QUARTERLY REVIEWS

THE APPLICATION OF MONTE CARLO METHODS TO PHYSICOCHEMICAL PROBLEMS

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WITH the advent of fast electronic computers the Monte Carlo method has become a powerful tool in the hands of the theoretical chemist. Based on random sampling, it can be used to solve complex problems for which analytical methods are powerless, with an accuracy limited only by statistical considerations. In many physical problems the basic elements of the calculation may be fully understood but the general complexity prevents solution by standard means. For such problems the Monte Carlo method is particularly appropriate, whereas for simple calculations it is generally inefficient. As yet no general review of the applications of the method to problems of chemical interest has been available. Monte Carlo techniques have been used with some success in three fields of particular interest to chemists and these will be reviewed separately: (1) the properties of dense gases, liquids, and solids; (2) the configuration of macromolecules; and (3) order–disorder phenomena. In each of these the appropriate analytical theories will be surveyed and their conclusions compared with the results obtained by Monte Carlo methods. The Monte Carlo methods to be described generally involve the simulation of physical systems (in a purely mathematical sense), and the method is not markedly different, in principle, from the physical simulation of such systems. There have been frequent attempts to use physical models as molecular analogues in order to obtain a better understanding of molecular processes and the structure of matter. Ball bearings, seeds, and similar objects have all been used to study the distribution of molecules in liquids and metals, though, because of the practical difficulties, much of the work has been confined to two dimensions. Morrell and Hildebrand,[1] however, constructed a model liquid by means of gelatine balls, hardened by chemical treatment, in a matrix of liquid gelatine of the same density. The "molecular" distribution in this liquid was very similar to that observed in real liquids by *X*-ray diffraction studies.

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[1] W. E. Morrell and J. H. Hildebrand, *J. Chem. Phys.*, 1936, **4**, 224.

The Monte Carlo Method[2, 3]

The difficulty of devising appropriate mechanical models has severely limited the value of physical simulations of molecular systems. However, the availability of fast electronic computers has made it possible to design calculations involving essentially the same approach. The Monte Carlo technique is, in its essential and simplest form, an experimental study of a mathematical model of some physical process. Thus, if we wished at a game of chance to estimate our probable losses due to the "house percentage," we could proceed in several ways. The simplest, but probably most expensive, would be a direct appeal to experiment; as an alternative we could attempt to analyse the statistics of the game and perform a direct calculation. For all but the simplest games this would be prohibitively difficult. In such a case the statistical approach of the Monte Carlo method may be applied. From our knowledge of the rules of the game we can construct a directly analogous mathematical scheme, using random numbers to represent the fall of dice or the distribution of playing cards. We can then "play" a large number of games until the average house winnings converge, as closely as desired, to a steady value: the house percentage. With the aid of a fast electronic computer this apparently inefficient method may produce a satisfactory result in a comparatively short time. The Monte Carlo method involving such sampling procedures can be applied to a very wide range of problems. A trivial but instructive example is the integration,

$$\bar{y} = \int_0^A \mathrm{f}(x)\mathrm{d}x.$$

By choosing N specific values of x $(x_1, x_2 \ldots x_i \ldots x_n,)$ at random we can compute

$$\hat{y} = \frac{A}{N}\sum_{i=1}^{i=N} \mathrm{f}(x_i).$$

The accuracy of the estimate $\hat{y}$ of $\bar{y}$ will depend on both the number of samples of x_i considered and on the nature of the function $\mathrm{f}(x)$. For example, if we wish to estimate $\hat{y} = \bar{y} \pm \epsilon$, with 95% certainty, the number of samples required (N) is given (when N is large) by

$$N = 3{\cdot}84 \text{ var } (\hat{y})/\epsilon^2.$$

The variance, var $(\hat{y})$, is defined as

$$\text{var } (\hat{y}) = \frac{1}{N}\left[\int_0^A \mathrm{f}(x)^2\mathrm{d}x - \bar{y}^2\right].$$

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[2] Monte Carlo Method, U.S. Dept. of Commerce, National Bureau of Standards, Applied Maths., Vol. XII.

[3] Symposium on Monte Carlo Methods (1954), University of Florida, John Wiley and Sons Inc., New York.

The efficiency of the method in the solution of any given problem will depend on the variance, and the key to the use of the Monte Carlo method is the devising of sampling schemes which will produce a small variance and so converge rapidly. Basically most methods of variance reduction presuppose some approximate knowledge of the final answer so that each sample may be classed according to the size of its contribution. Samples are chosen, not at random, but from some other probability function which is nowhere zero and varies so that the probability of picking a sample is greatest in the region of most importance. Samples selected in this manner are weighted (by the inverse probability of selection) to obtain an unbiased final value.

An example of both the Monte Carlo method and of the power of variance-reduction techniques in a very simple case is the determination of the area of a quadrant of a circle (Fig. 1). The simplest way would be to sample pairs of x_i and y_i randomly from 0 to 1, estimating the fraction of total points within the quadrant by using the condition:

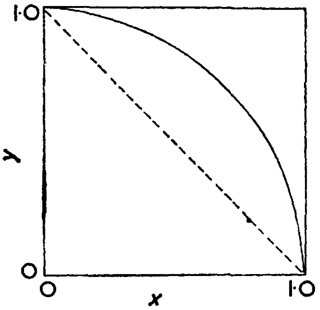

FIG. 1. *Quadrant of a circle, of which the area can be determined by both Monte Carlo and variance-reduction techniques.*

$$x_i^2 + y_i^2 \leqslant 1.$$

The ratio of such samples to the total number would give the area. In this case the variance may be shown to be 0·17/N. A superior method would involve sampling only x randomly from 0 to 1 to evaluate the integral

$$\int_0^1 (1 - x^2)^{\frac{1}{2}} \mathrm{d}x \approx \frac{1}{N} \sum_{i=1}^{i=N} (1 - x_i^2).^{\frac{1}{2}}$$

The variance is now

$$\operatorname{var}(\hat{y}) = \frac{1}{N}\left[\int_0^1 (1 - x^2)\mathrm{d}x - (\pi/4)^2\right] = 0{\cdot}05/N.$$

This method would be three times as efficient as the previous one if the computing time per iteration were unchanged—an assumption which is no more than approximately true. Had only those points lying above the 1,1 diagonal been considered, and the area of the segment been estimated, a variance as low as $0{\cdot}015/N$ could be obtained. In more complicated problems even greater savings can sometimes be attained. The evaluation of a simple integral of this type would never be carried out by a Monte Carlo method since, even if an analytical procedure were unavailable, a systematic numerical quadrature would be very much more efficient. However, for multiple integrations of four or more dimensions the Monte Carlo method is usually more powerful.

The Monte Carlo method has been used in two somewhat different types of problem. The first class comprises those problems to which, in principle, a numerical method could be applied but is impracticable owing to computational difficulties. High-order multiple integrations are a typical example. The second type of application is in the solution of statistical problems for which no concise mathematical formulation is available but only a set of rules for forming a population from which samples may be drawn. In the physical world there are many problems for which a good conceptual model of the individual events is available but in which the complex statistical nature of their interactions precludes any simple solution. This situation is particularly common in chemistry where the behaviour of dense gases and liquids, the structure of polymers, and order–disorder phenomena in the solid state and many similar problems have defied any quantitative understanding. The Monte Carlo method can therefore be expected to find considerable application in chemical problems. The remainder of this Review is concerned with the several attempts that have already been made to use Monte Carlo techniques to solve such problems. The three main areas are discussed separately. The recent applications of the method to the theory of absolute reaction rates are also reviewed.

The States of Matter

One of the most general problems which occur in physical chemistry is the evaluation of bulk properties of matter in terms of the forces acting between molecules (and *vice versa*). The problem in general cannot be solved; thus no adequate theoretical prediction of the properties of liquids or dense gases is possible. In the first place, we lack precise knowledge of the forces between molecules. The Lennard-Jones intermolecular potential is generally considered adequate for the inert gases but it is an oversimplification when applied to more complicated molecules. Nevertheless, even if an accurate knowledge of the forces between molecules were available, the major difficulty would still remain, that is, the purely statistical problem of accounting for the mutual interactions of large numbers of molecules. The properties of a molecular system can be expressed in terms of the partition function which, for a classical system, is given by

$$Z_N = \frac{1}{N!h^{3N}}\int \ldots \int \exp(-E/kT)\,\mathrm{d}q_1 \ldots \mathrm{d}q_{3N},\mathrm{d}p_1, \ldots \mathrm{d}p_{3N},$$

where p and q are the conjugate momenta and co-ordinates. The contribution of the kinetic energy can be evaluated by direct integration, but the contribution of the potential energy is not so easily evaluated. The so-called configurational integral may be written:

$$Q_N = \frac{1}{N!}\int \ldots \int \exp[-U(q)/kT]\,\mathrm{d}q_1 \ldots \mathrm{d}q_{3N},$$

where $U(q)$ is a function of all co-ordinates. As, in general, this integration cannot be performed, most theories attempt to simplify it by approximating the relation between the potential energy of the system and the co-ordinates of the molecules. Thus the potential energy might be expressed as a function of the co-ordinates of a few molecules only. The derived thermodynamic properties are valid only so far as the initial assumptions are valid.

Two such approaches are of particular interest. At low densities the equation of state of a gas can be expressed in terms of a series of virial coefficients

$$PV/RT = 1 + B(T)/V + C(\mathrm{T})/V^2 + \ldots\ldots$$

The second virial coefficient, $B(T)$, is related to the relative co-ordinates of two (spherically symmetrical) molecules by the equation

$$B(T) = -\,2\pi N\int_0^\infty [\exp(-\,U(r)/RT) - 1]r^2\mathrm{d}r,$$

where r is the separation of the molecular centres. If the variation of the intermolecular potential energy $U(r)$ with r is known, $B(T)$ can be evaluated. At high densities the cell (or free-volume) theory has been used extensively with moderate success. A reference molecule is considered to move in a potential field produced by its neighbours which are assumed to be fixed on lattice sites. The method is not very satisfactory for liquids but it has been the basis of a large amount of research.

The Monte Carlo method differs fundamentally from theories of this type as no attempt is made to simplify the configurational integral.[4] If the forces acting between molecules are known it is possible to sample the configurations of a large number of molecules and so evaluate the configurational integral with an accuracy limited only by statistical considerations. The assumption of the pairwise additive nature of the intermolecular

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[4] I. Z. Fisher, *Soviet Physics Review*, 1960, 2, 783.

energy is an approximation common to most analytical and Monte Carlo methods. The simplest type of Monte Carlo procedure would sample the configurations generated by a number of molecules placed at random in a regular volume.[5] The total energy of the system could be calculated from a knowledge of the form of the intermolecular potential, enabling each overall configuration to be weighted by the appropriate Boltzmann factor. The value of any equilibrium property can then be obtained by averaging over sufficient configurations. The limitation of this approach is that, except at the lowest densities, any randomly constructed molecular distribution is likely to be an extremely improbable one. Thus, in the case of hard-sphere molecules, an acceptable non-overlapping configuration is almost impossible to generate by this method at densities greater than those appropriate to the dilute gas.

The Monte Carlo method of Metropolis, Rosenbluth, Rosenbluth, Teller, and Teller.[6]—A more powerful method was devised by Metropolis *et al.*[6] The molecules are confined to a rectangular or cubic space by periodic boundary conditions which in effect give rise to an infinite space made up of unit translations of the basic cell. It is considered that at least 32 or 64 molecules in the basic cell are required to give an adequate picture of the condensed states of matter. Initially the molecules are distributed on a lattice and new configurations are generated by moving one molecule at a time. In the case of hard-sphere molecules the theory takes a particularly simple form. If a move were such as to cause an overlap, the potential energy would be infinite and the new configuration of the system would have zero probability and need not be considered. In such a case the system is returned to its original configuration. However, all configurations which do not involve overlapping molecules are equally probable and contribute to the final average of any property. Each acceptable configuration is analysed in terms of a pair distribution function, $g(r)$, of the molecules. This function defines the number density of molecular centres at a distance r from a reference molecule. Thus the number of molecular pairs which are separated by a distance r is $(N^2/2V)g(r)4\pi r^2 \mathrm{d}r$. After many configurations have been analysed the average pair distribution function is used to calculate the thermodynamic properties in the usual manner. Thus, for hard spheres,

$$PV/RT = 1 - (2\pi/3\mathrm{V})\ [g(\sigma)\sigma^3],$$

where σ is the diameter of the molecules and $g(\sigma)$ is the pair distribution function evaluated at the point of contact.

This method represents a great advance on the simple technique first described, in which molecules are introduced randomly into an appropriate space. In place of a series of independent samples, each weighted

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[5] B. J. Alder, S. P. Frankel, and V. A. Lewinson, *J. Chem. Phys.*, 1955, **23**, 417.

[6] Metropolis, Rosenbluth, Rosenbluth, Teller, and Teller, *J. Chem. Phys.*, 1953, **21**, 1087.

by the appropriate Boltzmann factor, this method generates new configurations in such a way that the probability of their occurrence is proportional to the Boltzmann factor and then weights all configurations equally. This corresponds to the generation of a Markov chain with constant transition probabilities.[7] Since the outcome of any trial is not independent but depends on the outcome of the trial immediately before it, the probability of configuration E_k is no longer associated with a fixed probability p_k, but to every pair E_j,E_k there corresponds a conditional probability p_{jk}. Thus if E_j occurs then the probability that E_k follows is p_{jk}. The various probabilities form a matrix of transition probabilities. A series of trials obeying statistics of this form is called a Markov chain. The absolute probability $a_k^{(n)}$, of state E_k after n steps starting from E_j can be expressed

$$a_k^{(n)} = \sum_j a_j\, p_{jk}^{(n)},$$

where a_j is the probability that E_j occurs in the initial trial. $a_k^{(n)}$ should be independent of a_j if n is large. This is the case if $p_{jk}^{(n)}$ converges to a finite limit independent of j. This is usually so if no periodicities occur. States which have a mean finite recurrence time but are not periodic are called ergodic states, and for a stationary distribution to occur all states must be ergodic. All such states can be attained from every other state. For such a system there is a stationary distribution which is unique and tends, as n gets large, to become independent of the initial state.

In a classical molecular system each state occurs with a frequency proportional to the Boltzmann factor for that state. The commonly used transition probabilities are given by:[8]

$$\left.\begin{aligned} p_{jk} &= A_{jk} && U_k \leqslant U_j \\ &= A_{jk}\exp[-(U_k - U_j)/kT]; && U_k > U_j \end{aligned}\right\} k \neq j;$$

$$p_{jj} = 1 - \sum_{j \neq k} p_{jk},$$

A_{jk} is only non-zero when the two states differ only in the co-ordinates of one molecule. A further restriction is that A_{jk} is zero if the move is such as to take the molecule a distance greater than that defined by an arbitrary fixed parameter, a condition which is included to increase the probability that moves will be acceptable. This parameter determines the rate of convergence of the method but not the final average. In the case of hard spheres the above conditions reduce to

$$\begin{aligned} p_{jk} &= A_{jk}; && U_k = 0; \\ p_{jk} &= 0; && U_k = \infty. \end{aligned}$$

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[7] W. Feller, "Probability Theory and Its Applications," John Wiley and Sons Inc., New York, 1950, Ch. 15.

[8] W. W. Wood and F. R. Parker, *J. Chem. Phys.*, 1957, **27**, 720.

The theory, together with many computational details, has been given by Wood *et al.*[8,9]

Molecular Dynamics.—The Monte Carlo method of Metropolis *et al.* is concerned only with the equilibrium properties of molecular systems, and the moves which the molecules undergo are not associated with real time but only with an arbitrary computer time. However, it is possible to solve with any required accuracy the simultaneous classical equations of motion of a number of molecules—this explicit simulation technique has been called molecular dynamics.[10,11] The molecules are again confined to cubic or rectangular boxes by periodic boundary conditions. To start with, the molecules are given equal kinetic energies with velocities in random directions, and after each collision the new velocities of the interacting molecules are calculated. The number of collisions as a function of time, and the sum of the momentum changes, are recorded to enable the collision rate and the pressure to be evaluated. This extension to transport properties represents a great advance in simulation techniques and enables a wide range of problems of a kinetic nature to be tackled.

Hard-sphere Systems.—Hard spheres exerting no attraction on each other are the simplest type of molecular model; consequently the properties of systems of such molecules are of particular interest. The potential is defined

$$U(r) = \infty;\ r \leqslant \sigma;$$
$$U(r) = 0;\ r > \sigma;$$

where σ is the collision diameter of the molecule. Before simulation calculations were undertaken it was a matter of controversy whether such systems could undergo phase transitions. The majority of studies have involved hard sphere molecules in two or three dimensions.*[12–15] Fig. 2 illustrates the Monte Carlo equation of state for three-dimensional hard-sphere systems and those predicted by various theories. Not unexpectedly the virial expansion provides an adequate model for the low-density results, whereas the cell theory is in poor agreement at all except the very highest densities. The most interesting feature of the Monte Carlo results is the phase transition which is observed in hard-sphere systems. The transition is between the fluid and the solid phase and, despite the absence of attractive forces, both phases are well defined. The Plate illustrates the change in the molecular motions in a system of hard spheres that has

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* "Two-dimensional hard spheres" are more properly called hard discs.

[9] W. W. Wood and J. D. Jacobson, Proc. Western Joint Computer Conference, San Francisco, California, 1959, p. 261.

[10] T. Wainwright and B. J. Alder, *Nuovo Cimento Suppl.*, 1958, **6**, 116.

[11] B. J. Alder and T. W Wainwright, *J. Chem. Phys.*, 1959, **31**, 459.

[12] M. N. Rosenbluth and A. W. Rosenbluth, *J. Chem Phys.*, 1954, **22**, 881.

[13] W. W. Wood and J. D. Jacobson, *J. Chem. Phys.*, 1957, **27**, 1207.

[14] B. J. Alder and T. Wainwright, *J. Chem. Phys.*, 1957, **27**, 1208.

[15] B. J. Alder and T. Wainwright, *J. Chem. Phys.*, 1960, **33**, 1439.

spontaneously undergone a transition from the fluid to the solid phase with no change in density. The photographs were obtained by following the molecular trajectories for 3000 collisions, and using the method of molecular dynamics. Hard-sphere systems undergo no gas–liquid transition and behave like substances above their critical temperature. The simplest form of intermolecular potential to give rise to all three states of matter is the square-well intermolecular potential which allows for molecular attraction.

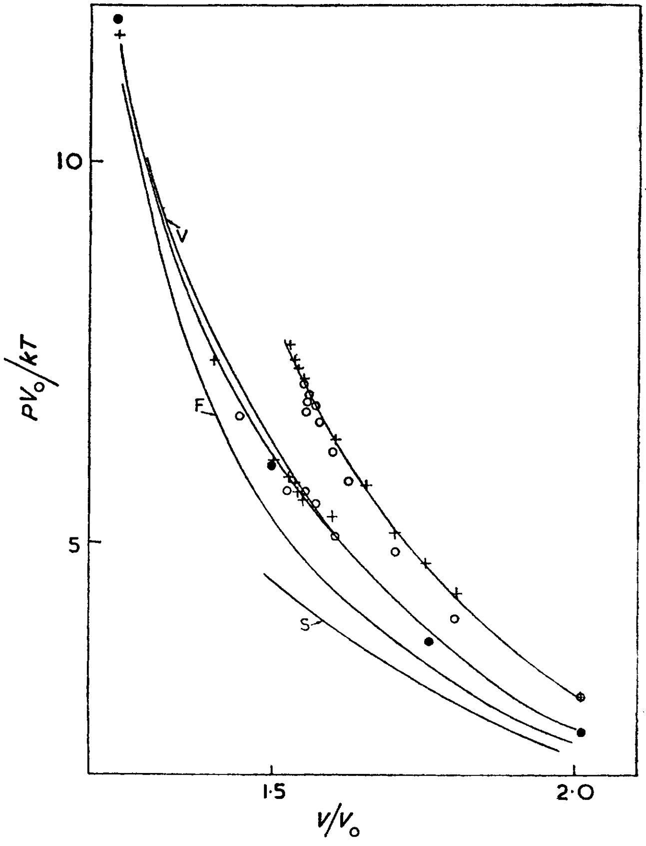

FIG. 2. *The equation of state for hard-spherical molecules.* The unlabelled solid curves represent the results obtained by molecular dynamics for system of 108 molecules. V_0 is the volume at close packing. The discontinuity at $V/V_0 \approx 1{\cdot}55$ is the fluid–solid phase transition. The predictions of various analytical methods are labelled: F, free-volume theory; V, virial expansion; S, superposition theory. Other symbols: + molecular dynamics for 32 molecules; O Monte Carlo results of Wood and Jacobson;[13] ● Monte Carlo results of Rosenbluth and Rosenbluth.[12]

(*Reproduced, by permission, from ref.* 13.)

Monte Carlo calculations have also been made on binary mixtures of hard-sphere molecules with a radius ratio 5:3.[16] Preliminary results showed that such systems undergo a contraction on mixing, and a feature of the results for such mixtures is that the cell model is found to be a somewhat better approximation when used to predict changes on mixing than when applied to the pure components. Further work is under way. Up to moderate densities the initial configuration of the mixture can be generated by distributing the two species randomly in a lattice. At high densities the problem of generating initial configurations is severe and special techniques are required involving a gradual expansion of the radii of the molecules.[17] At these densities the results indicate that transitions between certain types of configuration become very improbable and the total number of states may be effectively divided into more than one class between which transitions are extremely improbable. Wood, who has called this the quasi-ergodic problem, has pointed out that under these conditions spurious results will be attained.

The method of molecular dynamics has been applied to hard-sphere systems, and the equilibrium properties obtained agree well with the more recent Monte Carlo calculations. The phase transition was studied and found to be absent in systems of four or less molecules. Even with 500 molecules the two phases did not exist in the system simultaneously. The fact that more than four molecules must be involved makes it unlikely that the transition can be studied by analytical means. A full investigation of the dependence of the general thermodynamic properties on the number of molecules in the system has been made.[15] Thirty-two molecules give a reasonably adequate prediction of the equation of state in the fluid region whereas at least 64 molecules are required at higher densities. An interesting feature of the results was the speed with which the Maxwellian velocity distribution was attained. Whereas configurational distributions are modified only very slowly, the equilibrium velocity distribution is reached after 2—4 collisions per molecule. The equilibrium collision rate is given by the Enskog theory with considerable accuracy at all densities,[18] but this theory gives the self-diffusion coefficient correctly only in the fluid region. The exact results which have become available for this simple molecular model have already provided a stimulus to the development of analytical theories. Recently a new theory has been developed[19] which enables the equation of state of hard-sphere systems to be predicted with an accuracy never before attained. The use of the exact hard-sphere results as a basis for perturbation treatments of more realistic forms of intermolecular potential has also proved valuable.[20]

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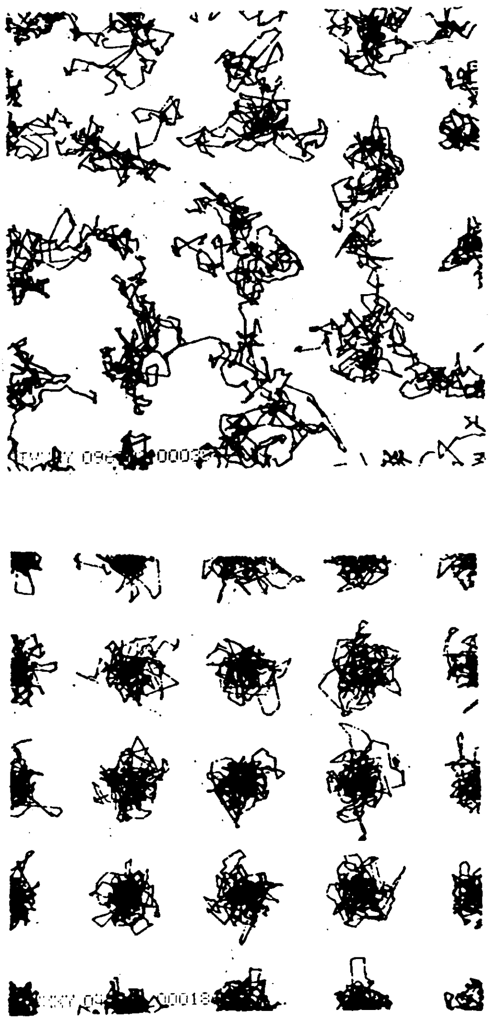
[16] E. B. Smith and K. R. Lea, *Nature*, 1960, **186**, 714.

[17] W. W. Wood, personal communication.

[18] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons Inc., New York, 1954, p. 634.

[19] H. Reiss, H. L. Frisch, and J. L. Lebowitz, *J. Chem. Phys.*, 1959, **31**, 369.

[20] E. B. Smith and B. J. Alder, *J. Chem. Phys.*, 1959, **30**, 1190.



The phase transition in hard-sphere systems. The traces were made by a succession of positions in a 32-particle hard-sphere system as determined by the method of molecular dynamics. 3000 collisions (a) in the liquid phase, and (b) in the solid region. The solidification has taken place spontaneously as both systems are under identical conditions ($V/V_0 = 1{\cdot}525$).

(Reproduced by permission from Alder and Wainwright.[11])

Lennard-Jones Molecules.—The success of the method of Metropolis *et al.* with simple molecular systems led to its application to a more realistic molecular model.[8] The Lennard-Jones intermolecular potential

$$U(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^{6}]$$

has been shown to be an adequate basis for the interpretation of the properties of the inert-gas molecules. The details of the calculation are somewhat different from that designed for hard-sphere systems. Any configuration j is changed to configuration k by moving one molecule. The potential energies U_j and U_k are then evaluated; if $U_k \leqslant U_j$ the new configuration is accepted. If $U_k > U_j$ then $\exp[-(U_k - U_j)/kT]$ is compared with a random number between 0 and 1, and, if the exponential is larger, the new configuration is accepted. If the reverse is true the original configuration is retained. These conditions make the probability of any configuration proportional to its Boltzmann factor. Because of the comparatively long-range nature of the Lennard-Jones forces the effect of distant neighbours was approximated in two ways, first, by assuming a lattice distribution and, secondly, by assuming a uniform distribution. The latter method proved satisfactory in most cases. The total potential energy of any configuration is estimated (for pairwise additive potentials) by

$$U = \tfrac{1}{2} \sum_{i=1}^{N} \sum_{\substack{j=1 \\ i \neq j}}^{N} U(r_{ij}).$$

The average potential energy over the Markov chain length gives the excess internal energy of the system. The excess heat capacity is calculated from the relation

$$C_v^E/R = N[<(U/NkT)^2>_{\text{av.}} - (U/NkT)^2],$$

and the equation of state from computations of the pair distribution function $g(r)$

$$\frac{PV}{RT} = 1 - \frac{2\pi N^2}{3NkT} \int_0^\infty g(r) \frac{\mathrm{d}u}{\mathrm{d}r} r^3 \mathrm{d}r.$$

The thermodynamic properties were calculated for Lennard-Jones molecules at the reduced temperature $kT/\epsilon = 2{\cdot}74$ and over a wide range of density to enable a comparison to be made with the experimental results of Michels *et al.*[21] and Bridgman[22] for argon at 55°C. Systems containing 32 and 108 molecules were studied and the results for both numbers were in good agreement. By using the potential parameters ϵ and σ, determined by Michels from a study of the second virial coefficient of argon, a comparison of the Monte Carlo and the experimental results can be made without the introduction of any adjustable parameters. As illustrated by Fig. 3 the Monte Carlo results and those of Michels from 150 to 2000 atm.

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[21] A. Michels, H. Wijker, and H. Wijker, *Physica*, 1949, **15**, 627.

[22] P. W. Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1935, **70**, 1.

are in excellent agreement but a discrepancy is evident between the calculations and Bridgman's results from 2000 to 15,000 atm. This may be due to the inadequacy of the Lennard-Jones intermolecular potential at high densities or to the fact that the pairwise additive potential approximation is no longer valid. However, the facts that the Monte Carlo results provide a better continuation of Michels's results (whereas there is a discontinuity between these and Bridgman's), and that Bridgman's results for nitrogen, reported in the same paper, have disagreed with more recent equation-of-state determinations, suggest that the Monte Carlo results may be more accurate than the experimental results at high densities.

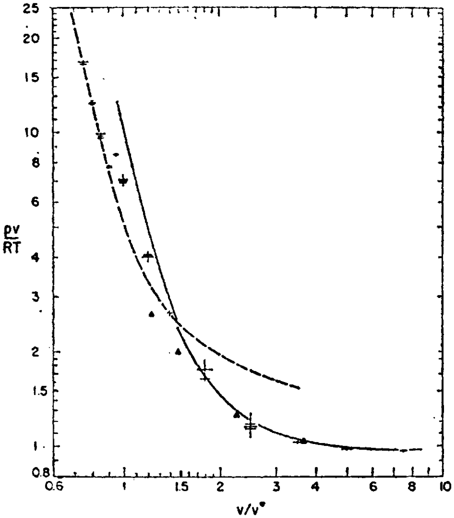

FIG. 3. *The equation of state of a system of Lennard-Jones molecules.* The crosses represent the Monte Carlo results. The upper solid curve represents Bridgman's results for argon at high pressures, and the lower one Michel's measurements up to 2000 atm. The broken curve is based on the results of the cell theory and the triangles on the superposition approximation. The discontinuity at $V/V^* \approx 1{\cdot}0$ is the phase transition. V^* is defined as $(\sqrt{2})N\sigma^3$, where σ is the collision diameter.

(Reproduced with permission from Wood and Parker.[8])

Order–Disorder Problems.

Many physical and chemical problems involve order–disorder processes on lattices. Superlattice transitions in alloys and the various co-operative transitions in many solid compounds are common examples. A theory of regular solutions has also been developed by using a lattice model. The general theory of order–disorder processes is appropriate to many similar phenomena.[23]

[23] E. A. Guggenheim, "Mixtures," Oxford University Press, London, 1952.

The simplest case involves two species A and B distributed on a lattice. The total interaction energy can be written

$$U = N_{AA}\,\omega_{AA} + N_{BB}\,\omega_{BB} + N_{AB}\,\omega_{AB},$$

where $N_{\alpha\beta}$ is the number of $\alpha\beta$ neighbour pairs and $\omega_{\alpha\beta}$ is the interaction energy of α and β species. An interchange energy ω is defined as

$$\omega = \omega_{AB} - \tfrac{1}{2}\omega_{AA} - \tfrac{1}{2}\omega_{BB},$$

which represents the energy of formation of an AB pair. The total energy is clearly dependent on the distribution of A and B on the lattice, that is, the degree of order present. The simplest treatment of this problem is to assume that the distribution is random despite the different energies of interaction. This has been called the zero-th approximation and was used by Bragg and Williams in their theory of superlattice transitions.[24] In the case of most liquid mixtures ω is positive and the tendency is towards phase separation, but for many metal alloys ω is negative and the tendency to form unlike pairs leads to a regular array called a superlattice in which the number of such pairs is maximum. Both tendencies are overcome by high temperatures, which favour random mixing, and definite transition temperatures exist at which randomness overcomes the ordering tendency. Such transitions are associated with a large rise in heat capacity. The transition temperature (T_c) is given by

$$T_c = z\omega/2\boldsymbol{k}$$

for the zero-th approximation, where z is the number of nearest neighbours. More sophisticated approximations make some allowance for the fact that the energy differences involved in the formation of various pair leads to a non-random distribution. Thus Guggenheim suggested that a parallel with chemical equilibrium could be drawn and proposed

$$N_{AA}N_{BB}/(N_{AB})^2 = e^{2\omega/\boldsymbol{k}T}/4.$$

This equation is the basis of the quasi-chemical theory which is a first-order approximation. This theory gives

$$T_c = \omega/\{\boldsymbol{k}\ln[z/(z-2)]\}.$$

Higher approximations are prohibitively difficult to evaluate by normal methods but the problem is most suitable for Monte Carlo study. Salsburg, Jacobson, Fickett, and Wood[25] applied the Monte Carlo method to a two-dimensional triangular lattice-gas (a lattice whose sites are only partly filled by interacting particles) for which an exact solution is available. The co-ordination number of the lattice is 6 and the molecules interact only

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[24] W. L. Bragg and J. E. Williams, *Proc. Roy. Soc.*, 1934, *A*, **145**, 699; *ibid.*, 1935, *A*, **151**, 540.

[25] Z. W. Salsburg, J. D. Jacobson, W. Fickett, and W. W. Wood, *J. Chem. Phys.*, 1959, **30**, 65.

with nearest neighbours, the interaction giving rise to a pair energy ϵ. N such particles are considered, distributed on M lattice sites. New configurations are generated by moving a "molecule" to an unoccupied site selected at random, and the system is contained by periodic boundary conditions. The details of the method are similar to that devised by Metropolis *et al.* If the new configuration has a lower energy it is accepted. If not, the exponential of the energy difference is compared with a random number between 0 and 1. An exponential greater than the random number leads to the acceptance of the new configuration, otherwise the system is returned to its original state. Systems of from 8 to 98 molecules were studied on lattices for which 50% of the sites were occupied ($N/M = 0{\cdot}5$) at a reduced temperature defined by

$$\exp(-\epsilon/kT) = 2.$$

The results were extrapolated to give values corresponding to an infinite number of molecules. The ratio U/ϵ, that is, the ratio of the average internal energy per molecule to that of a single pair interaction (or the average number of nearest-neighbour bonds per molecule), was found to be 1·896. The value given by exact treatment[26] was 1·8938. About 500,000 configurations were considered in each case. A further study was made of the variation of the properties of the system with the fraction of sites occupied. The results show the power of the Monte Carlo method in dealing with problems of this type. In a similar study, Fosdick[27] considered a two-dimensional lattice, and for a 20 × 20 lattice rapid convergence was reported except near the Curie point, but as yet only a preliminary notification of the research is available.

The Monte Carlo method has also been applied to more realistic lattices of interest to metallurgists. Guttman[28] investigated order–disorder phenomena in a body-cenrted cubic lattice containing two types of atom. He considered systems of from 256 to 1024 molecules at various composition ratios. With $\omega_{AA} = \omega_{BB} = 0$, and $\omega = \omega_{AB}$, the total energy is given by

$$U = -N_{AB}\,\omega,$$

where N_{AB} is the number of A–B interactions. The results for an infinite crystal are summarised in the annexed Table, together with the predictions of various theoretical approximations. ρ_c represents the value of the short-range order parameter at the transition temperature. ρ is defined by

$$\rho = \frac{N_{AB} - N_{AB\,(\text{random})}}{N_{AB\,(\text{perfect order})} - N_{AB\,(\text{random})}}$$

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[26] G. F. Newell and E. W. Montrose, *Rev. Mod. Phys.*, 1953, **25**, 353.
[27] L. D. Fosdick, *Bull. Amer. Phys. Soc.*, 1957, **2**, 239.
[28] L. Guttman, *J. Chem. Phys.*, 1961, **34**, 1024.

TABLE. *Comparison of the results for a* 1:1 *superlattice in a body-centred cubic lattice at the critical temperature.*[28]

Method	$kT_c/z\omega$	S_c/Nk	C_v/Nk	ρ_c
Bragg–Williams (zero-th order)	0·5	0·693	1·50	0
Quasi-chemical (1st order)	0·435	0·652	1·78	0·144
Domb[a]	0·385	0·548	(∞)	0·311
Monte Carlo	0·379	0·495	(∞)	0·418

[a] Domb, Changements de phases, Comp. rend. reunion ann. avec comm. thermodynamique, union intern. phys., Paris, 1952, p. 177.

The heat-capacity maximum in the region of order–disorder transition reaches a maximum in an asymmetric manner. The Monte Carlo results are in quite good agreement with the experimental heat capacities for $\beta_{\text{Cu-Zn}}$, considering the primitive nature of the model used. Guttman concludes that the power of such calculations lies, not so much in the fact that they can be adapted to give exact numerical solutions of these problems as in the insight they give towards the construction of a simple but adequate theoretical model.

Fosdick[29] investigated order–disorder phenomena in a A_3B alloy on a face-centred cubic lattice, using a rather more sophisticated model. He defined interaction parameters

$$\omega^{(n)} = \tfrac{1}{2}\omega_{\text{AA}}{}^{(n)} + \tfrac{1}{2}\,\omega_{\text{BB}}{}^{(n)} - \omega_{\text{AB}}{}^{(n)},$$

where n refers to the order of the neighbour. Considering only first- and second-nearest neighbours, two parameters are defined, $\omega^{(1)}$ and $\lambda = \omega^{(2)}/\omega^{(1)}$, the latter representing the ratio of the interchange energies of the first and the second series of neighbours. Using systems of 500 lattice sites in 5 × 5 × 5 unit-cell arrays, and with periodic boundary conditions, he studied the system when $\lambda = 0$, $-$ 0·25, and $-$ 0·50. The transition temperature at these values of λ is given by $kT_c/\omega^{(1)} = 1{\cdot}01$, 1·61, and 2·25, respectively. Taking $\lambda = -$ 0·25, for the Cu_3Au system, $\omega^{(1)}$ is calculated to be 816 cal./mole, compared with values of 802 and 711 suggested by previous workers.

The Properties of Macromolecular Systems

The properties of high polymers of both natural and synthetic origin have been of interest for many years. Their anomalous physical properties, such as viscosity, which is dependent on the shear rate, light scattering, and long-range elasticity have provided a challenge to theory. The aim of all work in this field is to explain these macroscopic properties in terms of the detailed molecular geometry of the long chains involved. Unfortunately a know-

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[29] L. D. Fosdick, *Phys. Rev.*, 1959, **116**, 565.

ledge of the molecular formula and geometry of a polymer in the normal chemical sense is not sufficient, since the properties of such molecules do depend directly, not upon the formal chemical structure, but upon the actual configurations adopted by the polymer chains. In most work, the geometric properties of these chain configurations have been reported in terms of the average square distance between the ends of a chain of N links, $<R_N{}^2>_{\mathrm{av}}$. This quantity furnishes an indication of the size of the molecule and can be used in the prediction of its viscous properties. For example it has been suggested[30] for polymer solutions that

$$\eta_0 = K[<R_N{}^2>_{\mathrm{av}}]^{\frac{3}{2}}/M,$$

where η_0 is the intrinsic viscosity, which is obtained by extrapolation to zero concentration and zero rate of shear, M is the molecular weight, and K a constant.

Thus the first step in any rigorous treatment of the properties of a macromolecule must be the evaluation of the "average configuration," ideally in terms of a probability density function (W) which defines the probability of finding a chain segment of the macromolecule in a given region of space. This function being given, the problem is reduced to one in mechanics, albeit a very complex one. It is with the calculation of W that we shall be concerned in the remainder of this discussion.

In principle it should be possible to calculate W exactly from a knowledge of the segment–segment interactions and the molecular geometry, but in practice the statistical complexity is too great. However, many approximate methods have been devised. The simplest models[31,32] consider a polymer molecule as a long, freely jointed chain or random walk of equal steps, a model directly analogous to Brownian motion and for which the geometric properties can be determined exactly. Attempts have been made to improve this model by allowing for the effect of restricted rotation and fixed bond angles on the mean chain configuration. In the first such attempt Kuhn[33] showed that the variations in end–end length due to these molecular factors over a chain of many links could be dealt with by grouping several molecular links together to form a "statistical length." The actual molecular chain could then be replaced in the calculation by a chain made up of an equivalent number of freely jointed statistical lengths. The exact physical relation of the statistical length to the link length depends principally upon the intramolecular forces assumed in the calculation of Boltzmann weighting factors for each configuration.

An alternative method (*e.g.*, ref. 34) confines the chain segments to a lattice, the tetrahedral diamond lattice being particularly suitable for use when discussing quadrivalent carbon chains. The relative probability for

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[30] M. L. Huggins, *J. Phys. Chem.*, 1938, **42**, 911.

[31] E. Guth and H. Mark, *Akad. Wiss. Wien. Sitzungber.*, II*b*, 1934, **143**, 445.

[32] W. Kuhn, *Kolloid Z.*, 1934, **68**, 2.

[33] W. Kuhn, *Kolloid Z.*, 1936, **76**, 258.

[34] R. P. Smith, *J. Chem. Phys.*, 1960, **33**, 876.

each possible step at every stage of the chains's growth is computed, as in the Kuhn model, by considering the Boltzmann weighting factor for the step. The random walk on a lattice is known as a Polya walk, and it is possible, as in the case of a walk in continuous space, to calculate the average configuration of the chain. In general the theoretical calculations predict that a limit of the form

$$\lim_{N \to \infty} \langle R_N{}^2 \rangle_{\text{av}} = N l^2 A$$

exists where l = the individual link length, and A is a constant depending on the molecular properties of the chain. Unfortunately all calculations based upon these types of model are deficient in one important respect. No account is taken of the impossibility that two chain segments occupy the same region of space. In other words no allowance is made for the "excluded volume".

The Problem of Excluded Volume.—Despite many attempts to incorporate this factor in calculations, only one exact result has been obtained (on the limiting-step entropy for walks on a lattice).* In general the theoretical treatments have given rise to widely divergent predictions. Indeed it would be little exaggeration to say that all possible predictions as to the effect of excluded volume on chain configuration have been made at one time or another. The difficulty seems to lie mainly in the mathematical complexities associated with problems such as this in which the probability of any step depends directly, not only upon the immediately prior step, but upon all the previous steps

Rubin[35] in an ambitious attempt to secure a solution to the problem of self-avoiding random walks in continuous space was able to show that it was a bad approximation to neglect even high-order interactions (*i.e.*, interactions between segments separated by many chain links) and that no useful approximate solution was likely to be found; however, he was able to set an upper bound of 0·5 on ϵ in the empirical equation

$$\lim_{N \to \infty} \langle R_N{}^2 \rangle_{\text{av}} = K N^{(1+\epsilon)}.$$

Flory and Fox[36] in a less fundamental approach assumed that the density distribution of the excluded volume chain about a central reference point was Gaussian in form but broadened by segment–segment interaction. Thus $\langle R_N{}^2 \rangle_{\text{av}} = \langle R_N{}^2 \rangle^{\text{o}}_{\text{av}} A^2$, where $\langle R_N{}^2 \rangle^{\text{o}}_{\text{av}}$ refers to the simple model involving no excluded volume corrections and A is an "expansion coefficient." From thermodynamic considerations they deduced that $A^5 - A^3 = BN^{\frac{1}{2}}$ and that $\langle R_N{}^2 \rangle_{\text{av}}/N$ increased with N. Unfortunately

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* The limiting step entropy dS_{∞} for walks on a lattice is defined as

$$dS_{\infty} = k \log \lim_{N \to \infty} \left(\frac{\text{Number of allowed } n \text{ step walks}}{\text{Number of allowed } (n-1) \text{ step walks}} \right)$$

[35] R. J. Rubin, *J. Chem. Phys.*, 1952, **20**, 1940.

[36] P. J. Flory and T. G. Fox, jun., *J. Amer. Chem. Soc.*, 1951, **73**, 1904.

the approximations are of doubtful validity and it has been shown recently[37] that $(A^5 - A^3)/N^{\frac{1}{2}}$ is not constant but is an increasing function of A. Other workers[38] have used the simple unrestricted random walk as a first approximation and have attempted to allow for the effect of the excluded volume by incorporating additional "volume perturbation" terms in equations such as the differential Fokker–Planck equation which describes the distribution of end–end distances for simple random walks. However, the solution is very sensitive to the nature of the terms included and conflicting conclusions have been obtained.

Work on the other model of a polymer—the self-avoiding random walk on a lattice (SARWL)—has followed a more purely mathematical course; use has been made of a method in which rigorous upper and lower bounds on ϵ in the relation $\lim_{N \to \infty} \langle R_N^2 \rangle_{\text{av}} = KN^{(1+\epsilon)}$ are calculated, thus enabling the true value to be bracketed.[39] Unfortunately, it is not possible to produce a very accurate estimate of ϵ in this way since the calculations become prohibitively difficult if any but drastic simplifications are made. A method of direct enumeration has also been used in which the number of allowed configurations is counted directly.[40] The self-avoiding random walk has provided the only exact theoretical result in the field. Hammersley and Morton[41] were able to show that the limit $\mu = \lim_{N \to \infty} C_N/C_{N-1}$ exists for certain lattices where C_N and C_{N-1} are the total numbers of N and $N - 1$ step self-avoiding walks possible on the given lattice. The actual value of μ cannot yet be deduced mathematically but must be found experimentally. The constant μ is often known as the attrition constant since it determines the probability that the SARWL will be disallowed at its next step owing to an intersection. It is in fact related to the limiting-step entropy.

Monte Carlo Calculations.—The disagreement between the various approximate theoretical treatments of the chain-configuration problem suggests that none of them is entirely satisfactory. Unfortunately it is difficult to use experimental evidence to resolve this conflict since all the experimentally accessible quantities depend upon some bulk property which, as yet, can only be related to the polymer configuration in a rather arbitrary fashion. In this situation it would obviously be valuable to have some means of checking the accuracy of the theoretical prediction at some intermediate stage. A Monte Carlo method is well suited to this purpose since it can supply "experimental" information about chain configuration that would not otherwise be available.

An electronic computer can readily be programmed to generate a lattice model of a macromolecule by selecting, at random, steps along the

[37] M. Kurata, W. H. Stockmayer, and A. Roig, *J. Phys. Chem.*, 1960, **33**, 151.

[38] E. W. Montroll, *J. Chem. Phys.*, 1950, **18**, 734; J. J. Hermans, M. S. Klamkin, and R. Ullman, *J. Chem. Phys.*, 1952, **20**, 1360; H. M. James, *ibid.*, 1953, **21**, 1629.

[39] M. E. Fisher and M. F. Sykes, *Phys. Rev.*, 1959, **114**, 45.

[40] M. E. Fisher and B. J. Hiley, *J. Chem. Phys.*, 1961, **34**, 1253; 1961, **34**, 1531.

[41] J. M. Hammersley and K. W. Morton, *J. Roy. Stat. Soc.*, 1954, *B*, **16**, 1, 23.

lattice vectors, disregarding all chains which intersect. The "population" of random walk self-avoiding chains so generated can then be used to determine the various averages, such as end–end length, of theoretical and practical interest.

The method used differs in one important respect from that applied in the simulation of systems of hard-sphere molecules at high densities (as in the equation of state investigations), where the new configurations were achieved by the random motion of the constituent molecules over comparatively short distances. Thus there was a strong correlation between the configurations at successive iterations, and the approach to equilibrium was, in some sense at least, kinetic. In the generation of model polymer chains the packing density is much smaller (though this might not apply to a polymer in a very unfavourable solvent or with strong intersegment attractive forces) and it is consequently possible to generate entirely new random configurations of the chain at each iteration (though we shall see later that in some cases greater efficiency can be achieved by retaining a certain amount of the previous configuration). Thus the averaging is carried out over a spatial or Gibbsian ensemble. This method of averaging has several advantages and in particular it should be noted that, if this method were not used, severe complications would arise due to the existence of certain classes of state—corresponding perhaps to knotted configurations of the polymer chain—between which the probability of transition, while not zero, would be very low. Thus the probability of the molecule's "escaping" from this state during the "time" over which the averaging is carried out may be effectively zero. This type of behaviour is effectively non-ergodic and convergence of the average to the true value for systems showing this behaviour cannot be expected in any reasonable computing time.

The first attempts to perform this type of calculation were made by King on simple punched-card equipment,[42] but most of the subsequent work has been due to Wall and his co-workers.[43] All the investigations have been concerned with self-avoiding walks on various lattices, the tetrahedral being the most intensively studied. Interest has been focused mainly on the variation of the mean-square end–end length as a function of the number of steps in the chain, although the radius of gyration, ring-closure, probability, and limiting-step entropy have all been considered. It was found that for most two- and four-dimensional lattices the ratio

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[42] G. W. King, Monte Carlo Method, U.S. Dept. of Commerce, Nat. Bureau of Standards, Appl. Maths., Vol. XII.

[43] F. T. Wall, L. A. Hiller, and D. J. Wheeler, *J. Chem. Phys.*, 1954, **22**, 1036; F. T. Wall and L. A. Hiller, *Ann. Rev. Phys. Chem.*, 1954, **5**, 267; M. N. Rosenbluth and A. W. Rosenbluth, *J. Chem. Phys.*, 1956, **23**, 356; F. T. Wall, L. A. Hiller, and W. F. Atchison, *ibid.*, 1955, **23**, 913; F. T. Wall, L. A. Hiller, and W. F. Atchison, *ibid.*, p. 2314; F. A. Cotton and F. E. Harris, *J. Phys. Chem.*, 1956, **60**, 1451; F. T. Wall, L. A. Hiller, and W. F. Atchison, *J. Chem. Phys.*, 1957, **26**, 1742; F. T. Wall, R. J. Rubin, and I. M. Isaacson, *ibid.*, 1957, **27**, 186; F. T. Wall and J. J. Erpenbeck, *ibid.*, 1959, **30**, 634; G. S. Rushbrooke and J. Eve, *ibid.*, 1959, **31**, 1333; P. J. Marcer, D.Phil. thesis, Oxford, 1960.

$<R_N^2>_{av}/N$ diverged and converged, respectively, as N increased. But for three-dimensional lattices of practical interest the trend of this ratio is less clear, and chains of greater length must be sampled. This is not easy, since, as the chain becomes longer, the probability of successfully adding a further step decreases. The probability that a step will be allowed was found[43] to decrease exponentially with increasing chain-length, *i.e.*,

if N_s = number of s step walks successful, and

N_0 = number of walks started,

then $N_s = N_0 \exp(-\lambda s)$,

where λ is called the attrition coefficient.

To counter this difficulty various "enrichment" procedures are used and much recent research has been concerned with developing satisfactory schemes for extending the chain lengths that can be sampled. One method, due to Wall and Erpenbeck,[43] utilises allowed chains of a certain length (say s steps) as a basis for the development of a number of longer chains so that a tree of such chains is produced (see Fig. 4). It can be seen that wasteful branching or attrition is minimised when the number of walks started at each level is equal to the number of walks expected to fail within s steps.

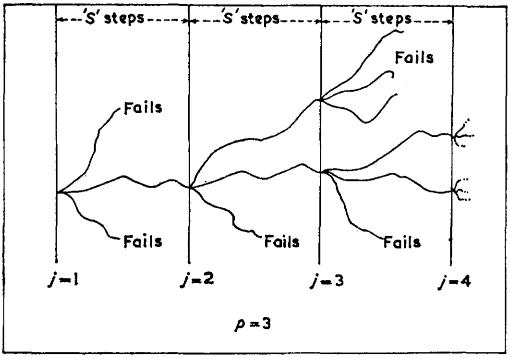

FIG. 4. *Chain enrichment by branching.*
If j is the number of levels at which branching occurs and p the number of branches started at each level, wasteful attrition or excess branching is minimised if $p = \exp(\lambda s)$ where λ is a constant and s the number of steps at each level.

A more sophisticated technique, devised by Marcer,[43] uses the branching procedure of Wall and Erpenbeck, but, instead of adding steps singly, whole sections of chain (40 step sections were in fact used) are added. These sections of self-avoiding chain are generated without difficulty by a straightforward Monte Carlo method. This technique is more efficient than the original Wall and Erpenbeck method since intersection within the individual lengths is prevented and the overall chain attrition much reduced. With this method reasonably large samples of chains up to 2000 links in length can be obtained. By these techniques a good knowledge of the properties of self-avoiding chains has been built up.

The results for tetrahedral chains have been fitted to the relation $\lim_{N\to\infty} \langle R_N{}^2\rangle_{\text{av}} = KN^{(1+\epsilon)}$ (by analogy with the simple random-walk problem).

As longer chains have been sampled it has been found necessary to change the parameters, *e.g.*, for $N \approx 200$, $\langle R_N{}^2\rangle_{\text{av}} = BN^{1.22}$ was suggested; for $N \approx 800$, $\langle R_N{}^2\rangle_{\text{av}} = B'N^{1.18}$ gave a better fit; for $N \approx 2000$, $\langle R_N{}^2\rangle_{\text{av}} = B''N^{1.13}$.

Most recently of all, Marcer has suggested that a relation of the form $\lim_{N\to\infty} \langle R_N{}^2\rangle_{\text{av}} = KN\log N$ gives a better fit, both to his values for chains up to 2000 links in length and to the previous data due to Wall. The typical behaviour of some SARWL's is illustrated in Fig. 5. In the case of the three-dimensional lattice at least, the limiting behaviour has not been reached and the plot is curved towards the log N axis.

Fig. 6 shows a comparison between the Monte Carlo results of Wall *et al.* and of Marcer, and some A factors determined by viscosity measure-

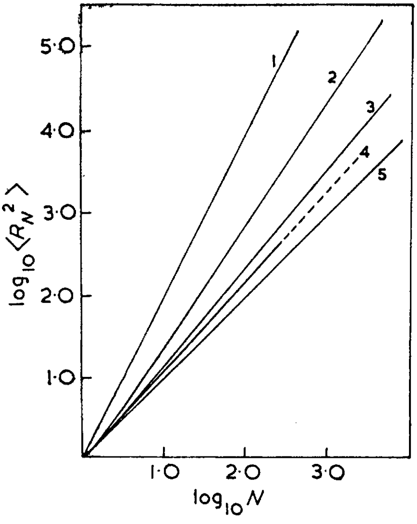

FIG. 5. *Typical behaviour of* $\langle R_N{}^2\rangle_{\text{av}}$ *for various types of lattice.*
(1) Self-avoiding random walk in one dimension (gradient = 2).
(2) Self-avoiding random walk on a two-dimensional square lattice.
(3) Self-avoiding random walk on a three-dimensional diamond lattice.
(4) Self-avoiding random walk on a typical four-dimensional lattice.
(5) Unrestricted random walk in three dimensions (gradient = 1).

(This Figure is based upon one given by Wall, Hiller, and Atchison.[43])

ments;[44] as can be seen, the Monte Carlo results conform quite well to the experimental values over the range of "A" values available and indeed suggest that even the comparatively primitive lattice model used in these calculations may form a reliable guide to the configuration of a polymer molecule. A more detailed comparision of theoretical and Monte Carlo results has been made by Kurata *et al.*[37]

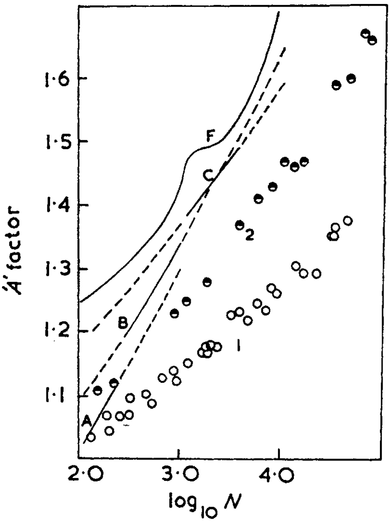

FIG. 6. *Comparison of "A" factors calculated from Monte Carlo results with factors obtained by viscosity measurements.*[47]

"A" factors from viscosity data for polyisobutenes: ○, at 20°C; ●, in cyclohexane at 30°C.

Limiting dependence of A on N from Monte Carlo results:

A, Wall, Hiller, and Wheeler;[43] B, Wall and Erpenbeck;[43] C, Marcer.[43]

Curve F shows the value of A as calculated from the Flory relation $A^5 - A^3 = BN^{\frac{1}{2}}$, B being taken arbitrarily as 100 for this plot.

The A factors from viscosity measurements were computed by using the relation $A^3 = [\eta_0]/KM^{\frac{1}{2}}$.

While for the Monte Carlo results A was calculated as $A^2 = \langle R_N^2 \rangle_{av} / \langle R_N^2 \rangle^{\circ}_{av}$ where $\langle R_N^2 \rangle^{\circ}_{av}$ was found by Tobolsky's method[34] using $E = 0{\cdot}8$ kcal. mole^{-1}.

Random Walks in Continuous Space.—The self-avoiding walk on a lattice is, of course, at best only an approximate model of the polymer molecule. A more realistic simulation would allow the walk to occur in continuous space and would incorporate as accurately as possible the various intramolecular-force fields. The application of a Monte Carlo method to a model of this type would correspond quite closely to the solution of the multidimensional integral formulated by Rubin. Naturally the greater mathematical complexity of this type of model will limit the

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[44] P. J. Flory and W. R. Krigbaum, *J. Polymer Sci.*, 1953, **11**, 37.

chain lengths accessible to computation, but it is possible to compute end-to-end length distributions and other characteristic properties which can be compared with experimental observations of, for example, the transition-state enthalpy in cyclisation reactions.[45]

Computation of Absolute Reaction Rate

The theoretical calculation of absolute reaction rates has long been the subject of investigation but, at present, progress is severely limited by the mathematical difficulties of the transition-state theory. Briefly, this theory involves the calculation of a multidimensional surface describing the potential energy of the reacting system as a function of the position of all the nuclei. This, of course, in itself is an immensely difficult task but in simple cases such as the H_2–H reaction a reasonable approximation to the potential-energy surface can be constructed.

If equilibrium is assumed between the reactants and the so-called "activated complex" which exists in the neighbourhood of the saddle point in the potential-energy surface, it is possible to calculate the concentration of the complex in the system. The activated complex can suffer one of two fates; it may decompose to yield the original reactants, or reaction may occur with the formation of products. The fraction of such fruitful collisions is known as the "transmission coefficient." Thus, if the potential-energy surface and the concentration of activated complex are known and the transmission coefficient can be calculated, our understanding of the reaction rate is complete.

The most elegant approach is the purely quantum-mechanical one in which the problem is regarded as the transmission of a wave packet through a potential-energy surface and a solution obtained by solving a time-dependent Schrödinger equation; unfortunately the mathematical difficulties of this method are at the moment almost prohibitive.[46]

An alternative procedure, possible in some cases, is to treat the assembly classically and, after computation of the potential-energy surface from quantum-mechanical considerations, to formulate the Hamiltonian equations of motion for the system of reacting nuclei. The track of all the nuclei can then be followed by solving these equations at successive short intervals of time, and hence the outcome of the collision, namely, reaction or no reaction, can be determined.

Wall, Hiller, and Mazur[47] have used this procedure in an attempt to study the reaction, $H + H_2 \rightarrow H_2 + H$. In their method the positions of all the nuclei throughout the interaction are "plotted" on a cathode-ray screen and photographed at short intervals, plots similar to Fig. 7 being obtained. By repeating this procedure many times for different initial

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[45] M. A. D. Fluendy, unpublished results.

[46] E. M. Mortensen and K. S. Pitzer, in "The Transition State," *Chem. Soc. Special Publ. No.* 16, 1962.

[47] F. T. Wall, L. A. Hiller, and J. Mazur, *J. Chem. Phys.*, 1958, **29**, 255; 1961, **35**, 1284.

conditions of translational, vibrational, and rotational energy, it was possible to determine the relation between these quantities and the probability of reaction. Though the results published so far are very limited, it is apparent that the vibrational energy plays only a small part in activating the complex and that molecules with little or no rotational energy are more likely to react with the colliding hydrogen atom.

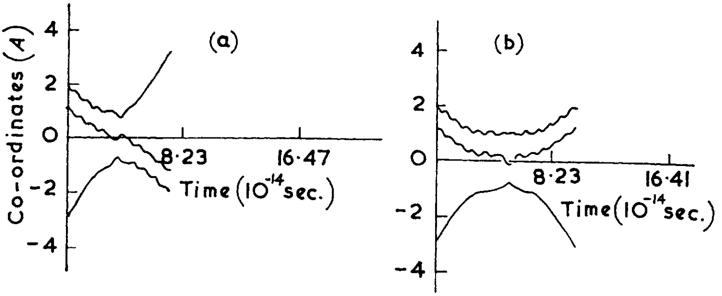

FIG. 7. *The figures show the tracks of all the reacting nuclei in the reaction* $H + H_2 \rightarrow H_2 + H$.

A hydrogen atom is shown coming from the bottom of the diagram to collide with a vibrating hydrogen molecule (the top two tracks). For clarity collinear collisions are illustrated

(a) Reaction (b) No reaction

(Reproduced with permission from ref. 47.)

Conclusion

From the preceding discussion it is clear that the Monte Carlo technique can be applied to a wide range of physicochemical problems, where it can be used, not only to provide numerical results, but also to guide the intuition in the construction of new theories. It must be remembered, however, that it is expensive of computer time and therefore a method of the last resort which should only be used for tackling those problems for which analytical or conventional numerical methods are useless. Whatever the application of the method, it is essential that the fullest use be made of any information available concerning the expected result, so that an efficient sampling scheme may be devised, since, in some cases, the computing time required to achieve a given accuracy may be reduced by several orders of magnitude by good sampling. Indeed, so important are the savings available that it may prove worthwhile to attempt to design a programme that would automatically optimise its sampling as the computation proceeded.

In fields outside chemistry the method has been shown to have wide applications. Successful applications range from scattering problems in nuclear physics to models of economic behaviour and the reorganisation of industrial stock piles. One thing seems certain; as electronic computers of the present generation are replaced by new models (at least 100 times faster) the scope of the Monte Carlo method must increase. In particular the properties of systems involving long-range interactions, such as plasmas and electrolytic solutions, may be studied. The method may also find application in the investigation of extended gravitational systems, surface-catalysis effects, the probability of knotting and similar topological problems in long-chain polymers, and in quantum mechanics.

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