

- HIRSHFELD, F. L. (1977). *Isr. J. Chem.* **16**, 226–229.
- JACKSON, J. D. (1975). *Classical Electrodynamics*, 2nd ed. New York, Chichester, Brisbane, Toronto, Singapore: John Wiley.
- JEFFREY, G. A., RUBLE, J. R., MCMULLAN, R. K. & POPLE, J. A. (1987). *Proc. R. Soc. London Ser. A*, **414**, 47–57.
- JEFFREY, G. A., RUBLE, J. R., YEON, Y. & LEHMANN, C. (1991). Private communication.
- KURKI-SUONIO, K. (1977) *Isr. J. Chem.* **16**, 115–123.
- LI, N., SU, Z., COPPENS, P. & LANDRUM, J. (1990). *J. Am. Chem. Soc.* **112**, 7294–7298.
- LSMOL90 (1990). Chemistry Department, State Univ. of New York at Buffalo, New York, USA.
- PANT, A. K. & STEVENS, E. D. (1988). *Phys. Rev. B*, **37**, 1109–1120.
- PROSSER, F. P. & BLANCHARD, C. H. (1962). *J. Chem. Phys.* **36**, 1112.
- SCHWARZENBACH, D. & THONG, N. (1979). *Acta Cryst.* **A35**, 652–658.
- SPACKMAN, M. & STEWART, R. F. (1981). In *Chemical Applications of Atomic and Molecular Electrostatic Potentials*, edited by P. POLITZER & D. G. TRUHLAR. New York, London: Plenum Press.
- STEVENS, E. D., DELUCIA, M. L. & COPPENS, P. (1980). *Inorg. Chem.* **19**, 813–820.
- STEWART, R. F. (1976). *Acta Cryst.* **A32**, 565–574.
- STEWART, R. F. (1979). *Chem. Phys. Lett.* **65**(2), 335–342.
- STEWART, R. F. (1991). In *Applications of Charge Density Research to Chemistry and Drug Design*, edited by G. A. JEFFREY & J. F. PINIELLA. New York: Plenum Press.
- SU, Z. (1991). *MOLPROP. Experimental Molecular Electrostatic Properties*. State Univ. of New York at Buffalo, New York, USA.
- SU, Z. & COPPENS, P. (1990). *J. Appl. Cryst.* **23**, 71–73.
- SWAMINANTHAN, S. & CRAVEN, B. M. (1984). *Acta Cryst.* **B40**, 511–518.

Acta Cryst. (1992). **A48**, 197–209

Minimizing Free Energy as a Direct Method for Phase Determination

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Abstract

A general joint probability distribution between structure factors is derived and is expressed as an exponential of the free energy for a system of interacting atoms. The free energy is an explicit function of the atomic densities and the interatomic potentials. In the limit of infinite temperature, energy effects are unimportant and the probability distribution becomes identical to those derived by Hauptman & Karle [*The Solution of the Phase Problem. I. The Centrosymmetric Crystal*. (1953). ACA Monogr. Wilmington: The Letter Shop; *Acta Cryst.* (1959), **12**, 93–97] and Bricogne [*Acta Cryst.* (1984), **A40**, 410–445].

1. Introduction

The principle of maximum entropy (PME) has been applied to crystallographic problems from a statistical inference viewpoint by Bricogne (1984) and Gull, Livesey & Sivia (1987). Navaza (1985, 1986) has shown that the type of constraint used with the PME determines the final form of the maximum-entropy functional. Recently, Bryan (1988) has also incorporated correlations into the entropy expression. However, no one has attempted to incorporate stereochemistry in a general way, although Wilson (1981) has considered the possibility. This paper shows that if chemical information can be represented as potential functions, then it can be applied with the

PME to yield the Helmholtz free energy as a function of the structure factors. Moreover, the free energy is shown to be, within a normalization factor, the log of a structure-factor joint probability distribution (j.p.d.). Phase determination can therefore be considered as a constrained free-energy minimization.

In calculating structure-factor j.p.d.s the crystal is usually modelled as a sample from an ensemble of structures in which all possible atomic configurations are equally represented. This assumption is free from stereochemical bias and is routinely used to solve small-molecule crystal structures. For larger structures, however, current procedures do not work well. From a theoretical point of view, one possible alternative for improving the success rate is to eliminate from the ensemble those configurations that are stereochemically impossible.

Energetic constraints yield preferred bond lengths and angles which alter the number of 'reasonably probable' configurations. Since the information theoretic entropy is a measure of reasonably probable configurations* and is equivalent to the entropy defined in statistical mechanics [up to a multiplicative Boltzmann constant k_B (Jaynes 1957)], it is clear that a physical approach offers an opportunity for extending the principle of maximum entropy within crystallography.

* And this measure is dependent only on a reasonable definition for 'reasonably probable' (Jaynes, 1965).

The main result in this paper is the explicit expression of the free energy as a function of single-atom density functionals (equation 3). That this is possible is a consequence of the Hohenberg–Kohen theorem, as shown by Evans (1979) (see also Parr, 1983). The derivation of (3) employs the grand canonical distribution which assumes that only the average number of each atomic type is known. [See Parr & Weitao (1989, p. 64) for a proof of the Hohenberg–Kohen theorem for the grand canonical ensemble.] Fortunately, the probability distribution based on a fixed number of atoms can be regained by a saddle-point integration in the manner of Darwin & Fowler (see Zubarev, 1974, p. 126).

The arguments in this paper are based on the well known cluster expansion and result in a j.p.d. between structure factors that does not depend on the assumption of independent identically distributed atoms. It should be noted that most of the necessary statistical mechanics concepts pre-date the proofs of direct-method j.p.d.s by a number of years.

2. Free energy

Standard equilibrium probability distributions such as the grand canonical distribution are constrained maximum-entropy (ME) distributions (McQuarrie, 1973, p. 37; Katz, 1967). The entropy functional $S \equiv -k_B \langle \log P \rangle$, evaluated at the ME distribution, is a function of the constraint values $\langle C_\mu \rangle$ (Jaynes, 1957) and has the form

$$k_B^{-1} S_{\max}[\langle C_1 \rangle, \langle C_2 \rangle, \dots] \\ = \log Z[\lambda_1, \lambda_2, \dots] - \lambda_1 \langle C_1 \rangle - \lambda_2 \langle C_2 \rangle - \dots \quad (1)$$

where Z is the partition function. The $\langle C_\mu \rangle$ are usually constrained averages of the constants of motion while the λ_μ are their corresponding Lagrange multipliers. The values of λ_μ are given by the solutions to the equations $\partial \log Z / \partial \lambda_\mu = \langle C_\mu \rangle$, $\mu = 1, 2, \dots$ (Jaynes, 1957). These conditions make (1) a Legendre transform between $\log Z[\lambda_1, \dots]$ and $S_{\max}[\partial \log Z / \partial \lambda_1, \dots] = S_{\max}[\langle C_1 \rangle, \dots]$ (McQuarrie, 1973, p. 15) and so, in principle, $\log Z$ and S_{\max} contain essentially the same information. Because $\partial S_{\max} / \partial \langle C_\mu \rangle = -k_B \lambda_\mu$, the derivatives of S_{\max} and $\log Z$ are complementary [the meaning of this term is more fully discussed by Mandelbrot (1989)] and their Hessians are, within a multiplicative factor, inverses of one another; *i.e.* $\partial^2 \log Z / \partial \lambda_\nu \partial \lambda_\mu = -k_B [\partial^2 S_{\max} / \partial \langle C_\nu \rangle \partial \langle C_\mu \rangle]^{-1}$. When the constraints $\langle C_\mu \rangle$ are taken to be number densities, $\langle N_\alpha(\mathbf{x}) \rangle \equiv \rho_\alpha(\mathbf{x})$, then the Hessian of the entropy is called the direct-correlation function and its inverse relationship to the Hessian of $\log Z$ is known as the Ornstein–Zernike equation (Zubarev, 1974, p. 290). In many statistical mechanics textbooks this equation is used to *define* the direct-correlation function. By compar-

ing (1) and its derivatives to thermodynamically derived Maxwell’s relations, an identification can be set up between variables so that if, for example, $\langle C_1 \rangle = \langle E \rangle$ is the average energy of the system, then it follows that $\lambda_1 = -\beta \equiv -1/k_B T$ where T is the temperature. Similarly, the Lagrange multiplier of the average number of atoms of type α , $\langle N_\alpha \rangle$, is related to the chemical potential (see Mohling, 1982). Free energies, such as the Helmholtz free energy, A , are related to one another and to the entropy *via* Legendre transforms,











$$-\beta A[\beta, \langle N_\alpha \rangle, \langle C_i \rangle, \dots] \\ = k_B^{-1} S_{\max}[\langle E \rangle, \langle N_\alpha \rangle, \langle C_i \rangle, \dots] - \beta \langle E \rangle. \quad (2)$$

The ellipsis make explicit the possibility that A still depends on other unspecified averages. Free-energy minimization can be used to determine the most probable values for the arguments. For example, at constant temperature and average number density, minimizing A with respect to an unknown average $\langle C_i \rangle$ is equivalent to maximizing S_{\max} . This implies that $\partial A / \partial \langle C_i \rangle = 0 \Rightarrow \partial S_{\max} / \partial \langle C_i \rangle = 0$ and hence that the corresponding Lagrange multiplier λ_i must be zero. The Lagrange multipliers are functions of the average values *via* the ME equations (Bricogne, 1984) so that the intersection of the hypersurface $\lambda_i(\langle E \rangle, \langle N_\alpha \rangle, \langle C_i \rangle, \dots) = 0$ determines the possible equilibrium points for $\langle C_i \rangle$. The idea of maximizing the maximum entropy as a phase-determination method is discussed by Navaza (1985). These arguments indicate that there is no essential difference to maximizing the entropy S_{\max} with respect to an unknown and minimizing a corresponding free energy (free energies must be minimized because of the negative $-\beta$). Preference of one free energy over another is based solely on those parameters which are of interest (temperature or energy, chemical potential or density *etc.*). Although the Lagrange multipliers appear explicitly, (1) represents the entropy as a function of the expectation values *only*. A major aim of this paper will be to determine the chemical potential *explicitly* as a function of the temperature and number densities and thus to remove any reference to it from the free-energy expression (2). This will be done in § 4 where it will be used to prove the following relationship: for M different types of atom in a crystal unit cell of volume V , the free energy A , under the condition that the average density for each atomic type is known, is given by

$$-\beta A = \sum_{\mu=1}^M \int_V \delta_\mu \rho_\mu(\mathbf{x}) \, d\mathbf{x} \\ - \sum_{\mu=1}^M \int_V \rho_\mu(\mathbf{x}) \log [\rho_\mu(\mathbf{x}) / \rho_\mu^0(\mathbf{x})] \, d\mathbf{x} \\ + \Gamma_\beta[\rho_1, \rho_2, \dots, \rho_M] \quad (3)$$

where $\delta_\mu = 1 - \log(\Lambda_\mu^3 / V)$ and Λ_μ is the de Broglie

Table 1. Table of low-order cluster integrals for Γ

Vertex	Integrand	Diagram
$\Gamma_{\{1,1\}}^\beta$	$\rho_\mu^0(\mathbf{x})f_{\mu\omega}(\mathbf{x}, \mathbf{y})\rho_\omega^0(\mathbf{y})$	
$\Gamma_{\{1,1,1\}}^\beta$	$\rho_\mu^0(\mathbf{x})f_{\mu\nu}(\mathbf{x}, \mathbf{y})\rho_\nu^0(\mathbf{y})f_{\nu\omega}(\mathbf{x}, \mathbf{z})\rho_\omega^0(\mathbf{z})f_{\nu\omega}(\mathbf{y}, \mathbf{z})$	
	$+\rho_\mu^0(\mathbf{x})\rho_\nu^0(\mathbf{y})\rho_\omega^0(\mathbf{z})f_{\mu\nu\omega}(\mathbf{x}, \mathbf{y}, \mathbf{z})$	
	$+\rho_\mu^0(\mathbf{x})\rho_\nu^0(\mathbf{y})\rho_\omega^0(\mathbf{z})f_{\nu\omega}(\mathbf{y}, \mathbf{z})f_{\mu\nu\omega}(\mathbf{x}, \mathbf{y}, \mathbf{z})$	
	$+\rho_\mu^0(\mathbf{x})\rho_\nu^0(\mathbf{y})\rho_\omega^0(\mathbf{z})f_{\mu\omega}(\mathbf{x}, \mathbf{z})f_{\mu\nu\omega}(\mathbf{x}, \mathbf{y}, \mathbf{z})$	
	$+\rho_\mu^0(\mathbf{x})\rho_\nu^0(\mathbf{y})\rho_\omega^0(\mathbf{z})f_{\mu\nu}(\mathbf{x}, \mathbf{y})f_{\mu\nu\omega}(\mathbf{x}, \mathbf{y}, \mathbf{z})$	
	$+\rho_\mu^0(\mathbf{x})\rho_\nu^0(\mathbf{y})\rho_\omega^0(\mathbf{z})f_{\mu\omega}(\mathbf{x}, \mathbf{z})f_{\mu\nu\omega}(\mathbf{x}, \mathbf{y}, \mathbf{z})$	
	$+\rho_\mu^0(\mathbf{x})\rho_\nu^0(\mathbf{y})\rho_\omega^0(\mathbf{z})f_{\mu\nu}(\mathbf{x}, \mathbf{y})f_{\nu\omega}(\mathbf{x}, \mathbf{z})f_{\mu\nu\omega}(\mathbf{x}, \mathbf{y}, \mathbf{z})$	
	$+\rho_\mu^0(\mathbf{x})\rho_\nu^0(\mathbf{y})\rho_\omega^0(\mathbf{z})f_{\mu\omega}(\mathbf{x}, \mathbf{z})f_{\nu\omega}(\mathbf{x}, \mathbf{z})f_{\mu\nu\omega}(\mathbf{x}, \mathbf{y}, \mathbf{z})$	
	$+\rho_\mu^0(\mathbf{x})\rho_\nu^0(\mathbf{y})\rho_\omega^0(\mathbf{z})f_{\mu\nu}(\mathbf{x}, \mathbf{y})f_{\mu\omega}(\mathbf{x}, \mathbf{z})f_{\nu\omega}(\mathbf{y}, \mathbf{z})f_{\mu\nu\omega}(\mathbf{x}, \mathbf{y}, \mathbf{z})$	

where $f_{\mu\nu}(\mathbf{x}, \mathbf{y}) = \exp[-\beta U_{\mu\nu}(\mathbf{x}, \mathbf{y})] - 1$ and $\rho_\mu^0(\mathbf{x}) = \exp[-\beta\lambda_\mu(\mathbf{x})]$. The function U defines the interatomic potential energy and $\lambda_\mu(\mathbf{x})$ a position-dependent external field or, equivalently, a position-dependent chemical potential. Higher-order irreducible diagrams when there is no three-atom interaction are given in Hoover & DeRocco (1962).

wavelength for atoms of type μ equal to $(2\pi\beta\hbar^2/m_\mu)^{1/2}$. The functions $\log \rho_\mu^0$ are external position-dependent chemical potentials. The functional $\Gamma_\beta[\tilde{\rho}]$ is the excess free energy given by

$$\begin{aligned} & \Gamma_\beta[\rho_1, \dots, \rho_M] \\ &= \sum_{n=2}^{\infty} \sum_{\{\tilde{\mathbf{n}}\}} [\prod n_\mu !]^{-1} \\ & \quad \times \int d\mathbf{x}_1 \dots d\mathbf{x}_n \rho_{\mu_1}(\mathbf{x}_1) \dots \rho_{\mu_M}(\mathbf{x}_n) \Gamma_{\{\tilde{\mathbf{n}}\}}^\beta(\mathbf{x}_1, \dots, \mathbf{x}_n) \end{aligned} \quad (4)$$

where $\{\tilde{\mathbf{n}}\}$ is the set of integers (n_1, n_2, \dots, n_M) that satisfy $\sum_{\mu=1}^M n_\mu = n$. The coefficients $\Gamma_{\{\tilde{\mathbf{n}}\}}^\beta$ are temperature-dependent irreducible cluster integrals (Morita & Hiroike, 1961), first introduced by Husimi (1950), which vanish if the interaction potentials vanish. Some of the lowest-order terms are given explicitly in Table 1. In quantum field theory they are equivalent to 'proper vertices' or one-particle-

irreducible (1PI) Green functions (Rivers, 1987, p. 34). The connection between statistical mechanics and quantum field theories, particularly in the use of cluster expansions, has a long history (see Landsman & Weert, 1987; de Dominicis & Martin, 1964).

3. Definitions

The starting point for the proof of (3) is the generating functional for the Green functions:

$$\begin{aligned} & Z_\beta[j_1, j_2, \dots, j_M] \\ &= \left\langle \left\langle \exp \left[\sum_{\mu=1}^M \int d\mathbf{x} j_\mu(\mathbf{x}) \hat{N}_\mu(\mathbf{x}) \right] \right\rangle \right\rangle. \end{aligned} \quad (5)$$

$\hat{N}_\mu(\mathbf{x})$ is the number density operator equal to $\hat{a}^\dagger(\mathbf{x})\hat{a}(\mathbf{x})$ where \hat{a}^\dagger and \hat{a} are atomic creation and annihilation operators respectively. $\langle\langle \hat{A} \rangle\rangle$ represents the statistical average of the operator \hat{A} with respect

to the Hamiltonian $\hat{\mathcal{H}}$:

$$\sum_{\alpha} \langle \Psi_{\alpha} | \exp[-\beta \hat{\mathcal{H}}] \hat{A} | \Psi_{\alpha} \rangle \quad (6)$$

where the summation α is over a complete set of states. This can be derived directly from the PME under the assumption of known average energy and particle density (Katz, 1967). The $j_{\mu}(\mathbf{x})$ are source terms for atoms of type μ and the derivatives of $\log Z$ with respect to these functions at the origin gives the sourceless Green functions $\langle\langle \hat{N}_{\mu_1}(\mathbf{x}_1) \hat{N}_{\mu_2}(\mathbf{x}_2) \dots \hat{N}_{\mu_M}(\mathbf{x}_M) \rangle\rangle$. Equation (5) can also be interpreted as the characteristic function of the probability distribution of atomic densities. With $j_{\mu}(\mathbf{x})$ purely complex, (5) is a Fourier transform of the unnormalized probability distribution $\exp[-\beta \hat{\mathcal{H}}]$. Taking α to be the quantum numbers $\{n_{\mu}(\mathbf{x})\}$, complete over the Fock space domain of the operator $\hat{\mathcal{H}}$, so that $\hat{N}_{\mu}(\mathbf{x}) | \Psi_{\{n_{\mu}(\mathbf{x})\}} \rangle = n_{\mu}(\mathbf{x}) | \Psi_{\{n_{\mu}(\mathbf{x})\}} \rangle$ and $n_{\mu}(\mathbf{x})$ specifies the particle number at point \mathbf{x} , then (5) can be expressed as

$$\begin{aligned} Z_{\beta}[j_1, \dots, j_M] &= \sum_{n=0}^{\infty} \sum_{\{\bar{n}\}} \int_V d\mathbf{x}_1 \dots d\mathbf{x}_n \\ &\quad \times \exp[j_{\mu_1}(\mathbf{x}_1)] \dots \exp[j_{\mu_M}(\mathbf{x}_n)] \\ &\quad \times Z_{\{\bar{n}\}}^{\beta}(\mathbf{x}_1, \dots, \mathbf{x}_n). \end{aligned} \quad (7)$$

The density matrices, $Z_{\{\bar{n}\}}^{\beta}$, are given explicitly by

$$\begin{aligned} Z_{\{n_1, \dots, n_M\}}^{\beta}(\mathbf{x}_1, \dots, \mathbf{x}_n) \\ = \sum_{\mathbf{p}} \Phi_{\mathbf{p}}^*(\mathbf{x}_1, \dots, \mathbf{x}_n) \exp[-\beta \mathcal{H}_{\mathbf{p}}] \Phi_{\mathbf{p}}(\mathbf{x}_1, \dots, \mathbf{x}_n) \end{aligned} \quad (8)$$

where \mathbf{p} is over a complete set of wavefunctions for an n -particle system composed of n_1 of type 1, n_2 of type 2 *etc.* The Hamiltonian $\mathcal{H}_{\mathbf{p}}$ is the sum of kinetic energies and position-dependent potential energies (see § 3.1) of n particles with external chemical potentials $\lambda_{\mu}(\mathbf{x})$ [equal to $\log \rho_{\mu}^0(\mathbf{x})$ of (3)]. Since $Z_{\{\bar{n}\}}^{\beta}(\tilde{\mathbf{x}})$ in (8) does not depend on the type of function $\Phi_{\mathbf{p}}$, only that they form a complete set, then symmetrized or anti-symmetrized Bloch plane-wave products, normalized to crystal volume V , can be used:

$$\begin{aligned} -\Phi_{\mathbf{p}} &= [\prod_{\mu} n_{\mu}!]^{-1/2} \sum_{\mu_1, \mu_2, \dots, \mu_M} (\pm 1)^{\mu_1} \dots (\pm 1)^{\mu_M} \\ &\quad \times \varphi_{\mu_1}(\mathbf{x}_1) \dots \varphi_{\mu_M}(\mathbf{x}_n) \end{aligned} \quad (9)$$

where $\mathbf{p} = (\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_n)$ and $\varphi_{\mathbf{p}}(\mathbf{x}) = V^{-1/2} \exp\{i\mathbf{p}\mathbf{x}/\hbar\}$. The plus sign corresponds to Bose statistics and the minus sign to Fermi statistics. To evaluate (8) the following approximation is made

$$\sum_{p_1, p_2, \dots, p_n} \rightarrow [\prod_{\nu} n_{\nu}!]^{-1} V^N / (2\pi\hbar)^{3N} \int \dots \int d\mathbf{p}_1 \dots d\mathbf{p}_N \quad (10)$$

where the factorials allow for the fact that a permutation of identical particles does not change the physical state. This transformation excludes the possibility of

Bose-gas degeneracy where there may be a macroscopically large number of particles in the ground state. The error introduced by the transformation (10) is equal to the difference between $\sum \exp(-\alpha n^2)$ and $\alpha^{1/2} \int \exp(-x^2) dx = \alpha^{-1/2}$ which is small only if α is small. This error can be rectified by replacing $\alpha^{-1/2}$ with $f(\alpha)$ for some suitable function f . The function can be absorbed into the density expression, introducing no effective error, as long as only the classical terms are included. In this case the δ_{μ} of (3) changes to $1 - \log f[(\lambda_{\mu}^3/V)^{-2}]$.

So far, care has been taken to keep the development quantum mechanically sound because the final application will be to systems with a large number of atoms in a restricted cell volume. However, in the thermodynamic limit of $N \rightarrow \infty$, the cell volume V will also approach infinity because real crystal densities, especially those of organic molecules, differ by less than an order of magnitude [for most organic molecules the densities range from 0.9 to 1.7 g ml⁻¹ (Stout & Jensen, 1989)] and hence $N/V \rightarrow \rho$ remains a finite constant. Keeping only the most important quantum exchange effects (the single permutations of the μ_i) and following standard analysis such as Zubarev (1974, p. 129), (8) reduces to

$$\begin{aligned} \prod_{\nu=1}^M (\Lambda_{\nu}^{-3n_{\nu}} / n_{\nu}!) \left\{ \exp(-\beta U) + \sum_{\mu=1}^M \sum_{\mu_i \neq \mu_j} (\pm 1)^{\mu} \right. \\ \left. \times \exp[-2\pi|\mathbf{x}_{ij}|^2 / \Lambda_{\mu}^2] [1 + O(\beta)] \right\}. \end{aligned} \quad (11)$$

U is a modification (a smearing) of the original potential V due to quantum diffraction effects caused by the wave-like nature of the atoms and can be interpreted as a consequence of Heisenberg's uncertainty principle. The approximate form of U was found by Feynman & Hibbs (1965) and is generalized here to

$$\begin{aligned} U(\mathbf{x}_1, \dots, \mathbf{x}_n) \\ \approx \prod_{\mu} (\Lambda_{\mu}^2/12)^{-1/2} \int_{-\infty}^{\infty} V(\mathbf{x}_1 + \mathbf{y}_1, \dots, \mathbf{x}_n + \mathbf{y}_n) \\ \times \prod_{\mu} \exp(-12\pi\mathbf{y}_{\mu}^2 / \Lambda_{\mu}^2) \prod_{\mu} d\mathbf{y}_{\mu}. \end{aligned} \quad (12)$$

This effective potential includes most of the significant quantum effects (Doll, 1984). The first term of (11) is essentially a classical result while the second term gives the quantum exchange effect. The exponential argument is numerically equal to $0.05 m x^2 T$ if m is expressed in atomic mass units, x in ångströms and T in kelvin. Carbon as a typical atom with a worst-case average separation of 1 Å at liquid-nitrogen temperature (72 K) gives $e^{-17} = 3 \times 10^{-8}$. A more typical value is around 10^{-30} . In any case, it will be assumed that β is set sufficiently small that the de Broglie wavelength is much smaller than the average atomic separation and hence the

second term can be ignored. [An acceptable compromise for all atomic types except helium near its lambda point (Larsen, Kilpatrick, Lieb & Jordan, 1965).]

3.1. Assumptions about the interatomic potential

A particular set of atomic positions will be called a 'configuration' and it will be assumed that the interaction energy for N atoms can be expressed as

$$U = \sum_{i < j} U_{ij} + \sum_{i < j < k} \Delta U_{ijk} + \dots + \Delta U_{ijk\dots N}. \quad (13)$$

The periodic boundary conditions imply that the pair potential must have the symmetry of the lattice. The second and higher terms in (13) occur because the atoms are not point particles but can affect one another *via* intermediaries as shown in Fig. 1. In many molecular modelling cases it is assumed that the first term dominates the total energy, although the second term may contribute up to 10% (Margenau & Kestner, 1969) while third- and higher-order terms, at least in the case of liquids, contribute less than 1%. (These numbers are known only indirectly.) Since it is *via* these potentials that stereochemical information is being introduced, their availability and accuracy are an important issue which will be discussed in § 10.

3.2. The cluster expansion

Following Stell (1976), the classical probability density distribution of N atoms can be expressed as

$$\prod_{\mu=1}^N \Lambda_{\mu}^{-3} \rho_{\mu}^0(\mathbf{x}_{\mu}) \prod_{\mu < \nu} (1 + f_{\mu\nu}) \prod_{\mu < \nu < \omega} (1 + f_{\mu\nu\omega}) \dots \quad (14)$$

where $f_{\mu\nu} = \exp\{-\beta U_{\mu\nu}(\mathbf{x}_{\mu}, \mathbf{x}_{\nu})\} - 1$ etc. and $\rho_{\mu}^0(\mathbf{x}_{\mu}) = \exp\{-\beta \lambda_{\mu}(\mathbf{x}_{\mu}) + j_{\mu}(\mathbf{x}_{\mu})\}$. This product can be expanded in terms of the $f_{\mu\nu}$ and can be represented graphically by assigning lines to the $f_{\mu\nu}$ and points to the ρ_{μ} as shown in Appendix II. A 'bond' (to μ) will be defined as the existence of one or more $f_{\mu k}$ or $f_{\mu kl}$ etc. in a particular diagram and a 'vertex' will be defined as the actual atom μ .

4. Derivation of the free-energy relation

A diagrammatic derivation based on Feynman diagrams is followed because it is both a simple and

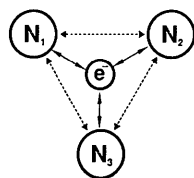


Fig. 1. If only nuclear configurations are of interest, as is the case for structure determination, then n -body effective potentials may be required to compensate for the neglected electron configurations.

a concise way of demonstrating the necessary steps. There are many other papers that confirm the arguments in this section. For example, the detailed combinatorial analysis that underlies the diagrammatic proofs can be found in Stillinger & Buff (1962) and also in the algebraic derivation of a related gas mixture problem by Fuchs (1941). (Appendix II gives an introduction to the cluster expansion terminology used in statistical mechanics).^{*} With expansion (14), the partition function can be expressed as an infinite sum of graphs or, borrowing from the terminology of quantum field theory, as an infinite sum of many-leg density functions (see, for example, Rivers, 1987). This is represented pictorially in Fig. 2. Some of the graphs that make up the partition function are disconnected (see Fig. 9 of Appendix II for an example) while the sum over the subset of connected graphs is important enough to be given the label W and is represented in Fig. 3. The act of differentiating these diagrams with respect to $j_{\mu}(\mathbf{x})$ is equivalent to producing a 'leg' of type μ at \mathbf{x} and is represented in Fig. 4 for the case of Z (see also Fig. 11 of Appendix II). Differentiating Z in this way will result in some of its graphs being connected to this leg and some not. 'Pulling' on this leg will yield two components: (i) a

^{*} See also the review by Stell (1976), Hansen & McDonald (1976), the umbral calculus approach of Roman (1979a, b), Mohanty (1982), Wilson & Rogers (1986); the cluster expansion theorems of Morita & Hiroike (1961) and the density functional methods based on the cluster expansion of de Dominicis (1962) and de Dominicis & Martin (1964). The cluster expansion is, in turn, a special case of a 'polymer expansion' (Glimm & Jaffe, 1981).

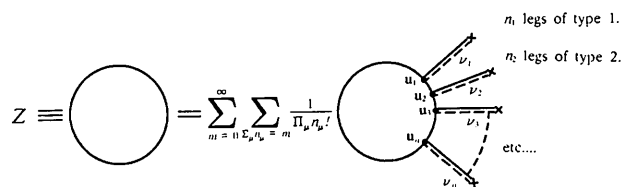


Fig. 2. The partition function is the sum over all topologically inequivalent diagrams. The ball and stick representations are taken from Rivers (1987).

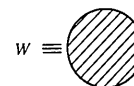


Fig. 3. The sum over all connected diagrams is represented as a hatched ball.

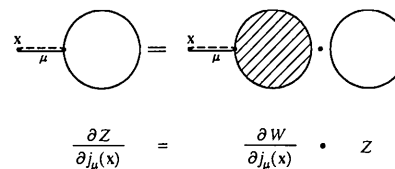


Fig. 4. The diagrammatic equivalent of differentiation is the addition of a 'leg'.

set of graphs connected to the leg which is equivalent to the derivative of W ; (ii) a leg-less set of connected graphs equivalent to Z . This is shown in Fig. 4 and the equivalent differential equation shown beneath has the solution $Z = \exp [W]$. This relationship was first found by Mayer (Mayer & Mayer, 1940) but has been rediscovered many times in different fields; for example, in the quantum many-body problem it is sometimes called the Goldstone theorem. It is important to note here that the derivative $\partial W / \partial j_\mu(\mathbf{x})$ is equal to the number density $\rho_\mu(\mathbf{x})$ of atom type μ for the conjugate distribution $\exp [-\beta \hat{\mathcal{H}} + \sum_\mu j_\mu(\mathbf{x}) \hat{N}_\mu(\mathbf{x})]$ (see Bricogne, 1984). [Just differentiate $\log Z$ in (5).]

Some of the vertices in the connected diagrams constituting $\partial W / \partial j_\mu(\mathbf{x})$ are only connected to other vertices *via* the leg. That is, removal of the leg splits a particular diagram into two or more disconnected sets. Hence the diagrams can be sorted into groups depending on the number of disconnected diagrams into which each one separates. Each vertex within such a disconnected diagram remains connected to the others as well as to \mathbf{x} (see Fig. 5 and Fig. 12 in Appendix II). The factorial terms make sure equivalent graphs are not counted more than once and so it can be seen that the series may be expressed as an exponential. Within this set there is a kernel that is 'doubly connected' to the leg at \mathbf{x} . That is, there are at least two independent paths that connect any atom to \mathbf{x} or the removal of any vertex (and its connections) will not affect the connectivity of any of the other vertices to \mathbf{x} . The rest of the diagrams are 'hung off' the vertices of this kernel (exclusive of \mathbf{x}) *via* a single leg. This is shown in Fig. 6. In other words, diagrams can be 'teased out' of the set until only a doubly connected set remains. These diagrams are singly connected diagrams with a single leg and

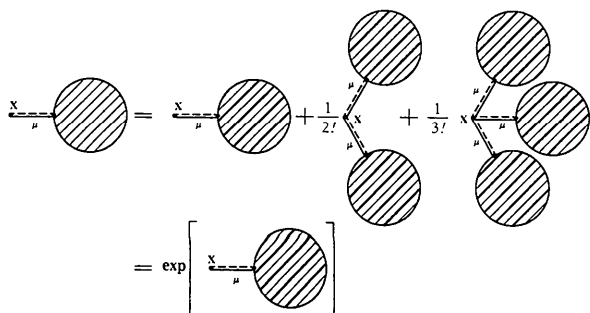


Fig. 5. The derivative of W can be rearranged to a sum over irreducibly connected diagrams. If the ball-and-stick representations are taken as overall 'templates' for diagrams then any diagram that satisfies the left-hand-side template (*i.e.* is connected with a single leg) can be matched with one and only one of the templates on the right-hand side. Conversely, any diagram that satisfies a template on the r.h.s. must exist on the l.h.s. because of the definition of W (*i.e.* it must be connected and have a single leg).

hence are equivalent to $\partial W / \partial j_\nu(\mathbf{y})$ (compare Fig. 6 with Fig. 4). Fig. 6 shows clearly that it is a power series in the densities. This series is labelled $\partial \Gamma / \partial \rho_\mu(\mathbf{x})$ so that

$$\rho_\mu(\mathbf{x}) = \Lambda_\mu^{-3} \rho_\mu^0(\mathbf{x}) \exp [j_\mu(\mathbf{x}) + \partial \Gamma / \partial \rho_\mu(\mathbf{x})] \quad (15)$$

which is called the Yvon equation (Yvon, 1935) by de Dominicis (1962) (see also Haymet, 1987). This is a crucial result which allows the source terms j_μ to be expressed in terms of the densities:

$$j_\mu(\mathbf{x}) = \log [\Lambda_\mu^3 \rho_\mu(\mathbf{x}) / \rho_\mu^0(\mathbf{x})] - \partial \Gamma / \partial \rho_\mu(\mathbf{x}). \quad (16)$$

This inversion is essential to obtaining the entropy in terms of the densities and is almost totally due to the assumption that only the average number of each atomic type is known. Moreover, no constraint is made on the certitude (or the lack thereof) with which these averages are specified.

The free energy $A[\beta, \partial W / \partial j_\mu]$ is given by the Legendre transform of $\log Z$ [Baus (1987), see also (1) and (2)]

$$\begin{aligned} -\beta A &\equiv \log Z - \sum_{\mu=1}^M \int_V j_\mu(\mathbf{x}) \partial \log Z / \partial j_\mu(\mathbf{x}) d\mathbf{x} \\ &= \int_V \left[\sum_{\mu=1}^M \int_{-\infty}^{j_\mu(\mathbf{x})} \partial \log Z / \partial j_\mu^*(\mathbf{x}) d[j_\mu^*(\mathbf{x})] \right] d\mathbf{x} \\ &\quad - \sum_{\mu=1}^M \int_V \{ \rho_\mu(\mathbf{x}) \log [\Lambda_\mu^3 \rho_\mu(\mathbf{x}) / \rho_\mu^0(\mathbf{x})] \\ &\quad - \rho_\mu(\mathbf{x}) \partial \Gamma / \partial \rho_\mu(\mathbf{x}) \} d\mathbf{x}. \end{aligned} \quad (17)$$

The first term can be expressed using (16) as

$$\begin{aligned} &\int_V \left(\sum_{\mu=1}^M \int_{-\infty}^{j_\mu(\mathbf{x})} \rho_\mu^*(\mathbf{x}) d \{ \log [\Lambda_\mu^3 \rho_\mu^*(\mathbf{x}) / \rho_\mu^0(\mathbf{x})] \right. \\ &\quad \left. - \partial \Gamma / \partial \rho_\mu^*(\mathbf{x}) \} \right) d\mathbf{x}. \end{aligned} \quad (18)$$

The first term of (18) gives the first part of (3) and the second can be combined with the last term of

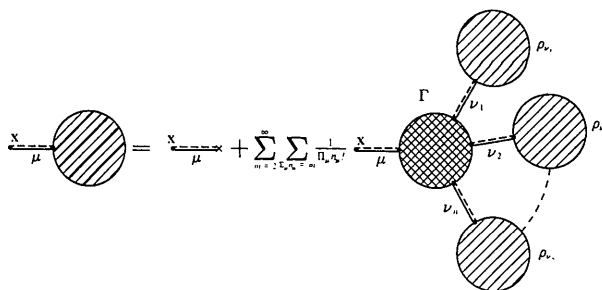


Fig. 6. The irreducibly connected diagrams can be rearranged as a sum of connected diagrams with a doubly irreducible kernel (shown cross-hatched).

(17) to give

$$\int_V \sum_{\mu=1}^M \left\{ \int_{-\infty}^{j_{\mu}(\mathbf{x})} -\rho_{\mu}^*(\mathbf{x}) d[\partial\Gamma/\partial\rho_{\mu}^*(\mathbf{x})] + \rho_{\mu}(\mathbf{x})\partial\Gamma/\partial\rho_{\mu}(\mathbf{x}) \right\} d\mathbf{x}. \quad (19)$$

The inner integral can be replaced with an integration by parts

$$d[\rho_{\mu}(\mathbf{x})\partial\Gamma/\partial\rho_{\mu}(\mathbf{x})] - [\partial\Gamma/\partial\rho_{\mu}(\mathbf{x})] d\rho_{\mu}(\mathbf{x}). \quad (20)$$

Some terms cancel leaving

$$\int_V \sum_{\mu=1}^M \int_{-\infty}^{j_{\mu}(\mathbf{x})} \partial\Gamma/\partial\rho_{\mu}^*(\mathbf{x}) d[\rho_{\mu}^*(\mathbf{x})] = \Gamma(\tilde{\rho}). \quad (21)$$

From this, the free-energy expression (3) follows directly. Because the Lagrange multipliers (effectively the chemical potentials) now only appear implicitly within the ρ_{μ} they can be set to zero without altering the result (3) and rendering $\partial W/\partial j_{\mu}$ equal to the atomic density described by the Hamiltonian \mathcal{H} .

5. Expressing the free energy in terms of structure factors

The free energy (3) is expressed in terms of the densities of each of the contributing atomic types but it can equally well be expressed in terms of their respective Fourier coefficients U_h^{μ} giving $-\beta A[U_h^1, \dots, U_h^N]$. Unfortunately, these individual values are not known (or measured) and only their sum,

$$\sum_{\mu=1}^N f_{\mu}(\mathbf{h})U_h^{\mu} = F_h, \quad (22)$$

weighted by their individual scattering factors $f_{\mu}(\mathbf{h})$, is of interest in crystallography. The U_h^{μ} will be termed atomic structure factors because they are formally different from (but numerically similar to; hence the notation) the unitary structure factors U_h . Equation (22) can be expressed in the matrix form $\mathbf{fU} = \mathbf{F}$ for which the 'inverse' is required. Because the matrix \mathbf{f} is not square it is necessary to use a generalized inverse, $\mathbf{f}^{\#}$, of which there are two choices: (1) if $\mathbf{f}^{\#} \equiv (\mathbf{f}^T \mathbf{f})^{-1} \mathbf{f}$ then $\mathbf{fU} = \mathbf{F} \Rightarrow \mathbf{U} = \mathbf{f}^{\#} \mathbf{F}$ (this does not imply that $\mathbf{fU} = \mathbf{F}$). (2) If $\mathbf{f}^{\#} \equiv \mathbf{f}^T (\mathbf{f} \mathbf{f}^T)^{-1}$ then $\mathbf{U} = \mathbf{f}^{\#} \mathbf{F} \Rightarrow \mathbf{fU} = \mathbf{F}$ (this does not imply that $\mathbf{U} = \mathbf{f}^{\#} \mathbf{F}$). Because the U_h^{μ} 's must be consistent with the F_h 's, it is the latter choice that is needed. This gives $U_h^{\mu} = f_{\mu}(\mathbf{h})F_h/\sigma_2$ which can be substituted into (3) to give the free energy as a function of the structure factors.

The problem of determining unknowns that are not uniquely specified by the data is best approached *via* the principle of maximum entropy (Levine, 1980). If the summations (22) are interpreted as expectation values from some underlying statistical model then a ME probability density $P(\mathbf{U})$ for the U_h^{μ} can be calcu-

lated. From this, inversion can be effected using $\int U_h^{\mu} P(\mathbf{U}) d\mathbf{U}$ which is a function of the constraints F_h via the Lagrange multipliers (as discussed in the *Introduction*). For example, if the U_h^{μ} are taken as random variables distributed within the circle of radius u_h^{μ} , then the log of the partition function must satisfy $\partial \log Z(\alpha_h)/\partial \alpha_h = |F_h|$ where α_h is the Lagrange multiplier of F_h . This equation has the form

$$-2(N/\alpha_h) + \sum_{\mu=1}^N u_h^{\mu} f_{\mu}(h) \times I_0(u_h^{\mu} f_{\mu}(h)\alpha_h)/I_1(u_h^{\mu} f_{\mu}(h)\alpha_h) = F_h. \quad (23)$$

If F_h is small (implying that α is also small) then α_h can be determined as a function of F_h . The atomic structure factors are independently distributed so that the partition function is separable ($Z = \prod_{\mu} Z_{\mu}$) and U_h^{μ} can be determined from $\partial \log Z_{\mu}/\partial \alpha_h$. This results in a value equivalent to that found from the generalized inverse described above. If $F_h \rightarrow \sum u^{\mu} f_{\mu}$ is large then α_h is also large and the atomic structure factor is given by

$$U_h^{\mu} = F_h/Nf_{\mu}(\mathbf{h}) \left[1 + u_h^{\mu} \sum_{\nu} \delta f_{\nu}(\mathbf{h}) / |F_h| \right] \quad (24)$$

where $\delta f_{\nu} = f_{\mu} - f_{\nu}$.

Clearly, the drawback with the above approach is that the j.p.d. for the atomic structure factors was based on an arbitrary statistical assumption about the distribution of the U_h^{μ} 's. This problem can be avoided by noting that since the entropy is equal to the expectation value of the log of the probability density, the function $\exp(-\beta A)/Z$ formally defines a probability distribution. With this in mind, let $P(\mathbf{U}^{\mu})$ be the j.p.d. between the individual atomic structure factors U_h^{μ} with the corresponding characteristic function $Z[\tilde{j}]$ [which is given by (5) substituting j_h^{μ} as the Fourier transform of $j_{\mu}(\mathbf{x})$]. Similarly, let $P(\tilde{\mathbf{F}})$ denote the j.p.d. between the actual structure factors F_h . Then, *via* the change-of-variables theorem (Gillespie, 1983), it is easy to show that the characteristic function $C[\tilde{\lambda}]$ of $P(\tilde{\mathbf{F}})$ is equal to $Z[\tilde{j}]$ under the condition that $j_h^{\mu} = f_{\mu}(\mathbf{h})\lambda_h$. The inverse Laplace transform gives the j.p.d. between structure factors,

$$P(\tilde{\mathbf{F}}) = \int_{\tau-i\infty}^{\tau+i\infty} \exp[W(f_{\mu}\lambda) - \tilde{\lambda}\tilde{\mathbf{F}}] d\tilde{\lambda} \quad (25)$$

which can be evaluated at a saddle point by solving $\partial W/\partial \lambda_h = F_h$ for $\lambda_h = \tau_h$. Integration of (25) at the saddle point gives

$$\begin{aligned} \log P(\tilde{\mathbf{F}}) &\equiv -\beta A_c(\tilde{\mathbf{F}}) \\ &= -\beta A(\tilde{\mathbf{F}}) \\ &\quad + \frac{1}{2} \log \det \{ \partial^2 [-\beta A(\tilde{\mathbf{F}})] / \partial F_h \partial F_k \} \end{aligned} \quad (26)$$

where the U_h^{μ} in (3) have been substituted by $U_h^{\mu} \equiv \partial W/\partial j_h^{\mu}|_{j_h^{\mu}=f_{\mu}(\mathbf{h})\lambda_h}$ and are indirectly functions of the

F_h by the λ_h s. This is possible in principle because W is a known function of the connected cluster integrals but it is unlikely that an analytic function, f , can be found that gives $\tilde{\lambda}_h = f(\tilde{F})$ in terms of the structure factors. On the other hand, if $j_\mu(\mathbf{x})$ is small, then $U_h^\mu \propto j_h^\mu(\mathbf{h} \neq 0)$ which gives $\lambda_h = F_h/\sigma_2$, the same value as predicted from the generalized inverse. Any value of λ_h can be used, although the saddle-point value gives the most accurate low-order expansion (Daniels, 1954). It is important to note that (26) is also the relation that connects the free energy of the canonical distribution to that of the grand canonical distribution (Fowler & Guggenheim, 1939). By construction, the left-hand side gives the log of the j.p.d. between structure factors for a fixed finite number of atoms as specified by the constraints (22) (see also Appendix I). Hence the minimization of $A_c(\tilde{F})$ with respect to the phases can be considered a direct method of phase determination if interatomic potentials can be supplied *ab initio* from general chemical knowledge.

The generalized inverse permits a simple extension to incorporate multiple isomorphous replacement (MIR) data sets. M different isomorphous structures with reflections G_h^i , $i = 1, \dots, M$, imply a set of relations of the form

$$\sum_{\mu=1}^N g_\mu^i(\mathbf{h}) U_h^\mu = G_h^i. \quad (27)$$

The meaning of the term isomorphous is clearly defined by forcing the U_h^μ to be identical in all of the structures (only the g_μ^i distinguish between structures). Application of the generalized inverse gives

$$U_h^\mu = \sum_{i,j}^M g_\mu^j(\mathbf{h}) \left[\sum_{\nu} g_\nu^i(\mathbf{h}) g_\nu^j(\mathbf{h}) \right]^{-1} G_h^i. \quad (28)$$

This inversion, when substituted into (3), gives the j.p.d. between the structure factors of the isomorphous structures. The idea can be applied to the saddle-point integration (25) using $j_h^\mu \rightarrow \sum_i g_\mu^i(\mathbf{h}) \lambda_h^i$, but now (26) cannot be considered the log of the free energy of any particular structure. Symmetry can also be accommodated by substituting

$$\rho_\mu(\mathbf{x}) = G^{-1} \sum_g^G \rho_\mu(S_g \mathbf{x}) \quad (29)$$

for each atom or, if it is a non-crystallographic symmetry, for each of the participating atoms. It is not hard to show that this yields similar relationships to those used in molecular replacement methods (Main & Rossmann, 1966).

6. Convergence of the excess free-energy summation

If the $f_{\mu\nu}$ are all short range, the integrals of Γ are effectively volume independent and hence can be expanded rigorously as powers of $N\epsilon/kT$, where N

is the average number of atoms in the unit cell and ϵ is the average energy per atom. The Mayer cluster expansion on which the derivation of (3) is based has been shown, for the simple virial expansion, to converge after seven terms or so for densities approaching half the crystallization density of simple close-packed lattices (see Ree & Hoover, 1967). Also Γ can be expanded about any preferred reference density as

$$\Gamma = \sum_{n=0}^{\infty} \sum_{\{\bar{n}\}} [\prod n_\mu !]^{-1} (\partial^n \Gamma / \prod \partial \rho^{n_\mu}) \times \prod_{\mu} [\rho_\mu(\mathbf{x}) - \rho_\mu^0]^{n_\mu} \quad (30)$$

thereby improving the chances of fast convergence. The derivatives of Γ form part of the direct-correlation functions and can be related to the actual correlation functions by generalized Ornstein-Zernike relations (Bławdziewicz, Cichocki & Holyst, 1989). Expansions of Γ to a third order have been successfully applied to computational crystallization problems by Haymet & Oxtoby (1981) and Bagchi, Cerjan, Mohanty & Rice (1984) and thus it would seem that the excess free-energy expansion (4) is unlikely to be divergent or otherwise pathological.

It could be asked if the free energy (26) predicts any kind of phase change as the temperature is lowered. Such a change would be indicated by a divergence in the hessian of $\log Z$ and, due to the Ornstein-Zernike equation (see § 2), would mean that some eigenvalues of the hessian of A must vanish. In fact the free energy of the grand canonical [the first term of (26)] remains finite and at the critical points becomes insensitive to wild fluctuations in the density [as might be expected (Fisher & Jasnow, 1975)]. Indeed, the direct-correlation functions remain short ranged even at critical points (Hansen & McDonald, 1976) roughly equal to the range of the interatomic forces. On the other hand, the second term of (26) does diverge, reflecting the well known fact that the canonical and grand canonical partition functions cannot be equivalenced at critical points (Zubarev, 1974).

Since it is envisaged that the free energy (26) will be used as a weighting function to determine the most likely phases for a structure, the temperature becomes, computationally, no more than a variable parameter weighting the effects of interatomic potentials. Thus, in practice, it may be possible to set the temperature high enough to ensure quick convergence of Γ but still permit the potentials to be effective in the phasing process.

7. Hard-core potential

It is not yet clear how the energy interaction terms appearing in the excess free energy alter the phase indications of the reflections. In this section the effect of a simple hard-core potential will be investigated.

Assuming that all atoms have the same radius, such a potential f_{ij} has the form

$$f(\mathbf{x}, \mathbf{y}) = \begin{cases} -1 & \text{if } \exists |\mathbf{x} - \mathbf{y} \pm \mathbf{1}| < \sigma \\ 0 & \text{otherwise.} \end{cases} \quad (31)$$

Because of the infinite core repulsion this is a temperature-independent potential. The function (31) is easily expressed as a Fourier series

$$f(\mathbf{x}, \mathbf{y}) = \sum_{\mathbf{h}} \mathbf{V}_{\mathbf{h}} \exp [2\pi \mathbf{h} \cdot (\mathbf{x} - \mathbf{y})]. \quad (32)$$

Approximation of the step function as a Gaussian of width $\varepsilon = 2\sigma$ gives $\mathbf{V}_{\mathbf{h}} \approx -\varepsilon \exp(\varepsilon^{2/3} h^2)$ and $\varepsilon = \nu_{\text{atom}}/V$ is the ratio of the volume of a single atom to the volume of the unit cell. For ε small and with the configurational entropy term approximated by a simple polynomial, the triplet term can be calculated as

$$\sum_{\mathbf{h}, \mathbf{k}} \sigma_2^{-3/2} [\sigma_3 - K\varepsilon^2 \sigma_1^3] \mathbf{E}_{\mathbf{h}} \mathbf{E}_{\mathbf{k}} \mathbf{E}_{-\mathbf{h}-\mathbf{k}} \quad (33)$$

where K is a positive constant < 1 , whose exact value depends on the form of $\mathbf{V}_{\mathbf{h}}$. Notice that $\sigma_3 \approx N^{-1/2}$ but that $\sigma_1 \approx N^{1/2}$. Because, as pointed out in § 3, crystal densities do not vary by more than an order of magnitude, $\varepsilon \approx N^{-1}$ so that $\varepsilon^2 \sigma_1^3 \approx N^{-1/2}$ has the same dependence upon the number of atoms as σ_3 . Much has been said about the lack of any physical justification for permitting the atoms to be uniformly distributed about the unit cell without regard to their proximity to one another (Wilson, 1981), but as Goedkoop, MacGillavry & Pepinsky (1951) have shown, an isotropic exclusion zone around each atom (a result of hard-core repulsion) has no phasing power because it already exists in the Patterson map. On the other hand, Rius & Miravittles (1991) have shown that if significant areas in the Patterson map are void of density then some phase information can be extracted. In this case one can infer an effective repulsion potential that is not necessarily isotropic and for which ε is not necessarily small. As can be seen from (33) the hard-core potential affects the triplets by reducing their weights by a constant amount. From this result it is possible to say that, although the direct-method procedures are based on a random-atom assumption, to a first approximation there is no practical difference between this and a phase procedure based on hard-core repulsion.

8. Extensions

If consideration is given to the proof in § 4, it can be seen that there is no need to interpret the parameters \mathbf{x} in (3) as atomic positions. It is possible to extend $\mathbf{x} \rightarrow \mathbf{x}$, $\boldsymbol{\theta}$ to include other degrees of freedom such

as action angle variables between fragments. The densities now have to be interpreted in terms of this larger space and the interatomic potentials $f_{\mu\nu}$ become correspondingly more complicated. Unfortunately it is not clear how to express $\rho_{\mu}(\mathbf{x}, \boldsymbol{\theta})$ in terms of the scattering factor. On the other hand, Bayes's theorem can be applied with the probability distribution (26) to get $P(\tilde{\mathbf{F}}, \tilde{\boldsymbol{\theta}}) \propto P(\tilde{\mathbf{F}}|\tilde{\boldsymbol{\theta}})P_{\text{prior}}(\tilde{\boldsymbol{\theta}})$. In this case the second term of (26) is crucial because it provides normalization for the probability. This extra 'power' of the probability distribution over simple entropy maximization (or in this case, free-energy minimization) has already been noted in the crystallographic area by Bricogne (1988).

9. Simulated annealing

The expression of the free energy as a j.p.d. between structure factors raises the question of the applicability of simulated annealing techniques to phase solution. Original attempts by Semenovskaya, Khachatryan & Khachatryan (1981, 1985) to determine crystal structures *via* statistical mechanics arguments based on an 'R-factor' free energy have not been shown to be advantageous. Recently, Sheldrick (1990) has reported a practical application of phase annealing to real structure-factor data. Unfortunately it is not possible to relate his practical approach to the free-energy relations (3) or (26) even though simulated annealing techniques were originally developed for free-energy minimizations in 'rugged landscapes'. The major difference is that (3) gives the standard invariant relations in the high-temperature limit whereas Sheldrick's B parameter must be lowered to regain them. Further, the phase dependence of the configurational part of the free energy is temperature independent.

10. Discussion

The requirement that stereochemical information be supplied in the form of potential functions (13) is possibly too exigent, given the current state of chemical knowledge. For example, in accurate molecular-dynamics calculations of local order in silicon, Mistriotis, Flytzanis & Farantos (1989) had to employ four-body potential functions. These results were only applicable to clusters of more than six atoms (where π bonding is insignificant due to the large degree of coordination). Others have used three-body potentials based on two-body sums (Biswas & Hamann, 1985) or a pair potential dependent upon the chemical environment (Tersoff, 1986). This last method is used in the application of molecular dynamics to crystallographic refinement where the known environment surrounding each atom permits atomic interactions to be separated into

bonded and non-bonded types (Brünger, Kuriyan & Karplus, 1987). One can incorporate this idea into the free energy (3) by making the potentials dependent upon the densities, *i.e.* $V(\rho_\mu, \rho_\nu)$, but the complication this entails may introduce more error than it eliminates.

It would seem that the only unambiguous information available is the hard-core repulsion potential between atoms which Goedkoop, MacGillavry & Pepinsky (1951) have already shown to hold no phase information. Equation (33) shows, however, that the weights of the invariants are different and this should serve as a caution to the efforts being launched to calculate triplet weights 'accurately' from the random-atom assumption (Shmueli, Rabinovich & Weiss, 1989).

In some cases it is not necessary to work at the atomic level. The scattering factors in (22) could equally well be those of groups [or the 'globs' of Harker (1953)]. This approach has been used by Rabinovich & Shakked (1984) to solve some DNA structures. They effectively used a simple hard-core potential between DNA fragments to exclude certain configurations from consideration. This is exactly the idea behind the derivation of the free-energy distribution. Rabinovich & Shakked have reported some success with their brute-force search through configuration space. This method has also been used by Major, Guatheret, Lapalme, Jolicoeur, Fillion & Cedergren (1990), but without the aid of reflection intensity information. Their potentials (simple topological constraints) are extremely crude due to the large grid spacings employed but have aided in a successful, if limited, search for RNA loops. With (26) this search has already been completed *via* the integration over configurations (7) and only the average effect on the structure factors remains. Moreover, it is not necessary to restrict the potential functions to the chemical domain. For example, knowledge of non-crystallographic symmetry, S , implies the potential $V_{\mu\nu}(\mathbf{x}_\mu, \mathbf{x}_\nu) = \delta(\mathbf{x}_\mu - S[\mathbf{x}_\nu])$. The recycling of fragments found in direct-method maps to improve invariant phase relationships (Main, 1976) is now a standard part of crystallographic practice. The combination of fragments with simple exclusion potentials and the free energy (26) into a more general phasing scheme is therefore a promising possibility.

The generalization of the j.p.d. between structure factors has provided insight into requirements for improving on the random-atom approximation. These requirements involve a knowledge of stereochemistry in the form of potentials and, maybe more importantly, a clearer understanding of what level to consider 'atomic'.

Financial assistance from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

APPENDIX I

(i) Corrections to the j.p.d.

It is possible to extend the standard methods used to derive j.p.d.s for uniform atomic distributions just as the free energy was extended from the configurational entropy; that is, *via* the potential functions. By taking the atomic probability density ρ as proportional to (14) and expanding to lowest order in $f_{\mu\nu}$, the distribution

$$\rho(\mathbf{r}_1, \dots, \mathbf{r}_N) = \prod_{\mu=1}^N \rho_\mu^0(\mathbf{r}_\mu) \left[1 + \sum_{\mu < \nu} f_{\mu\nu}(\mathbf{r}_\mu, \mathbf{r}_\nu) \right] \quad (A1)$$

is obtained. Expressing the interaction potentials, f , in terms of their Fourier transform as was done in (32) and assuming that the ρ^0 are uniform (an assumption that can be dropped), one can use the technique of Castleden (1987, 1988) to derive the j.p.d. between structure factors:

$$P(\mathbf{F}) = P_o(\mathbf{F}) + \sum_{\mathbf{h}} \sum_{\mu < \nu} |\mathbf{V}_{\mathbf{h}}^{\mu\nu}| \sum_{\{\mathbf{n}\}} \prod_{\mathbf{h}} G(\mathbf{n}, f, F_{\mathbf{h}}) \times \cos \left\{ \sum_1 \left[\sum_{\alpha} n_{\alpha 1} \right] \varphi_1 + \varphi_{\mathbf{h}}^{\mu\nu} \right\} \quad (A2)$$

where P_o is the ordinary j.p.d. and the notation is taken from Castleden (1988). The set of integers $\{\mathbf{n}\}$ satisfies

$$\left\{ n_{\alpha\mathbf{h}} \left| \sum_{\mathbf{k}} n_{\alpha\mathbf{k}} \mathbf{k} + \mathbf{h} = \mathbf{0} \right. \right\} \text{ if } \alpha = \mu, \nu$$

and

$$\left\{ n_{\alpha\mathbf{h}} \left| \sum_{\mathbf{k}} n_{\alpha\mathbf{k}} \mathbf{k} = \mathbf{0} \right. \right\} \text{ otherwise.} \quad (A3)$$

The combinatorial problems encountered by Peschar & Schenk (1986) and Castleden (1987) in calculating a sufficient number of terms to ensure the convergence of the series $P_o(\mathbf{F})$ are, here, even more acute and make (A2) far more difficult to compute than (26). However, the derivation shows that the free energy and the j.p.d. must be similar as they both stem from the same prior atomic probability distribution and that the coefficients calculated from (A2) (and the higher-order terms) should, for large N , be equal to those calculated from (26).

(ii) Atomic correlations with the central limit theorem

Heinerman, Krabbendam & Kroon (1977) have used the central limit theorem (CLT) to derive the j.p.d. of a triplet invariant. The CLT also applies when correlation between random variables exists (Serfling, 1968) although the correlation length has to remain finite. With this restriction, an interatomic probability distribution $p(\mathbf{r}_i - \mathbf{r}_j)$ can be defined with Fourier

coefficients $G_{ij}(\mathbf{h}) \equiv \langle \exp \{2\pi i \mathbf{h} \cdot (\mathbf{r}_i - \mathbf{r}_j)\} \rangle_p$. With the terminology of Heinerman *et al.*, it can be shown that the triplet invariant $\psi_{\mathbf{h}} + \psi_{\mathbf{k}} + \psi_{-\mathbf{h}-\mathbf{k}}$ equals φ where

$$k \exp(i\varphi) = 2\sigma_2^{-3} |F_{\mathbf{h}_1} F_{\mathbf{h}_2} F_{-\mathbf{h}_1-\mathbf{h}_2}| \Delta. \quad (A4)$$

Assuming that the scattering factors f are independent of \mathbf{h} , Δ is given by

$$\sigma_3 + [\sigma_1\sigma_2 - \sigma_3][G(\mathbf{h}_1) + G(\mathbf{h}_2) + G(-\mathbf{h}_1 - \mathbf{h}_2)] + [\sigma_1^3 - 3\sigma_1\sigma_2 + 2\sigma_3]G(\mathbf{h}_1)G(\mathbf{h}_2). \quad (A5)$$

Because the G s are real-valued, the only possible values for the triplet sum φ are 0 or π . This is in agreement with (33).

APPENDIX II

The use of diagrams

After careful definition of a few terms, the arguments of § 4 and the proof of (16) can be made rigorous with the aid of theorems derived by Morita & Hiroike (1961). These theorems are reproduced in Hansen & McDonald (1976, Appendix A) and are hereafter referred to as lemmas I, II and III. They apply only to 'simple' diagrams; that is, no third- or higher-order interactions, and a single atomic type (see Fig. 7), but it is not difficult to drop these restrictions and generalize the results.

Ignoring the product over densities, (14) can be written in the form $\prod_k (1 + \delta_k)$ where $\delta_s = f_{ij}$ *etc.* Expanding the product produces sums over terms of the form $\delta_i \delta_j \dots \delta_k$ with each set of indices $[ij \dots k]$

distinct. This means that no permutations can transform it into a set of indices for another member of the sum. Each product, when integrated, has associated with it a distinct labelled diagram (see Fig. 8). Since Z is the sum over all possible ensembles of atoms, it follows that Z is the sum over all topologically distinct labelled diagrams. Here, topologically distinct means that no deformation, rotation, inversion *etc.* of the diagrams which does not break any 'bonds' can superimpose one distinct diagram onto another. Labelled diagrams which share the same topology when their labels are ignored can be grouped together to form an unlabelled diagram (see Figs. 8 and 9). Conversely, for any unlabelled diagram, all its distinct labelled equivalents can be matched with a product of deltas. (The proof can be made by construction. Note, in particular, the form of the fourth-order bond in Fig. 7; any permutation of labels on like atoms leaves it invariant. This must also be true of all higher-order bonds in order to match the symmetry of the potential function they represent.)

Let $z \in \{Z\}$. Because this diagram can be constructed from a product,

$$z = \prod_{i=1}^N [w_i^{n_i}], \quad (A6)$$

where $w_i \in \{W\} \forall i$ (see Fig. 10) and where n_i are certain integers, then by lemma I, $Z = \exp [W]$.

Since differentiation of a closed diagram produces a sum over all distinct diagrams with one open vertex (lemma II, see Figs. 11 and 12), lemma I can be used

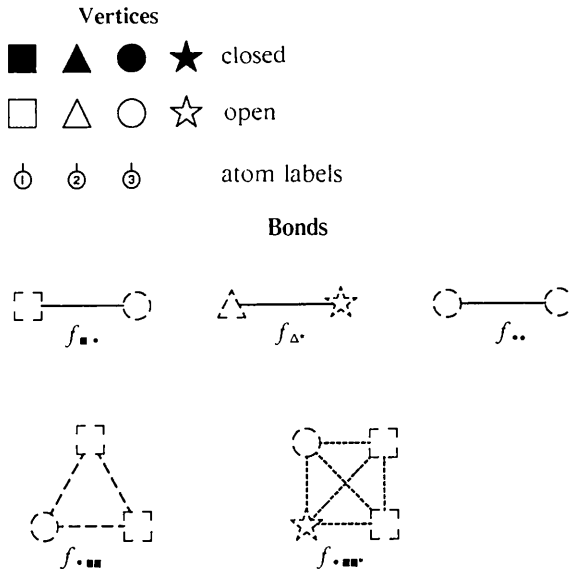


Fig 7. Diagrams are made up of vertices and bonds. Vertices may be open or closed. Closed vertices may or may not be labelled but open vertices are always labelled. Bonds represent the interatomic potentials. Each 'shape' represents an atomic type.

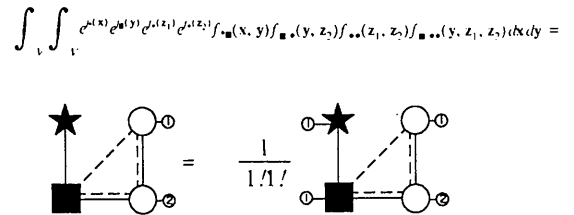


Fig. 8. Each unlabelled diagram is shorthand for a particular set of integrals. Each topologically distinct way of labelling the diagram (permuting only between vertices of the same type) corresponds one to one with a particular integral. For example, setting $-\beta\lambda_{\mu}(x)$ to zero gives the above result.

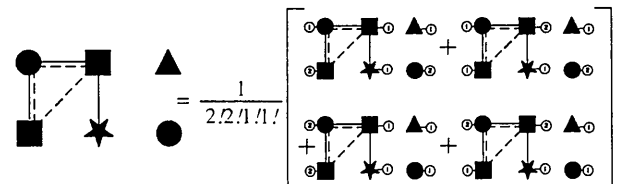


Fig. 9. The partition function is the sum over all topologically distinct unlabelled diagrams. The set of these diagrams is denoted by $\{Z\}$ and the sum by Z , e.g. $z \in \{Z\}$ = the above formula.

to prove that $\partial W/\partial j_\mu(\mathbf{r}) = \exp[G_\mu(\mathbf{r})]$ where $G_\mu(\mathbf{r})$ is the sum over the set of diagrams with no open articulation vertices (Fig. 13). This is because if $w_\mu(\mathbf{r})$ is an element of the set $\{\partial W/\partial j_\mu(\mathbf{r})\}$ then it can be

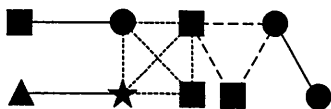


Fig. 10. An element of the set $\{W\}$. From the set $\{Z\}$ all connected diagrams are selected. This set is denoted by $\{W\}$ and the sum of its elements by W .

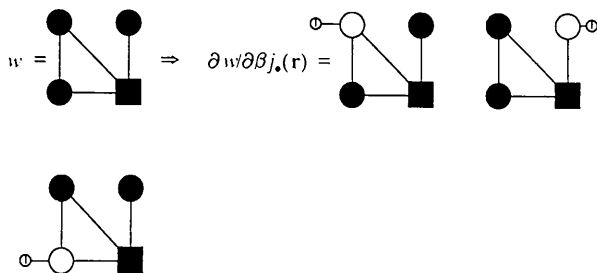


Fig. 11. Any element $w \in \{W\}$ can be differentiated. The diagrammatic equivalent of differentiation is given by lemma II: the derivative of a closed diagram with respect to some Lagrange multiplier $j_\mu(\mathbf{r})$ is equal to the function $f(\mathbf{r})$ represented by the sum over all topologically distinct diagrams obtained by replacing a closed μ vertex by an open μ vertex, all multiplied by β . For example, let $w \in \{W\}$ so that the first formula is obtained, but not the lower diagram since this is topologically identical to the first diagram.

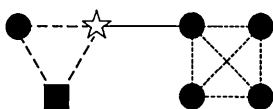


Fig. 12. All elements of the set $\{W\}$ can be differentiated [for example and w.l.o.g. by $j^*(\mathbf{r})$]. This set of diagrams is denoted by $\{\partial W/\partial j^*(\mathbf{r})\}$. The sets $\{W\}$ and $\{\partial W/\partial j^*(\mathbf{r})\}$ have diagrams which contain 'articulation vertices'. These are vertices which, if removed, result in two or more disconnected diagrams.



Fig. 13. An element of the set $\{G^*(\mathbf{r})\}$. All the diagrams in $\{\partial W/\partial j^*(\mathbf{r})\}$ that have no open articulation vertices form a set.

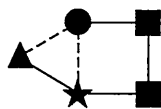


Fig. 14. An element of the set $\{I\}$. The set $\{I\}$ is the set of diagrams in $\{W\}$ with no articulation points.

constructed from a product

$$w_\mu(\mathbf{r}) = \prod_{i=1}^n [g_\mu^i(\mathbf{r})]^n, \quad (A7)$$

where $g_\mu^i(\mathbf{r}) \in \{G_\mu(\mathbf{r})\} \forall i$.

The final step giving the expansion in terms of densities is a direct result of (a simple generalization of) lemma III. An element of the set I is shown in Fig. 14.

References

- BAGCHI, B., CERJAN, C., MOHANTY, U. & RICE, S. A. (1984). *Phys. Rev. B*, **29**, 2857-2860.
- BAUS, M. (1987). *J. Stat. Phys.* **48**, 1129-1146.
- BISWAS, R. & HAMANN, D. R. (1985). *Phys. Rev. Lett.* **55**(19), 2001-2004.
- BLAWZDZIEWICZ, J., CICHOCKI, B. & HOLYST, R. (1989). *Physica (Utrecht)*, **A157**, 857-890.
- BRICOGNE, G. (1984). *Acta Cryst.* **A40**, 410-445.
- BRICOGNE, G. (1988). *Acta Cryst.* **A44**, 517-545.
- BRÜNGER, A. T., KURIYAN, J. & KARPLUS, M. (1987). *Science*, **235**, 458-460.
- BRYAN, R. K. (1988). In *Improving Protein Phases*, compiled by S. BAILEY, E. DODSON & S. PHILLIPS, from the Study Weekend held at Daresbury Laboratory, 5-6 February 1988.
- CASTLEDEN, I. R. (1987). *Acta Cryst.* **A43**, 384-393.
- CASTLEDEN, I. R. (1988). PhD thesis, Univ. of Western Australia.
- DANIELS, H. E. (1954). *Ann. Math. Stat.* **25**, 631-650.
- DOLL, J. D. (1984). *J. Chem. Phys.* **81**, 3536-3541.
- DOMINICIS, C. DE (1962). *J. Math. Phys.* **3**, 983-1002.
- DOMINICIS, C. DE & MARTIN, P. C. (1964). *J. Math. Phys.* **5**, 14-30, 31-59.
- EVANS, R. (1979). *Adv. Phys.* **28**, 143-200.
- FEYNMAN, R. P. & HIBBS, A. R. (1965). *Quantum Mechanics and Path Integrals*. New York: McGraw-Hill.
- FISHER, M. E. & JASNOW, D. (1975). In *Phase Transitions and Critical Phenomena*, Vol. 4, edited by C. DOMB & M. S. GREEN. London: Academic Press.
- FOWLER, R. H. & GUGGENHEIM, E. A. (1939). *Statistical Thermodynamics*. Cambridge Univ. Press.
- FUCHS, K. (1941). *Proc. R. Soc. London. Ser. A*, **179**, 408-432.
- GILLESPIE, D. T. (1983). *Am. J. Phys.* **51**(6), 520-533.
- GLIMM, J. & JAFFE, A. (1981). *Quantum Mechanics - a Functional Integral Point of View*. Berlin: Springer-Verlag.
- GOEDKOOP, J. A., MACGILLAVRY, C. H. & PEPINSKY, R. (1951). *Acta Cryst.* **4**, 491-492.
- GULL, S. F., LIVESEY, A. K. & SIVIA, D. S. (1987). *Acta Cryst.* **A43**, 112-117.
- HANSEN, J. P. & McDONALD, I. R. (1976). *Theory of Simple Liquids*. London: Academic Press.
- HARKER, D. (1953). *Acta Cryst.* **6**, 731-736.
- HAUPTMAN, H. & KARLE, J. (1953). *The Solution of the Phase Problem. I. The Centrosymmetric Crystal*. ACA Monogr. Wilmington: The Letter Shop.
- HAUPTMAN, H. & KARLE, J. (1959). *Acta Cryst.* **12**, 93-97.
- HAYMET, A. D. J. (1987). *Ann. Rev. Phys. Chem.* **38**, 89-109.
- HAYMET, A. D. J. & OXTOBY, D. W. (1981). *J. Chem. Phys.* **74**, 2559-2565.
- HEINERMAN, J. J. L., KRABBENDAM, H. & KROON, J. (1977). *Acta Cryst.* **A33**, 873-878.
- HOOVER, W. G. & DEROCOCCO, A. G. (1962). *J. Chem. Phys.* **36**, 3141-3162.
- HUSIMI, K. (1950). *J. Chem. Phys.* **18**, 682-684.
- JAYNES, E. T. (1957). *Phys. Rev.* **106**, 620-630.
- JAYNES, E. T. (1965). *Am. J. Phys.* **33**, 391-398.
- KATZ, A. (1967). *Principles of Statistical Mechanics*. San Francisco: W. H. Freeman & Co.
- LANDSMAN, N. P. & WEERT, CH. G. (1987). *Phys. Rev. Rep.* **145**, 141-249.

- LARSEN, S. E., KILPATRICK, J. E., LIEB, E. H. & JORDAN, H. F. (1965). *Phys. Rev. A*, **140**, 1129–1130.
- LEVINE, R. D. (1980). *J. Phys. A: Math. Nucl. Gen.* **13**, 91–108.
- MCQUARRIE, D. A. (1973). *Statistical Thermodynamics*. Mill Valley, California: Univ. Science Books.
- MAIN, P. (1976). In *Crystallographic Computing Techniques*, edited by F. R. AHMED. Copenhagen: Munksgaard.
- MAIN, P. & ROSSMANN, M. G. (1966). *Acta Cryst.* **21**, 67–72.
- MAJOR, F., GUATHERET, D., LAPALME, G., JOLICOEUR, L., FILLION, E. & CEDERGREN, R. (1990). In PhD thesis (François Major), Univ de Montréal, Canada.
- MANDELBROT, B. B. (1989). *Phys. Today*, **42**, 71–73.
- MARGENAU, H. & KESTNER, N. R. (1969). *Theory of Intermolecular Forces*. New York: Pergamon.
- MAYER, J. E. & MAYER, M. G. (1940). *Statistical Mechanics*. New York: Wiley.
- MISTRIOTIS, A. D., FLYTZANIS, N. & FARANTOS, S. C. (1989). *Phys. Rev. B*, **39**(2), 1212–1218.
- MOHANTY, U. (1982). *J. Math. Phys.* **23**, 1489–1492.
- MOHLING, F. (1982). *Statistical Mechanics: Methods and Applications*. Publishers Creative Services Inc.
- MORITA, T. & HIROIKE, K. (1961). *Prog. Theor. Phys.* **25**, 537–543.
- NAVAZA, J. (1985). *Acta Cryst.* **A41**, 232–244.
- NAVAZA, J. (1986). *Acta Cryst.* **A33**, 212–223.
- PARR, R. G. (1983). *Ann. Rev. Phys. Chem.* **34**, 631–656.
- PARR, R. G. & WEITAO, (1989). *Density-Functional Theory of Atoms and Molecules*. Oxford Univ. Press.
- PESCHAR, R. & SCHENK, H. (1986). *Acta Cryst.* **A42**, 309–317.
- RABINOVICH, D. & SHAKKED, Z. (1984). *Acta Cryst.* **A40**, 195–200.
- REE, F. H. & HOOVER, W. G. (1967). *J. Chem. Phys.* **46**, 4181–4196.
- RIUS, J. & MIRAVITLLES, C. (1991). *Acta Cryst.* **A47**, 52–55.
- RIVERS, R. J. (1987). *Path Integral Methods in Quantum Field Theory*. Cambridge Univ. Press.
- ROMAN, S. (1979a). *J. Approx. Theory*, **26**, 340–381.
- ROMAN, S. (1979b). *Adv. Math.* **31**, 309–329.
- SEMENOVSKAYA, S. V., KHACHATURYAN, K. A. & KHACHATURYAN, A. G. (1981). *Acta Cryst.* **A37**, 742–754.
- SEMENOVSKAYA, S. V., KHACHATURYAN, K. A. & KHACHATURYAN, A. G. (1985). *Acta Cryst.* **A41**, 268–273.
- SERFLING, R. J. (1968). *Ann. Math. Stat.* **39**, 1158–1175.
- SHELDRIK, G. (1990). *Acta Cryst.* **A46**, 467–473.
- SHMUELI, U., RABINOVICH, S. & WEISS, G. H. (1989). *Acta Cryst.* **A45**, 361–367.
- STELL, G. (1976). In *Phase Transitions and Critical Phenomena*, Vol. 5B, edited by C. DOMB & M. S. GREEN. London: Academic Press.
- STILLINGER, F. H. & BUFF, J. (1962). *J. Chem. Phys.* **37**, 1–12.
- STOUT, G. H. & JENSEN, L. H. (1989). *X-ray Structure Determination: a Practical Guide*, 2nd ed. New York: John Wiley.
- TERSOFF, J. (1986). *Phys. Rev. Lett.* **55**(6), 632–635.
- WILSON, A. J. C. (1981). *Acta Cryst.* **A37**, 808–810.
- WILSON, B. G. & ROGERS, F. J. (1986). *Physica (Utrecht)*, **A139**, 359–386.
- YVON, J. (1935). *Actual. Sci. Ind.* **203**, 67–72.
- ZUBAREV, D. N. (1974). *Nonequilibrium Statistical Thermodynamics*. New York: Consultants Bureau.

Acta Cryst. (1992). **A48**, 209–215

R Factors in X-ray Fiber Diffraction. IV. Analytic Expressions for Largest Likely R Factors

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Abstract

The largest likely R factor is useful for evaluating the significance of R factors obtained in structure determinations. Numerical expressions have been derived previously for calculating largest likely R factors in fiber diffraction analyses. Analytical approximations to largest likely R factors (\mathcal{R}) in fiber diffraction are derived here that show the dependence on resolution ($\hat{\rho}$), helix symmetry (u_0) and molecular radius (\hat{r}). The simplest approximation is $\mathcal{R} \propto (u/\hat{r}\hat{\rho})^{1/2}$ which represents the overall behavior of R factors reasonably well. More accurate approximations are also derived. These are applied to various structures and the dependence on different structural parameters is examined. These results provide insight into the behavior of R factors in fiber diffraction and may be useful in further analysis.

1. Introduction

The significance of an R factor obtained in a structure determination can be assessed by comparison with the largest likely R factor; that for a structure uncorrelated with the correct structure (Wilson, 1950). R factors in fiber diffraction are generally smaller than in single-crystal analyses because the diffraction pattern is cylindrically averaged, and the largest likely R factor in fiber diffraction has been studied by Stubbs (1989) and Millane (1989a, b, 1990). The largest likely R factor depends on the number of overlapping complex Fourier-Bessel structure factors at different positions in reciprocal space, and therefore on the diameter and symmetry of the diffracting particle and the maximum resolution of the diffraction data. The largest likely R factor in fiber diffraction, while easily calculated, is a rather complicated