Relationship between pair and higher-order correlations in solid solutions and other Ising systems

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D M C Nicholson[1]**, R I Barabash**[1]**, G E Ice**[1]**, C J Sparks**[1,3]**, J Lee Robertson**[1] **and C Wolverton**[2]

[1] Oak Ridge National Laboratory, Oak Ridge, TN 37831-6118, USA
[2] Ford Research and Advanced Engineering, MD 3083/SRL, PO Box 2053, Dearborn, MI 48121-2053, USA

Abstract
Atomic structure is perhaps the information most critical to the understanding of materials behaviour, hence the great importance of x-rays and neutrons as probes. Although scattering is sensitive to pair and higher-order correlations, in most applications only the pair correlation is recovered. However, pair correlation is inadequate for a complete description of homogeneous systems in thermodynamic equilibrium; all correlations are required. It is often assumed that the pair correlations extracted from scattering experiments either uniquely determine or greatly restrict higher-order correlations. Here we argue on the basis of simulations and classical density functional theory that when the Hamiltonian is of pair-potential form the pair correlations do uniquely determine all higher-order correlations. However, we also demonstrate by simulation and prove algebraically that for specific many-body Hamiltonians additional information beyond pair correlations is needed to determine higher-order correlations. The derivations are underpinned by the close connection between fluctuations, applied fields, and correlations and identify approaches that hold promise for extracting higher-order correlations.

For many materials systems, all that is known about the atomic-scale structure is the pair correlation (PC). Therefore, the relationship between PC and the totality of structural information is very important. However, in general, correlations to all orders are needed to completely define the structure [1]. Additional constraints may sometimes result in relationships between pair and higher-order correlations that remould this requirement into the requirement that the constraints together with lower-order correlations completely determine the structure. Rozman [2] showed that for several periodic, piecewise uniform structures with smooth boundaries the PCs were sufficient to define the structure. In that study structures were

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[3] Deceased.

found that could be reconstructed from their PC but the particular constraints that allowed this were left as a matter of speculation.

In this paper we consider systems 'constrained' to be either canonical or grand canonical ensembles at temperature T; furthermore, each member of the ensemble is completely specified by the occupation of each site on a lattice. It is also assumed that the Hamiltonian can be cluster expanded. We will focus on binary solid solutions but the results are directly applicable to other Ising models and are easily generalized to liquids by substitution of closely related quantities, i.e. pair correlation function for short range order parameter or by the more cumbersome approach of treating liquids as solid solutions of atoms and vacancies in the limit that the lattice parameter goes to zero.

The set of coefficients that specify the Hamiltonian provides an alternative, compact, and complete specification of the structure, albeit one that is usually unknown and if known still requires considerable work to obtain a typical structural description in terms of ensemble averaged properties. The relationship between structure, correlations, and constraints is a longstanding problem in many fields [3–5]. Diagrammatic methods have been used for liquids to express the grand potential in terms of the point and pair correlation functions [6]. In the tradition of the study of short-range order (SRO) and diffuse scattering it can be traced to the work of Krivoglaz [7] and others [8–16].

Henderson [17] used the minimum condition on the free energy attributed to Bogoliubov [18] to show that for pair potential Hamiltonians (PPHs) the pair correlation was unique. Henderson did not address higher-order correlations for either pair or for many-body Hamiltonians (MBH). Evans [19] commented on Henderson's work and asserted without proof that an MBH of order n is uniquely determined by correlations to order n. In a recent paper Stillinger and Torquato [20] studied short (15 sites maximum) linear chains in which they could enumerate all configurations. They found chains with lengths between 11 and 15 sites for which a range of many-body correlations was consistent with a single pair correlation. Because their configurations are very small and far from the thermodynamic limit, their results show a strong dependence on the chain length. Their approach is very different from ours but their conclusions corroborate ours. Specifically, they also point out the need for caution when interpreting higher-order correlations based on reverse Monte Carlo.

The need for continued discussion of the relationship between pair and higher-order correlations is evidenced by the continued practice of drawing conclusions about higher-order correlations from analysis of scattering data [11, 13, 21] on disordered systems. For ordered systems with unit cells smaller than the coherence length of the scattering wave the scattered amplitude contains complete information about the structure and the scattered intensity can in many cases determine the structure. Furthermore, it is a property of some ordered structures that due to a limited number of symmetry groups being consistent with periodicity they are uniquely specified by their scattering intensity or even by their spherically averaged intensity, i.e. powder pattern. These can be considered special cases, where auxiliary information supplements pair correlations to allow a complete description. It is in these systems, which have been very important to materials science, that the Rietveld refinement has made its great contribution. The delineation between ordered structures that can and cannot be determined in this way is interesting and important but will not be addressed here. We restrict discussion to structural features characterized by long wavelengths greatly exceeding available coherence lengths. We focus on binary disordered substitutional alloys composed of elements A and B.

To place Rietveld refinement in to the context of this paper we note that the refinement process is the minimization of an artificial pair potential Hamiltonian constructed solely to provide a metric for the level of agreement between powder scattering data and a set of proposed structures. Results presented below prove that the result of this process if it can be

carried to convergence will provide unique higher-order correlations but that these higher-order correlations need not be those of the material under study. Only if the Hamiltonian governing the energy of the material is a pair potential Hamiltonian will the higher-order correlation be determined. The reproducibility of the analysis can mislead practitioners as to the validity of the higher-order correlations. We further caution that if the system being analysed is not in equilibrium or representative of an equilibrium structure such as a quenched sample then there is no proof that the higher-order correlations are determined even if the Hamiltonian is strictly pair potential.

The immediate predecessor of the work presented here is that of Wolverton *et al* [21], who showed by inverse Monte Carlo based on 35 shells of SRO parameters that a given set of pair correlations at a particular temperature can be generated by two different Hamiltonians, one pair and one many body. These authors did not examine the issue of whether the two Hamiltonians give different higher-order correlations. Such a result would have numerically proved by counter-example that PCs do not in general determine higher-order correlations.

Here, we present algebraic arguments that support the hypothesis that PCs determine higher-order correlations for pair potential Hamiltonians (PPHs), then prove this hypothesis using arguments familiar from classical density functional theory [22]; we also prove for Hamiltonians of higher order than pair that correlations up to the order of the Hamiltonian determine all higher-order correlations. We also prove that for a many-body Hamiltonian (MBH) the higher-order correlations are not determined by the pair correlations; finally, simulations are presented that illustrate these principles.

Gragg *et al* [23] used simple constraints to show that for a given order of correlation all correlations are determined by one of each of the lower-order correlations and by one of the correlations at the given level. This is a familiar result for the case of PC, where if the concentration and probability of AA pairs is known the probability of BB and AB pairs is easily determined because the sum of probability of an A atom having an A as a particular neighbour and that it has a B at the particular neighbour position is unity. For three-body correlations, the concentration of A atoms, c, and the probability of AA pairs, P_{ij}^{AA}, together with the probability of a triangle, ijk, of all A atoms, P_{ijk}^{AAA}, determines the other probabilities $P_{ijk}^{AAB}, P_{ijk}^{ABB}$ etc; therefore, we can, without loss of generality, consider at each level of correlation exclusively the averages of products of Ising spin variables $\sigma_i = 1$ (-1) for occupation A (B). These averages are related to other familiar descriptions by

$$\sigma = 1/N \sum_{i=1}^{N} \langle \sigma_i \rangle = 2c - 1$$

$$\sigma_j^{(2)} = 1/N \sum_{i=1}^{N} \langle \sigma_i \sigma_{i+j} \rangle = 4(c^2 - c(1-c)\alpha_j) - 2c - 1 \tag{1}$$

$$\sigma_{j,k}^{(3)} = 1/N \sum_{i=1}^{N} \langle \sigma_i \sigma_{i+j} \sigma_{i+k} \rangle = 8P_{jk}^{AAA} - \sigma_j^{(2)} - \sigma_k^{(2)} - \sigma_{j-k}^{(2)} - 3c - 1$$

where α is the Warren Cowley SRO parameter.

The Hamiltonian is assumed to be cluster expanded as follows:

$$H(\{\sigma_n\}) = \sum_i^{N} \Delta V \sigma_i + \sum_i^{N} V_i^{ext} \sigma_i + \frac{1}{2} \sum_{ij}^{N} V_{ij} \sigma_i \sigma_j + \frac{1}{6} \sum_{ijk}^{N} V_{ijk} \sigma_i \sigma_j \sigma_k + \cdots \tag{2}$$

where ΔV is the difference in energy of pure A and B material and can be incorporated into the definition of the chemical potential in the grand canonical ensemble or the definition of the zero of energy in the canonical ensemble. The V_i^{ext} is a possible external site dependent

Table 1. Values of Δ_{jk} and $\sigma_{jk}^{(3)}$ for the PPH.

c	$\sigma_{jk}^{(3)}$	$\frac{d\sigma_{jk}^{(3)}}{dc}$	Δ_{jk}	$\frac{d\Delta_{jk}}{dc}$
0	-1	6	0	0
1/2	0	0	0	0
1	1	6	0	0

potential that will be zero for a homogeneous system but is included as a formal device because derivatives with respect to it generate correlation functions. The pair and three-body potentials are V_{ij} and V_{ijk} respectively.

We use a variable Δ_{jk} to quantify, for a given jk, the difference between the maximum and minimum values $\sigma_{jk}^{(3)}$ can have for a specified set $\{\sigma_j^{(2)}\}$; if $\Delta_{jk} = 0$ then $\sigma_{jk}^{(3)}$ is completely determined. Clapp [24] showed that for PPH in samples with equal concentrations the three-body correlations are completely determined by the pair correlations ($\Delta_{jk} = 0$ at $c = \frac{1}{2}$) because the former are exactly zero. This follows from the symmetry of the energy under simultaneous interchange of all A and B atoms (this only holds at $c = \frac{1}{2}$), the equality of the occupation probability for configurations with equal energy, and the change in sign of the triplet function under the interchange. We augment this result with the trivial observations (valid for all Hamiltonians) that for concentrations of zero (unity) the triplet correlations are exactly -1 (1) and the derivative of the triplet correlation is exactly six at $c = 0$ or 1. It is less trivial to show that $\frac{d\Delta_{jk}}{dc}|_{c=\frac{1}{2}} = 0$. Even though $V_i^{ext} = 0$ in the homogeneous system, the derivative with respect to V_i^{ext} can be used to prove $\frac{d\Delta_{jk}}{dc}|_{c=\frac{1}{2}} = \frac{d\sigma_{jk}^{(3)}}{dc}|_{c=\frac{1}{2}} = 0$. These results apply to ordered and disordered systems at all temperatures; however, some care must be taken when considering the low-temperature limit. Even for nominally ordered systems one should picture a sample that approaches infinite size so that derivatives with respect to concentration are easily defined in terms of anti-site defects. Even at low temperature, where a few ordered structures may dominate the observed configurations, the correlation functions we address are ensemble averages not quantities associated with individual ensemble members.

For the PPH exact properties of Δ_{jk} and $\sigma_{jk}^{(3)}$ are summarized in table 1.

The table indicates that for the PPH the PCs determine the triplet correlations for many concentrations; it would be surprising if Δ_{jk} could be this tightly restricted and yet not be identically zero. These results support the hypothesis that for the PPH the pair correlations determine higher-order correlations. Furthermore, symmetry arguments similar to those of Clapp can be used to prove that for the MBH at $c = 1/2$ PCs do not determine triplet correlations. This is proved starting with a PPH and evaluating the derivatives of the PC and triplet correlation as the three-body potential is turned on. Odd products of spin operators change sign under the A $\leftrightarrow$ B transformation and therefore vanish at $c = 1/2$.

$$\frac{1}{N}\sum_{l}^{N}\frac{d\sigma_j^{(2)}}{dV_{l,l+m,l+n}^{(3)}}\bigg|_{c=\frac{1}{2}} = \frac{1}{N^2}\sum_{i,l}^{N}\langle\sigma_i\sigma_{i+j}\sigma_l\sigma_{l+m}\sigma_{l+n}\rangle|_{c=\frac{1}{2}} = 0$$

$$\frac{1}{N}\sum_{l}^{N}\frac{d\sigma_{jk}^{(3)}}{dV_{l,l+m,l+n}^{(3)}}\bigg|_{c=\frac{1}{2}} = \frac{1}{N^2}\sum_{i,l}^{N}\langle\sigma_i\sigma_{i+j}\sigma_{i+k}\sigma_l\sigma_{l+m}\sigma_{l+n}\rangle|_{c=\frac{1}{2}} \neq 0.$$

(3)

Because the third-order correlation can be changed without affecting the PC, the third-order correlations cannot be functions of the PC.

We now prove the hypothesis that for a given order of Hamiltonian, n, the correlations to order n determine all correlations of order greater than n. For each Hamiltonian and

temperature the equilibrium probability of being in a particular configuration is given by the density matrix

$$\rho = \frac{e^{-\beta(H-\mu)}}{Z}$$
$$Z = \text{Tr}(e^{-\beta(H-\mu)}). \tag{4}$$

The trace above is the classical trace over all configurations. The algebra given here is for the grand canonical ensemble; however, the example simulations presented below are performed in the canonical ensemble. The corresponding algebra for the canonical ensemble may be obtained by setting $\mu = 0$ and taking the trace to be over all configurations at fixed concentration. In general, the density matrix determines all average quantities through

$$\langle o \rangle = \text{Tr}(o\rho). \tag{5}$$

It is clear that all correlation functions are determined by ρ, which in turn is uniquely determined by the Hamiltonian. A more difficult question is whether the Hamiltonian is uniquely determined by the correlation functions; in particular, is the Hamiltonian determined by the PCs? If so, then all higher-order correlations are determined by the PCs because the former are obviously determined by the Hamiltonian. The numerical results of Wolverton *et al* [21] show that the PCs do not, in general, uniquely determine the Hamiltonian. We query whether, if the Hamiltonian is limited to order n, there is more than one choice of potential of order n that gives the same correlations to order n. We extend the work of Evans [22] and Hohenberg [25] by following their approach, that gives a proof based on *reductio ad absurdum*. We assume that there are two Hamiltonians of order n, H and H', that give the same correlation to order n, and show that this assumption cannot be true because it leads to absurd results. The Hamiltonians H and H' have density matrices ρ and ρ' that are different and which, together with H and H', determine the grand potentials Ω and Ω'. As a preliminary step consider

$$\text{Tr}[(\rho - \rho')H] = \sum_i^N \Delta V[\text{Tr}\,\rho\sigma_i - \text{Tr}\,\rho'\sigma_i] + \sum_i^N V_i^{\text{ext}}[\text{Tr}\,\rho\sigma_i - \text{Tr}\,\rho'\sigma_i]$$

$$+ \tfrac{1}{2}\sum_{ij}^N V_{ij}[\text{Tr}\,\rho\sigma_i\sigma_j - \text{Tr}\,\rho'\sigma_i\sigma_j]$$

$$+ \tfrac{1}{6}\sum_{ijk}^N V_{ijk}[\text{Tr}\,\rho\sigma_i\sigma_j\sigma_k - \text{Tr}\,\rho'\sigma_i\sigma_j\sigma_k] + \cdots. \tag{6}$$

Note that the series above is to be terminated at the order of the potential. The statement that the correlations given by ρ and ρ' are the same up to order n can be written

$$\bar{\sigma}_j^2 = \frac{1}{N}\text{Tr}\left(\sum_{i=1}^N \sigma_i\sigma_{i+j}\rho\right) = \frac{1}{N}\text{Tr}\left(\sum_{i=1}^N \sigma_i\sigma_{i+j}\rho'\right),$$

$$\bar{\sigma}_{jk}^3 = \frac{1}{N}\text{Tr}\left(\sum_{i=1}^N \sigma_i\sigma_{i+j}\sigma_{i+k}\rho\right) = \frac{1}{N}\text{Tr}\left(\sum_{i=1}^N \sigma_i\sigma_{i+j}\sigma_{i+k}\rho'\right), \tag{7}$$

$$\cdots,$$

$$\bar{\sigma}_{jk\ldots}^n = \cdots.$$

Therefore, at any order for which the correlations are the same for ρ and ρ', the corresponding term is zero. This applies for either H or H'. The value of Ω' is given by

$$\Omega'[\rho'] = \text{Tr}[\rho'(H' - \mu(N_A - N_B) + \beta^{-1}\ln(\rho'))]. \tag{8}$$

Using equation (6) and the identity $\mathrm{Tr}(\rho - \rho') = 0$, Ω' can be related to Ω by

$$\Omega[\rho] + \mathrm{Tr}[\rho(H' - H)] = \Omega'[\rho'] + \beta^{-1}\,\mathrm{Tr}[\rho \ln \rho - \rho \ln \rho']. \tag{9}$$

The last term is positive definite [26]; therefore,

$$\Omega' < \Omega + \mathrm{Tr}[\rho'(H' - H)]. \tag{10}$$

Exactly the same argument can be made with the primed and unprimed variables interchanged; therefore, interchanging primed and unprimed variables

$$\Omega < \Omega' + \mathrm{Tr}[\rho(H - H')]. \tag{11}$$

Adding the previous two equations we obtain

$$\Omega' + \Omega < \Omega' + \Omega + \mathrm{Tr}[(\rho - \rho')H] + \mathrm{Tr}[(\rho' - \rho)H']. \tag{12}$$

Referring back to the cluster expansion of H in equation (6), we obtain

$$\Omega' + \Omega < \Omega' + \Omega. \tag{13}$$

If, for example, the expansion is terminated at the pair terms and if the concentration is fixed, the traces on the rhs of equation (13) are zero because we have required that ρ and ρ' give the same pair correlation. The resulting inequality cannot be satisfied; hence, our assumption that two separate potentials lead to the same PC cannot be true; therefore, the potential that generates a given PC is unique. This is clearly a generalization of classical density functional theory for a heterogeneous system, which states that if the Hamiltonians can differ only in V_i^{ext} then V_i^{ext} is uniquely determined by the concentration set $\{c_i\}$. Note that the same argument can be made when equation (12) is truncated at higher order. Therefore, our result shows that if a Hamiltonian is truncated at order n then the correlations up to and including order n determine all higher-order correlations.

We have performed numerical simulations, which serve to further illustrate our analytic results. We begin with two distinct Hamiltonians: a pair-only one (PPH), and a pair + many-body Hamiltonian (MBH). These Hamiltonians were then used in equilibrium Monte Carlo simulations (the Hamiltonians and simulation procedure are described in [21]) to generate two sets of equilibrium PCs, $\{\sigma_j^{(2)}\}_{\text{PPH}}$ and $\{\sigma_j^{(2)}\}_{\text{MBH}}$ respectively, as well as many-body correlations, some of which are depicted in figures 1 and 2. We refer to these correlations from Monte Carlo as 'equilibrium' correlations. We next generated configurations with PCs statistically identical to $\{\sigma_j^{(2)}\}_{\text{PPH}}$ and $\{\sigma_j^{(2)}\}_{\text{MBH}}$ respectively by starting from a random configuration and repeatedly introducing pair interchanges until agreement was reached out to 150 atomic shells. We refer to these generated structures as 'constructed'. By construction, 'equilibrium' and 'constructed' values of PCs are equal, so the relevant comparison is between the many-body correlations in the 'equilibrium' and 'constructed' samples. The probability of 'AAA' neighbour triangles is shown for the various cases in figure 1. Results are shown for triangles formed by a central atom, a second atom that is its first nearest neighbour, and a nearest neighbour of the second atom that is either a first, second, third, or fourth neighbour of the central atom. We observe that for the PPH the equilibrium and constructed samples have almost equal P^{AAA}. We determined that they are equal to within the limitations imposed by our sample size (64 000 for the equilibrium structures and 108 000 for the constructed structures). This determination was made by comparison to the spread in values for identical calculations for the case $H = 0$, where for our sample size the relative error in P^{AAA} is also given algebraically to be 1.5%, which corresponds to an error bar of about 0.008 in the plot below. Thus, consistent with our analytical results, for the PPH, we find that PCs effectively constrain the values of many-body correlations.

However, we note further that for the MBH the P^{AAA} of the equilibrium and constructed structure differ appreciably. These differences impact physical properties such as electron
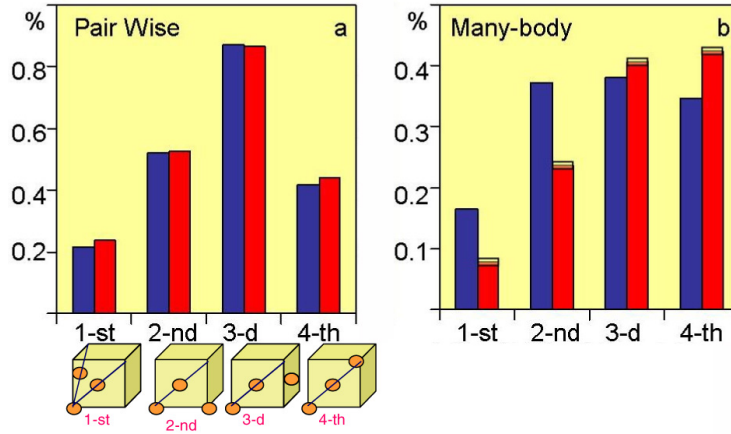
Figure 1. Percentage of triplets that are all A atoms in four different kinds of triplet configurations. Blue—equilibrium lattice, red—constructed lattice with same pair correlation as equilibrium lattice. Kinds of triplets: first, (000), (101), (011); second, (000), (101), (202); third, (000), (101), (200); fourth, (000), (101), (211). For constructed MBH lattice error bars are indicated by empty boxes.
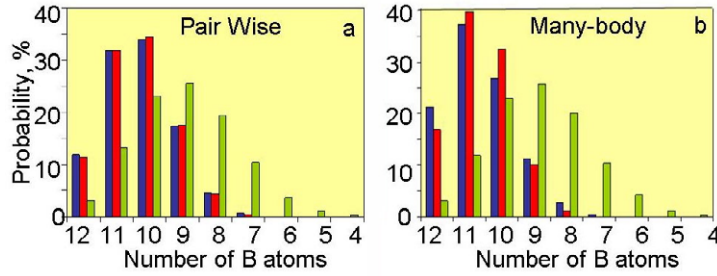
Figure 2. Percentage of A sites with n B atoms as nearest neighbours. Green—random lattice, blue—equilibrium lattice, red—constructed lattice with same pair correlation as equilibrium lattice.

transport which can depend on probability of linear paths of a particular species [30]. We also checked that the differences are statistically significant, i.e. they are much larger than statistical fluctuations in the random case. We further checked the sensitivity of our results to the precision with which the constructed PCs agreed with the equilibrium values. This was done by constructing samples with PCs given by $\{\sigma_j^2\}_{\mathrm{MBH}} + \delta\sigma_i^2$. The resulting $\frac{\mathrm{d}P^{\mathrm{AAA}}}{\mathrm{d}\sigma_i^{(2)}}\Delta\sigma_i^{(2)}$ values were small compared to observed differences in figure 1, indicating that small errors, $\Delta\sigma_j^{(2)}$, in reproduction of the PCs do not affect our conclusion. The difference in three-body correlations shown in figure 2(b) is statistically significant. This supports our analytic results; for the MBH, our numerical results show that PCs do not constrain the values of many-body correlations.

Note that the different constructed samples yield the same higher-order correlations to within a small range, for example indicated by the error bars in figure 1(b). One might assume that because the three-body correlation is not determined by the PC the values of the three-body correlation would vary greatly depending on the random initial configuration used in the construction process. This is not the case because the construction process is itself dependent on albeit an artificial many-body Hamiltonian based on the sum of the squares of the difference

between the sample PC and the target equilibrium values. In fact, the Monte Carlo simulated annealing method is used to obtain the constructed samples. In general, equilibrium correlation functions are determined by their underlying Hamiltonian, so, even the artificial Hamiltonian used in the construction process to constrain the PCs is expected to give specific values for the three-body correlations, as are shown in figures 1(b) and 2(b). This is also the reason for the reproducibility of the Rietveld refinement process.

In figure 2 the distribution of first nearest neighbours is shown. This is, in a sense, a less fundamental set of quantities than the probability of triangles, in that the distribution is composed of sums over 13-body correlations having the same numbers of B atoms. However, the number and distribution of nearest neighbours is so fundamental to descriptions of materials behaviour that it warrants detailed consideration. For the PPH the equilibrium and constructed samples have 'identical' distributions while for the MBH the differences are significant. This result cautions of the dangers of using higher-order correlations obtained from fitting measured PCs without auxiliary information indicating that the Hamiltonian is well approximated by a pair potential model (which is rarely the case, for real physical systems). It is often possible to judge the size of the many-body terms in the Hamiltonian by observing the concentration dependence of the pair potentials obtained from reverse Monte Carlo.

The analysis above emphasized the connection between higher-order correlation and the response of lower-order correlation to external fields and to the fluctuations of lower-order correlations. If external fields could be controlled at the atomic scale it would be straightforward to determine higher-order correlations by measuring the PC in the presence of the appropriate external field. Typical fields such magnetic and stress fields have a global effect. They change the difference in the average chemical potential of the species and the higher-order potentials. The change in chemical potential can be measured at equilibrium by thermodynamic methods. The derivative of the PC with respect to chemical potential difference is related to a sum over the three-body correlation:

$$\frac{\mathrm{d}\sigma_j^{(2)}}{\mathrm{d}\mu} = \sum_{k=1}^{N} \sigma_{j,k}^{(3)}.$$

(14)

Unfortunately, the sum on the right-hand side is simply related to the PC (see equation (1)); therefore, changes in the chemical potential do provide new information about three-body correlations. Changes in the higher-order interactions do give new information but usually require knowledge of the relationship between the interactions and the applied field. These relationships can be determined from first-principles calculations or from measurements with some caveats. The change in ordering temperature with strain could indicate the dependence of near-neighbour interactions on strain.

In the case of magnetic alloys, models for the local moment depend on the number of magnetic neighbours [31, 32]. For example, in $Ni_{0.75}Cu_{0.25}$ the difference between the equilibrium and constructed first-nearest-neighbour distributions shown in figure 2 would result in saturation moments that differed by 10%. The combination of first-principles modelling of the moment, measurement of the saturation magnetization, and measurement of the PC both in a high magnetic field and with no field are likely to reveal the many-body correlations seen in figure 2.

Alternatively, if the PC could be measured in regions small enough that the change from one region to another was observable, then the higher-order information could be ascertained from the fluctuations. Extraction of higher order correlations via the application of fields assumes that the system is in thermal equilibrium and hence would have to be done *in situ* at a temperature where equilibrium could be achieved in reasonable times. More commonly, experiments are done at room temperature on samples that have been rapidly quenched so as
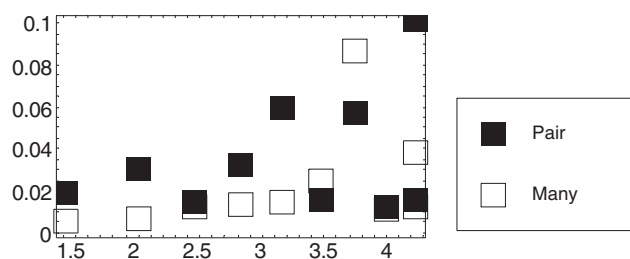
Figure 3. The fluctuations in alpha calculated from our small set of PPH and MBH structures.

to maintain the SRO resembling that of the temperature just prior to the quench. In *in situ* experiments at high T fluctuations in either space or time could be analysed. In the case of quenched samples spatial fluctuations in PC are 'frozen in' and only the spatial fluctuations can possibly be observed. Although spatial fluctuations will be present and they do contain information about higher-order correlation they will be difficult to observe because the signal from several very small volumes will have to be compared. To illustrate this point we compare in figure 3 the fluctuations in alpha calculated from our small set of PPH and MBH structures. It is encouraging that the fluctuations are significantly different in the two cases.

These fluctuations provide constraints on the four-body correlations because they describe the probability of, for example, an AA pair being located in a particular relationship to another AA pair. The four-body correlations impact the three-body correlations through constraints as described by Gragg *et al* [23]. More direct information about three-body correlations is related to fluctuations in the product of the concentration and alpha. Our samples are only 64 000 atoms and this is not sufficiently many atoms to provide the needed scattering intensity. By straining, and/or bending, thin samples below the elastic limit the intensity from small thicknesses will be scattered into different angles. Such a procedure allows the full x-ray flux to be used. If the intensity of the unstrained sample is subtracted from the intensity of the strained sample suitably transformed to account for the affine strain the difference will be zero when there are no fluctuations in the PC. This is a challenging approach for directly obtaining information about higher order correlations.

An alternative approach requires additional assumptions but may be more fruitful in the short run. It is based on the fact that the lattice is strained differently at the atomic level depending on the local configuration. The richest source of this information is the displacement SRO which has been measured in [27–29]. The local displacements clearly reflect the higher-order correlations but a model relating them is needed in order to extract information about the correlation from the displacements. Models can be based on measurements of elastic constants as a function of concentrations and SRO (different SRO can be induced by quenching from different temperatures) or they can be based on first principles calculations.

In summary, we have performed simulations of realistic PPH (MBH) systems for which the higher-order correlations are (are not) determined by the PCs. Classical density functional theory was used to prove the general result that for Hamiltonians cluster expanded to order n the correlations of order n determine all higher-order correlations. It was also proved that for the MBH in at least one set of circumstances the PCs do not determine the higher-order correlations. Our simulated results for a realistic MBH indicate that significant errors in higher-order correlations can result from assuming that they are determined by PCs. Equations (3) indicate that at $c = 1/2$ increasing the triplet potential can increase triplet correlation without a concomitant change in the PC and therefore lead us to doubt that PC restricts triplet correlation

significantly. These results call into question inferences about higher-order correlations based purely on PC.

Commonly used procedures such as Rietveld which construct configurations that fit measured PCs and provide higher-order correlations based on the constructed configurations should be modified to incorporate the constraint of particular higher-order correlation. The range of possible values of the particular higher-order correlation could be determined based on the existence of a solution to the fitting problem to within a prescribed tolerance. Research efforts should move on to analysis of higher-order reflections and simultaneous application of external forces that can provide derivatives of the PCs and hence information about higher-order correlations.

Acknowledgments

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