1}{L} \int_0^L dM \int d^3s \int \delta\chi G(\mathbf{r}-\mathbf{s}, L-M[\chi]) G(\mathbf{s}, M, [\chi]) W. \quad (4.2)$$

Now average using the JWKB for the G

$$p = \frac{1}{L} \int_0^L dM \int d^3s \int \delta\chi |\mathbf{r}-\mathbf{s}|^{-1} |\mathbf{s}|^{-1} \int dE_1 \int dE_2 \exp \left\{ -\frac{l^2}{2r} \int \chi^2 d^3a + \left(\frac{6i}{l}\right)^{1/2} \int_0^s \frac{d^3a}{a^2} (E_2 + \chi)^{1/2} + \left(\frac{6i}{l}\right)^{1/2} \int_s^r \frac{d^3a}{|a-s|^2} (E_1 + \chi)^{1/2} - iE_1(L-M) - iE_2M \right\}. \quad (4.3)$$

$$\bar{\chi}(a) = \frac{v}{l^2} \frac{\Theta(|a| \leq |s|)}{a^2} (E_2 + \chi)^{-1/2} \left(\frac{6i}{l}\right) + \frac{v}{l^2} \frac{\Theta(|\mathbf{a}-\mathbf{s}| \leq |\mathbf{r}-\mathbf{s}|)}{|\mathbf{a}-\mathbf{s}|^2 (E_1 + \chi)^{1/2}} \quad (4.4)$$

$$i(L-M) = \left(\frac{6i}{l}\right)^{1/2} \int_{|\mathbf{a}-\mathbf{s}| \leq |\mathbf{r}-\mathbf{s}|} \frac{d^3a}{|s-a|^2} (E_1 + \chi)^{-1/2} \quad (4.5)$$

$$vM = \left(\frac{6i}{l}\right)^{1/2} \int_{|\mathbf{a}| \leq |s|} \frac{d^3a}{a^2} (E_2 + \chi)^{-1/2}. \quad (4.6)$$

In particular to get back to $\mathbf{r}=0$ one has

$$\bar{\chi} = \left(\frac{6i}{l}\right)^{1/2} \left\{ \frac{\Theta(|\mathbf{a}| \leq |s|)}{a^2} (E_2 + \chi)^{-1/2} + \frac{\Theta(|\mathbf{a}-\mathbf{s}| \leq |s|)}{|\mathbf{a}-\mathbf{s}|^2} (E_1 + \chi)^{-1/2} \right\} \quad (4.7)$$

$$iL = \left(\frac{6i}{l}\right)^{1/2} \int d^3a \left(\frac{\Theta(|\mathbf{a}| \leq |s|)}{a^2} (E_2 + \chi)^{-1/2} + \frac{\Theta(|\mathbf{a}-\mathbf{s}| \leq |s|)}{|\mathbf{a}-\mathbf{s}|^2} (E_1 + \chi)^{-1/2} \right). \quad (4.8)$$

I won't write out the details from here on for the answer is defined dimensionally and must be

$$p(\mathbf{0}, L) \propto L^{-9/5} \text{ i.e., } n^{-9/5}. \quad (4.9)$$

The details of the integration serve to fix the constant. Presumably one could break up G at more

than one point and get a better value for this constant, but the $n^{-9/5}$ would still come the same.¹

Having sketched out the entire function one can now normalize and get the height of the peak $L^{-17/10}$ which clearly dominates the rest of the function. By evaluating \bar{r}^2 one finds a series, the expansion parameter being $(L^{-1/10} v^{-1/3} l^{7/10})$ which must be small for the above analysis to be valid.

Finally, the number of walks can be remarked upon since it is an interesting combinatorial point even if it has little bearing on polymers. As has been noted, the dominant feature will be the local effect of the effective phase space available per molecule. The long range effect will come from the unnormalized Green function which is

$$\frac{\mu^{L/l}}{r} \frac{1}{r^{3/2}} \exp \left(- \int (L - gr^{5/3})^2 / r^3 \right). \quad (4.10)$$

Integrating over r one gets the leading term to be $\sim \mu^n n^{1/5}$.

5. The Collapse of Polymers

What happens when the virial coefficient changes sign?² Instead of the repulsion pushing the polymer out faster than the random configurations, it will now be pulled in. For v large and attractive the polymer will condense into a solid ball, a state easily obtained experimentally even for a single chain. But for v near zero a new semicondensed state appears possible, and passage through the Flory temperature (i.e., $v=0$) will produce a phase change for a very long chain [3]. The physical picture will be of the polymer repeatedly passing through the same region of space so that again a polymer density is set up which now traps the polymer. Consider this problem from the point of view of I i.e., study the probability that, after a chain length $L' (0 < L' < L)$, the polymer will be at $\mathbf{r}, q(r, L', [L])$. As in I (where the present q is called p) one can argue that the polymer field can be represented by approximating

¹ This value has been conjectured by Fisher, Faraday Society Discussion 25, p. 200.
² Dr. J. Mazur has pointed out to me that $v=0$ may be much more complicated than is generally supposed. The discussion of this point due to Flory assumes that chains with $v=0$ are Gaussian, but a single chain is a distinctly nonuniform entity having a high "polymer density" at its center of gravity, tending to a low value at the end points. So one could have a ' $\bar{r}^2(L)$ ' effect from the middle to the ends. The following discussion may need modifying in the light of this comment.

$$\int_0^L \int_0^L V(\mathbf{R}(L') - \mathbf{R}(L'')) dL' dL'' \\ \cong \int_0^L V(\mathbf{R}(L') - \mathbf{s}) q(\mathbf{s}, L') dL' dL'' \quad (3.32)$$

But $q(r, L')$ can now be argued to be independent of L' since the self trapped polymer will repeatedly go through every point of its density; it will, of course, still be a function of L . Since V is short range one may now approximate by writing

$$\int_0^L \int_0^L V(\mathbf{R}(L') - \mathbf{S}) q(\mathbf{S}, L'') dL' dL'' \\ \cong \frac{w}{L} \int_0^L \int_0^L q(\mathbf{R}(L'), L'') dL' dL'' \quad (5.1) \\ = w \int_0^L \bar{q}(\mathbf{R}(L')) dL'$$

where w is Lvl^{-2} . This now gives a functional integral in the Markov form so that one can break the functional integral up to L at an intermediate L' and define

$$q(r', L') = \mathcal{N}(L') \int \exp \left[-\frac{3l}{2} \int_0^{L'} \left(\frac{\partial \mathbf{R}}{\partial L''} \right)^2 dL'' \right. \\ \left. - w \int_0^{L'} \bar{q}(\mathbf{R}(L'')) \right] \delta \mathbf{R} \quad (5.2)$$

which satisfies

$$\left(\frac{\partial}{\partial L'} - \frac{l}{6} \nabla^2 + w \bar{q}(r) - C(L') \right) q = \delta(r). \quad (5.3)$$

Ignoring C for the moment, the resulting differential equation will have eigenfunctions E_n ,

$$\left(\frac{\partial}{\partial L'} - \frac{l}{6} \nabla^2 + w \bar{q}(r) \right) q_n e^{E_n L} = 0 \quad (5.4)$$

$$\left(\frac{\partial}{\partial L'} - \frac{l}{6} \nabla^2 + w \bar{q}(r) \right) g(r, L) = \delta(r) \delta(L')$$

$$g(r, L) = \sum q_n(r) q_n^*(0) e^{E_n L} \Theta(L'). \quad (5.5)$$

There will be positive and negative eigenvalues. As $L' \rightarrow \infty$ only the positive ones survive and unless the largest positive eigenvalue tends also to zero the whole expression will diverge i.e., this eigenvalue is brought to zero by the normalization.

Thus one is led to the eq (5.6) in which C' now takes the role usually taken by the eigenvalue, and since q will not depend on L' , \bar{q} can be identified with it:

$$\left(\frac{l}{6} \nabla^2 + w(q(r) - q^2) \right) q(r) = 0 \\ \int q(r) d^3 r = 1 \\ \bar{q}^2 = \int q^2(r) d^3 r. \quad (5.6)$$

By redefining $r = r' w/l$ one brings the equation into the final form

$$-\frac{1}{3} \left(\frac{d^2}{dr'^2} + \frac{2}{r'} \frac{d}{dr'} \right) q + \left(\frac{w}{l} \right)^3 (q - \bar{q}^2) q = 0 \quad (5.4)$$

rather like the Schrödinger equation with an attractive potential and eigenvalue \bar{q}^2 . The solution has to be obtained numerically and clearly will have the form

$$q = Q(r l^3 / v L) \left(\frac{l^3}{v L} \right)^3, \quad (5.5)$$

where Q is a dimensionless function. Clearly in this case

$$\bar{r}^2 \propto v^2 L^2 l^{-6} \quad (5.6)$$

which is quite different both from the $L^{6/5}$ and the Einstein Law, $\bar{r}^2 \propto L l$. The distribution changes abruptly as

$$v > 0 \rightarrow v = 0 \rightarrow v < 0.$$

I have been greatly helped by discussions with Professor G. Gee, Professor C. Domb, Professor M. E. Fisher and Dr. J. Mazur.

6. References

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- [3] The standard text particularly with reference to $v=0$ is Flory, P. J., Principles of Polymer Chemistry, Cornell University (1953).

Some Comments on Techniques of Modern Low-Temperature Calorimetry

I. M. Firth

University of St. Andrews, St. Andrews, Scotland

Introduction

Precision calorimetry at low temperatures started in 1929 when a sensitive phosphor-bronze thermometer was made by Keesom and Van Den Ende [1]. This led shortly to the discovery of the heat capacity connected with the superconductive phase transition [2] and also the electronic heat capacity in metals [3] was discovered and found to be in reasonable agreement with the theoretical predictions. Recently with the use of carbon resistance thermometers [4] and a-c bridge lock-in amplifier methods of measurement [5], a new era of precision has been entered. This has allowed the more exciting phase transitions at low temperatures to be checked. This era has come opportunely for at a recent meeting in Washington on "Phenomena in the Neighborhood of Critical Points" [6] it was emphasized that to obtain agreement with theoretical predictions very great care and precision must be taken in experimental measurements, not only of heat capacities, but of all properties related to such critical phenomena: e.g., magnetization, thermal conductivity, optical and neutron diffraction.

In considering the present situation in calorimetry, it is useful to review the way in which the main requirements of low temperature calorimetry were introduced. Although Gaede [7] used a metal calorimeter isolated somewhat from its surroundings it was Nernst [8] who recognized a few years later in 1909, that on account of surroundings there was usually a temperature gradient inside a calorimeter which would prevent making accurate, or often meaningful, measurements. To obviate this he placed the calorimeter in a vacuum realizing that, radiation being small at low temperatures, it was possible to obtain excellent thermal isolation and reduce the above error to a minimum.

Of course, it was necessary to change the temperature of the calorimeter and to do this he used an exchange gas, noting in the course of his work the drawback of remnant gas on the thermal isolation and, absorbed gas on the calorimeter on the

heat capacity measured. Temperature was measured by a platinum resistance thermometer the wire of which also acted as the electrical heating element for the calorimeter. Measurements with this arrangement were uncertain even with the most careful calibration of the resistance, because of irregular changes in the resistance of the platinum wire heating the calorimeter. Nernst avoided this disadvantage and at the same time made his method more simple, by measuring the variations of temperature resulting from electrical heating by using a thermocouple [9]. One junction was fixed to the calorimeter and the other lay on a lead block also in the vacuum chamber, figure 1. The heat capacity of lead being large, the temperature of the block remained nearly constant and any small drift took place slowly and uniformly so that the temperature of that junction could be corrected. A copper shield that enclosed the calorimeter was soldered to the lead block and this refinement was a great improvement on the open calorimeter. Nernst could measure temperature to 0.1 °K and specific heat to ~2 percent.

It is easy to see from this arrangement how adiabatic methods developed. The thermal insulation of this device can never be perfect so long as there

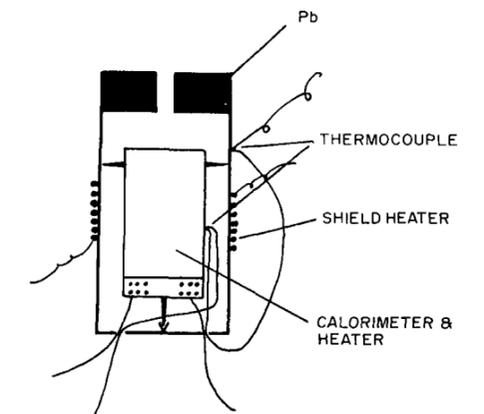


FIGURE 1. Calorimeter of Nernst showing the lead block, copper shield, heaters, and measuring thermocouple.