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Peter Palffy-Muhoray, *Kent State University - Kent Campus*



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# The single particle potential in mean-field theory

Peter Palffy-Muhoray<sup>a)</sup>

Liquid Crystal Institute, Kent State University, Kent, Ohio 44242

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The problem of determining the single particle energy in a mean-field description of interacting particles is considered. It is shown that the single particle energy must satisfy two consistency conditions, and a general procedure for obtaining the single particle energy from the pair energy is proposed. Interacting dipolar systems are examined, current approaches in the literature are discussed, and the usefulness of the proposed method is demonstrated. © 2002 American Association of Physics Teachers.

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## I. INTRODUCTION

Statistical mechanics provides beautiful and effective tools for describing the behavior of condensed matter systems. One approach to describing systems in equilibrium is to evaluate the partition function, then the free energy, and finally obtain the quantities of interest from the free energy. For systems of interacting particles, it is usually not possible to evaluate the partition function exactly. One popular approximation is mean-field theory. In mean-field theory, the energy of a system is approximated by the sum of identical single particle energies that describe the interactions of each particle with an effective mean field. In order for mean-field theory to provide a satisfactory description, the single particle potential must accurately describe not only the average energy of the particle, but also the forces and torques acting on it. This requirement is a subtle and interesting point that is not usually described in textbooks. We show that the single particle energy must satisfy two consistency conditions that encompass these two requirements. We then propose a general procedure for constructing a consistent single particle energy from the energy of two particles. Finally, by way of illustration, we consider the mean-field description of interacting systems of dipoles.

## II. THE SINGLE PARTICLE ENERGY IN THE MEAN-FIELD APPROXIMATION

In the standard statistical mechanical description,<sup>1-4</sup> consideration of the canonical ensemble leads to the result that the probability that a system in equilibrium at temperature  $T$  is in state  $r$  is given by

$$\mathcal{P}_r = \frac{e^{-\beta\mathcal{E}_r}}{Z}, \quad (1)$$

where  $\mathcal{E}_r$  is the total energy of the system in state  $r$ ,  $T$  is the absolute temperature,  $k$  is Boltzmann's constant, and  $\beta = 1/kT$ . The partition function  $Z$  is defined as

$$Z = \sum_r e^{-\beta\mathcal{E}_r}, \quad (2)$$

where the sum is over all accessible states  $r$ . The mean energy of the system is

$$\langle \mathcal{E} \rangle = \sum_r \mathcal{E}_r \mathcal{P}_r = - \frac{\partial}{\partial (1/kT)} \ln Z, \quad (3)$$

and the entropy is

$$S = \frac{\langle \mathcal{E} \rangle}{T} + k \ln Z. \quad (4)$$

The Helmholtz free energy is

$$F = \langle \mathcal{E} \rangle - TS = -kT \ln Z, \quad (5)$$

which can be evaluated at once if the partition function is known.

It is interesting to ask about the free energy in the presence of constraints. A typical constraint is the requirement that an order parameter of the system, say the magnitude  $M$  of the magnetization, has some specific value. The probability that this constraint is obeyed is simply the sum of the probabilities of the states  $r'$  that are compatible with the constraint, that is,

$$\mathcal{P}(M) = \frac{\sum_{r'} e^{-\beta\mathcal{E}_{r'}}}{Z} = \frac{Z_{\text{trial}}}{Z}. \quad (6)$$

The sum in the numerator is the trial partition function and is over the states that are compatible with the constraint; the corresponding trial free energy is

$$F(M) = -kT \ln Z_{\text{trial}}. \quad (7)$$

Because

$$\mathcal{P}(M) = \frac{e^{-\beta F(M)}}{Z}, \quad (8)$$

the most probable value of the order parameter is that which minimizes the trial free energy.

The essence of mean-field theory is to approximate the partition function of a system of  $N$  identical particles by the product of single particle partition functions, that is,

$$Z = \sum_r e^{-\beta\mathcal{E}_r} \approx \frac{1}{N!} \left( \sum_s e^{-\beta\epsilon_s} \right)^N = \frac{1}{N!} z^N. \quad (9)$$

Here  $\epsilon_s$  is the energy of a single particle in state  $s$ , interacting with an effective mean field that represents the effects of all the other particles. The mean field may be the magnetization or some other order parameter of the system;  $\epsilon_s$  is then a function of the order parameter. The mean-field assumption amounts to replacing the total energy  $\mathcal{E}_r$  of the system by the sum of single particle energies  $\epsilon_s$ . The factor  $N!$  ensures invariance under the interchange of indistinguishable particles;  $z$  is the single particle partition function. Us-

ing Stirling's approximation, the mean-field free energy becomes

$$F \simeq -NkT \ln \frac{1}{N} \sum_s e^{-\beta \epsilon_s}. \quad (10)$$

Because  $\epsilon_s$  depends on the effective mean field,  $F$  is the free energy of a system with a specified mean-field or order parameter; that is,  $F$  is a trial free energy.

We next consider the consistency requirements on the single particle energy. If we use the mean-field approximation to the partition function in Eq. (9) to evaluate the average energy of the system, we obtain

$$\langle \mathcal{E} \rangle = -\frac{\partial}{\partial \beta} \ln Z \simeq N \frac{\sum_s \epsilon_s e^{-\beta \epsilon_s}}{\sum_s e^{-\beta \epsilon_s}} = N \langle \epsilon_s \rangle. \quad (11)$$

By minimizing the mean-field trial free energy in Eq. (10) with respect to the order parameter, we obtain

$$\frac{\partial F}{\partial M} = 0 = N \frac{\sum_s (\partial \epsilon_s / \partial M) e^{-\beta \epsilon_s}}{\sum_s e^{-\beta \epsilon_s}} = N \left\langle \frac{\partial \epsilon_s}{\partial M} \right\rangle. \quad (12)$$

Consistency requires that the single particle energy satisfy

$$\langle \epsilon_s \rangle = \frac{\langle \mathcal{E} \rangle}{N}, \quad (13)$$

and

$$\left\langle \frac{\partial \epsilon_s}{\partial M} \right\rangle = 0. \quad (14)$$

The requirement in Eq. (13) is well known and obvious; the second requirement is less well known and more subtle.

We now consider a general method of constructing the single particle energy  $\epsilon_s$ . First, we note that the probability that a single particle is in state  $s$  is

$$\mathcal{P}_s = \frac{e^{-\beta \epsilon_s}}{z}. \quad (15)$$

The total energy  $\mathcal{H}_{12}$  of particles 1 and 2 includes the kinetic energy as well as the potential energy of interaction between the particles, and depends on the single particle states. We now construct

$$\epsilon_{s_1} = \sum_{j=2}^N \sum_{s_j} \mathcal{H}_{1j} \mathcal{P}_{s_j} - \frac{1}{2} \sum_{j=2}^N \sum_{s_1} \sum_{s_j} \mathcal{H}_{1j} \mathcal{P}_{s_1} \mathcal{P}_{s_j}, \quad (16)$$

where the sums are over the particles, identified by the index  $j$ , and single particle states  $s_1$  of particle 1 and  $s_j$  of particle  $j$ . The first term on the right-hand side of Eq. (16) may be thought of as the effective Hamiltonian of particle 1, which ascribes to particle 1 the energy of every pair involving particle 1 and from which the correct forces and torques can be obtained, while the second term is a constant that corrects for the overcounting of the energy by the first term. We now look at the consistency conditions. For the first of these, Eq. (16) gives

$$\begin{aligned} \langle \epsilon_{s_1} \rangle &= \sum_{s_1} \epsilon_{s_1} \mathcal{P}_{s_1} = \frac{1}{2} \sum_{j=2}^N \sum_{s_1} \sum_{s_j} \mathcal{H}_{1j} \mathcal{P}_{s_1} \mathcal{P}_{s_j} \\ &= \frac{1}{2} (N-1) \langle \mathcal{H}_{1j} \rangle = \frac{\langle \mathcal{E} \rangle}{N}, \end{aligned} \quad (17)$$

and so the first requirement is satisfied. In considering the second condition, we note that  $\epsilon_s$  is a function of the order parameter, but the pair energy  $\mathcal{H}_{1j}$  is not. If we take the derivative of  $\epsilon_{s_1}$  in Eq. (16) with respect to the order parameter, we find

$$\begin{aligned} \frac{\partial \epsilon_{s_1}}{\partial M} &= \sum_{j=2}^N \sum_{s_j} \mathcal{H}_{1j} \frac{\partial \mathcal{P}_{s_j}}{\partial \epsilon_{s_j}} \frac{\partial \epsilon_{s_j}}{\partial M} \\ &\quad - \frac{1}{2} \sum_{j=2}^N \sum_{s_1} \sum_{s_j} \mathcal{H}_{1j} \left[ \frac{\partial \mathcal{P}_{s_1}}{\partial \epsilon_{s_1}} \frac{\partial \epsilon_{s_1}}{\partial M} \mathcal{P}_{s_j} \right. \\ &\quad \left. + \frac{\partial \mathcal{P}_{s_j}}{\partial \epsilon_{s_j}} \frac{\partial \epsilon_{s_j}}{\partial M} \mathcal{P}_{s_1} \right], \end{aligned} \quad (18)$$

which, due to symmetry, can be written as

$$\begin{aligned} \frac{\partial \epsilon_{s_1}}{\partial M} &= \sum_{j=2}^N \sum_{s_j} \mathcal{H}_{1j} \frac{\partial \mathcal{P}_{s_j}}{\partial \epsilon_{s_j}} \frac{\partial \epsilon_{s_j}}{\partial M} \\ &\quad - \sum_{j=2}^N \sum_{s_1} \sum_{s_j} \mathcal{H}_{1j} \frac{\partial \mathcal{P}_{s_j}}{\partial \epsilon_{s_j}} \frac{\partial \epsilon_{s_j}}{\partial M} \mathcal{P}_{s_1}. \end{aligned} \quad (19)$$

By taking the average, we obtain

$$\sum_{s_1} \frac{\partial \epsilon_{s_1}}{\partial M} \mathcal{P}_{s_1} = 0, \quad (20)$$

and so the second requirement is satisfied.

Our general strategy for constructing the single particle potential from the pair energy,  $\mathcal{H}_{12}$ , is to form the quantity

$$\tilde{\epsilon}_{s_1} = \sum_{j=2}^N \sum_{s_2} \mathcal{H}_{1j} \mathcal{P}_{s_j}, \quad (21)$$

and its average

$$\langle \tilde{\epsilon}_{s_1} \rangle = \sum_{s_1} \tilde{\epsilon}_{s_1} \mathcal{P}_{s_1} = \sum_{j=2}^N \sum_{s_1} \sum_{s_j} \mathcal{H}_{1j} \mathcal{P}_{s_1} \mathcal{P}_{s_j}, \quad (22)$$

and construct the single particle energy  $\epsilon_{s_1}$  of Eq. (16) as

$$\epsilon_{s_1} = \tilde{\epsilon}_{s_1} - \frac{1}{2} \langle \tilde{\epsilon}_{s_1} \rangle. \quad (23)$$

It is useful to consider the role of the two terms in Eq. (23). The first term on the right-hand side, the sum of the pair energies of all pairs of particles involving particle 1, depends on the state of particle 1. Because this term contains the interaction energy of particle 1 with all the other particles in the system (assuming pairwise interactions), this term will contain the correct effective potential, and therefore give the correct forces and torques. The first term by itself overcounts the energy, because it is the sum of  $(N-1)$  pair energies; the second term, which does not contribute to forces and torques, corrects this overcounting and ensures that the average total energy is the correct value, one-half of the sum of  $(N-1)$  pair energies. We will show in the examples that using  $\epsilon_{s_1}$  as the single particle energy gives the expected correct results.

In many systems, the sum over momentum states can be carried out separately. In such systems, the above arguments hold if the energies refer to the potential energy only. The momentum contribution is a multiplicative term in the parti-

tion function and an additive term in the free energy; neither of these terms depends on the order parameter.

In the literature, the quantity  $\bar{\epsilon}_s$  is often used as the single particle energy instead of  $\epsilon_{s_1}$ . Although the latter gives the correct value for the single particle probability distribution, it does not give the correct free energy. Because it does not satisfy the consistency conditions, its use is not well justified and can be confusing.

We now consider specific examples of systems of interacting dipoles and examine the single particle energy.

### III. MEAN-FIELD THEORY OF DIPOLAR SYSTEMS

Although the study of dipolar systems has inherent difficulties associated with the long-range nature of dipolar forces, we consider such systems because the basic interactions are well established and familiar.

We first develop a mean-field description of a uniformly polarized ferroelectric system and consider a system of identical molecules on a lattice with permanent electric point dipoles. We also assume that there are no external fields. The interaction energy of the pair of dipoles  $\mathbf{p}_1$  and  $\mathbf{p}_2$  is given by

$$\mathcal{H}_{12} = -\frac{1}{4\pi\epsilon_0} \frac{3(\hat{\mathbf{r}}_{12} \cdot \mathbf{p}_1)(\hat{\mathbf{r}}_{12} \cdot \mathbf{p}_2) - \mathbf{p}_1 \cdot \mathbf{p}_2}{r_{12}^3}, \quad (24)$$

where  $\mathbf{r}_{12}$  is the intermolecular vector. The potential energy of molecule 1 due to its interactions with all other molecules in the system is

$$\sum_{j=2}^N \mathcal{H}_{1j} = -\mathbf{p}_1 \cdot \sum_{j=2}^N \frac{3(\hat{\mathbf{r}}_{1j} \cdot \mathbf{p}_j)\hat{\mathbf{r}}_{1j} - \mathbf{p}_j}{4\pi\epsilon_0 r_{1j}^3}. \quad (25)$$

As in Eq. (21), in the mean-field approximation, we average over the orientations of molecule  $j$ , and hence replace  $\mathbf{p}_j$  by its average,  $\langle \mathbf{p} \rangle$ , in the sum. This average gives

$$\bar{\epsilon}_1 = -\mathbf{p}_1 \cdot \sum_j \frac{3(\hat{\mathbf{r}}_{1j} \cdot \langle \mathbf{p} \rangle)\hat{\mathbf{r}}_{1j} - \langle \mathbf{p} \rangle}{4\pi\epsilon_0 r_{1j}^3} = -\mathbf{p}_1 \cdot \mathbf{E}_{\text{loc}}. \quad (26)$$

The dipole sum is the local electric field acting at the site of molecule 1, due to all the identical dipoles  $\langle \mathbf{p} \rangle$  at the other lattice sites. This sum vanishes for an infinite cubic lattice or for a spherically symmetric distribution. We note that for uniform polarization in a sphere, the Maxwell field is  $-\mathbf{P}/3\epsilon_0$ , where  $\mathbf{P}$  is the polarization, but the local electric field vanishes at the center.

We assume that the dipole distribution is not spherically symmetric and that translational invariance can be ignored. In this case, the local field has the form

$$\mathbf{E}_{\text{loc}} = \sum_j \frac{3(\hat{\mathbf{r}}_{1j} \cdot \langle \mathbf{p} \rangle)\hat{\mathbf{r}}_{1j} - \langle \mathbf{p} \rangle}{4\pi\epsilon_0 r_{1j}^3} \approx \frac{a}{4\pi\epsilon_0} \rho \langle \mathbf{p} \rangle = \frac{a}{4\pi\epsilon_0} \mathbf{P}, \quad (27)$$

where  $a$  is a dimensionless factor arising from the lattice structure and sample shape, and  $\rho$  is the number density. The interaction energy of molecule 1 with the other molecules in the system is

$$\bar{\epsilon}_1 = -\mathbf{p}_1 \cdot \mathbf{E}_{\text{loc}} \approx -\frac{a}{4\pi\epsilon_0} \mathbf{p}_1 \cdot \mathbf{P}. \quad (28)$$

It is convenient to write

$$\bar{\epsilon}_1 = -b\rho\mathbf{p}_1 \cdot \mathbf{P},$$

where  $b = a/(4\pi\epsilon_0\rho)$ . Because the dipoles have equal magnitudes  $p$ , we write

$$\bar{\epsilon}_1 = -b\rho p P \cos \theta, \quad (29)$$

where  $\theta$  is the angle between  $\mathbf{p}_1$  and  $\mathbf{P}$ .

It is tempting to regard  $\bar{\epsilon}_1$  as the single particle potential. It correctly describes the torque acting on molecule 1 due to the other molecules. However, it does *not* satisfy the consistency requirements of Eqs. (13) and (14). First, because  $\bar{\epsilon}_1$  is the sum of the energies of the pairs of molecules involving molecule 1,

$$N\langle \bar{\epsilon}_1 \rangle \neq \bar{\epsilon}, \quad (30)$$

and, in fact,  $N\langle \bar{\epsilon}_1 \rangle$  overcounts the mean energy by a factor of 2. Next, we note that in the ordered phase where  $P \neq 0$ , the requirement of Eq. (14) is violated; instead we have

$$\left\langle \frac{\partial \bar{\epsilon}_1}{\partial P} \right\rangle = -b\rho p \langle \cos \theta \rangle = -bP \neq 0. \quad (31)$$

Because  $\bar{\epsilon}_1$  does not satisfy the consistency requirements, it is not suitable as the single particle potential. The appropriate single particle potential is

$$\epsilon_s = \bar{\epsilon}_1 - \frac{1}{2}\langle \bar{\epsilon}_1 \rangle, \quad (32)$$

which is, explicitly,

$$\epsilon_s = -b\rho\mathbf{p}_1 \cdot \mathbf{P} + \frac{1}{2}b\rho\langle \mathbf{p}_1 \rangle \cdot \mathbf{P} = -b\rho p P \cos \theta + \frac{1}{2}bP^2. \quad (33)$$

We note that  $\epsilon_s$  gives the correct torque, the same as given by  $\bar{\epsilon}_1$ , on particle 1. Furthermore,  $\epsilon_s$  satisfies both consistency requirements:

$$N\langle \epsilon_s \rangle = \frac{1}{2}N\langle \bar{\epsilon}_1 \rangle = \langle \mathcal{E} \rangle, \quad (34)$$

and

$$\left\langle \frac{\partial \epsilon_s}{\partial P} \right\rangle = -b\rho p \langle \cos \theta \rangle + bP = 0. \quad (35)$$

From the single particle potential  $\epsilon_s$ , we can construct the single particle configurational partition function

$$z = \sum_s e^{-\beta\epsilon_s} \approx \int e^{-\beta\epsilon_s} d\Omega, \quad (36)$$

where  $d\Omega$  is the element of solid angle. The free energy is

$$F = -NkT \ln \frac{1}{N} \int e^{-\beta\epsilon_s} d\Omega, \quad (37)$$

or, explicitly,

$$\begin{aligned} F &= \frac{1}{2}NbP^2 - NkT \ln \frac{2\pi}{N} \int_{-1}^1 e^{\beta b\rho p P \cos \theta} d(\cos \theta) \\ &= \frac{1}{2}NbP^2 - NkT \left[ \ln \frac{kT}{b\rho p P} \sinh(\beta b\rho p P) + \ln \frac{4\pi}{N} \right]. \end{aligned} \quad (38)$$

If we minimize the free energy with respect to the order parameter  $P$ , we obtain the self-consistent equation

$$P = \rho p \frac{\int_{-1}^1 \cos \theta e^{\beta b\rho p P \cos \theta} d(\cos \theta)}{\int_{-1}^1 e^{\beta b\rho p P \cos \theta} d(\cos \theta)} = \rho p L(\beta b\rho p P), \quad (39)$$

where  $L(x) = \coth(x) - 1/x$  is the Langevin function. If we expand the free energy as a Taylor series in the polarization, we obtain the Devonshire expression<sup>5</sup>

$$F = \frac{1}{2}A_0\left(\frac{T}{T_c} - 1\right)P^2 + \frac{1}{4}BP^4 + \dots \quad (40)$$

Here  $A_0 = N((b\rho p)^2/3kT)$ ,  $T_c = b\rho^2 p^2/3k$ , and  $B = N((b\rho p)^4/45(kT)^3)$ .

We emphasize that although it is tempting to interpret the quantity  $\tilde{\epsilon}_1$  as the single particle potential, this use is not justified, because  $\tilde{\epsilon}_1$  does not satisfy the required consistency conditions. Interestingly, using  $\tilde{\epsilon}_1$  in the Boltzmann factor does give the correct probability distribution

$$P_s = \frac{e^{-\beta\epsilon_s}}{\sum_s e^{-\beta\epsilon_s}} = \frac{e^{-\beta(\tilde{\epsilon}_1 - (1/2)\langle\tilde{\epsilon}_1\rangle)}}{\sum_s e^{-\beta(\tilde{\epsilon}_1 - (1/2)\langle\tilde{\epsilon}_1\rangle)}} = \frac{e^{-\beta\tilde{\epsilon}_1}}{\sum_s e^{-\beta\tilde{\epsilon}_1}}, \quad (41)$$

because  $\langle\tilde{\epsilon}_1\rangle$  is a constant, independent of  $s$ . However, using  $\tilde{\epsilon}_1$  as the single particle potential does not give the correct expression for the partition function in Eq. (9) or the free energy in Eq. (10).

The argument for magnetic systems is similar. The energy of a single magnetic moment due to its interaction with its neighbors is

$$\tilde{\epsilon}_1 = -\mathbf{m}_1 \cdot \mathbf{B}_{\text{loc}} = -\frac{a\mu_0}{4\pi}\mathbf{m}_1 \cdot \mathbf{M} = -b\rho\mathbf{m}_1 \cdot \mathbf{M}, \quad (42)$$

where the magnetization may be interpreted as the Weiss molecular field.

The single particle potential is

$$\epsilon_s = \tilde{\epsilon}_1 - \frac{1}{2}\langle\tilde{\epsilon}_1\rangle = -b\rho\mathbf{m}_1 \cdot \mathbf{M} + \frac{1}{2}bM^2, \quad (43)$$

with the corresponding free energy

$$F = \frac{1}{2}NbM^2 - NkT \ln \sum_{\mathbf{m}_1} e^{\beta b\rho\mathbf{m}_1 \cdot \mathbf{M}}. \quad (44)$$

By minimizing the free energy with respect to the order parameter, we obtain

$$M = \rho m \frac{\sum_{\mathbf{m}_1} \hat{\mathbf{m}}_1 \cdot \hat{\mathbf{M}} e^{\beta b\rho\mathbf{m}_1 \cdot \mathbf{M}}}{\sum_{\mathbf{m}_1} e^{\beta b\rho\mathbf{m}_1 \cdot \mathbf{M}}}. \quad (45)$$

If the projection of the magnetic moment on the field direction can only take on two discrete values, then  $\hat{\mathbf{m}}_1 \cdot \hat{\mathbf{M}} = \pm 1$ , and

$$M = \rho m \tanh(\beta b\rho m M). \quad (46)$$

If the projection can take on  $2J+1$  discrete values, then  $\hat{\mathbf{m}}_1 \cdot \hat{\mathbf{M}} = -1, \dots, -1/J, 0, 1/J, \dots, 1$ , and

$$M = \rho m B_J(\beta b\rho m M), \quad (47)$$

where  $B_J(x) = (1/J) [(J + \frac{1}{2})\coth(x(J + \frac{1}{2})) - \frac{1}{2}\coth(x\frac{1}{2})]$  is the Brillouin function.

If the projection can take on continuous values, then  $\hat{\mathbf{m}}_1 \cdot \hat{\mathbf{M}} = \cos \theta$ , and

$$M = \rho m L(\beta b\rho m M). \quad (48)$$

In the literature, the quantity (in our notation)

$$\tilde{\epsilon}_1 = -b\rho \mathbf{m}_1 \cdot \mathbf{M} \quad (49)$$

is often regarded as the single particle potential. For example, in Ref. 2, we read on p. 430, “The interactions of this atom are described by the Hamiltonian ...”

$$\mathcal{H}_j = -g\mu_0 S_{jz} H_m = -2JS_{jz} \left\langle \sum_{k=1}^n S_{kz} \right\rangle. \quad (50)$$

Other authors<sup>1,3</sup> simply evaluate the expectation value of the magnetization, as in Eq. (45), as

$$\langle\mu_i\rangle = \frac{\text{Tr} \mu_i e^{\beta\mu_i\langle H_i\rangle}}{\text{Tr} e^{\beta\mu_i\langle H_i\rangle}}, \quad (51)$$

without much discussion of the significance of the quantity  $-\mu_i\langle H_i\rangle$  and the justification for its use as the single particle energy in the Boltzmann factor. Reference 3 is particularly opaque on this subject. The author writes that “The energy is then formed from  $-\mu_i\langle H_i\rangle$ ,” and cautions that “due care must be taken to introduce the factor 1/2 in the spin-spin interaction in order to avoid counting each interaction twice.” In much of the literature<sup>6-16</sup> the approach of Weiss is followed. That is, to describe the energy of a single spin in the interacting system, the external magnetic field in the result for noninteracting particles is simply replaced by the Weiss field. Although this approach gives the correct probability distribution and average magnetization, it is not consistent and does not give the correct free energy.

In the literature of the mean-field theory of nematic liquid crystals, where the anisotropic part of the interaction is taken to be the anisotropic van der Waals interaction,<sup>17</sup> the quantity

$$\tilde{\epsilon}_1 = -\epsilon\langle P_2\rangle P_2(\cos \theta) \quad (52)$$

is often taken to be the single particle potential, where  $P_2$  is the second Legendre polynomial and  $\langle P_2\rangle$  is the orientational order parameter.<sup>18,19</sup> It has been shown,<sup>20</sup> as we have argued here, that the appropriate form for the single particle potential is

$$\epsilon_r = \tilde{\epsilon}_1 - \frac{1}{2}\langle\tilde{\epsilon}_1\rangle = -\epsilon\langle P_2\rangle P_2(\cos \theta) + \frac{1}{2}\epsilon\langle P_2\rangle^2. \quad (53)$$

If we substitute Eq. (53) into Eq. (10), we find the free energy

$$F = N \frac{1}{2} \epsilon \langle P_2 \rangle^2 - NkT \ln \int_{-1}^{+1} e^{\beta\epsilon\langle P_2 \rangle P_2(\cos \theta)} d(\cos \theta), \quad (54)$$

whose minimization with respect to  $\langle P_2 \rangle$  gives the usual self-consistent equation<sup>21</sup> for the order parameter.

#### IV. CONCLUSION

We have argued that in the mean-field theory of interacting particle systems, the single particle energy must satisfy two consistency requirements. The first is that the average single particle energy must equal the mean energy per particle. The second is that the average derivative of the single particle energy with respect to the order parameter must vanish.

A quantity, often considered in the literature of dipolar systems, is the sum of the pair energies involving a given molecule, averaged over the states its neighbors. We showed that this quantity, defined in Eq. (21) and which we call  $\tilde{\epsilon}_1$ , is not suitable as the single particle energy. Although it gives the correct single particle probability distribution, it does not satisfy the consistency requirements and does not give the correct partition function or free energy. We have shown that

the appropriate single particle energy  $\epsilon_s$  that satisfies the two consistency requirements and gives the correct partition function and free energy is

$$\epsilon_s = \bar{\epsilon}_1 - \frac{1}{2} \langle \bar{\epsilon}_1 \rangle. \quad (55)$$

The first term, consisting of the sum of effective pair energies, provides the correct effective potential and hence the correct forces and torques acting on the particle, while the second corrects for the overcounting of the mean energy by the first term. We have shown the usefulness of this approach in calculating the free energy in the mean-field description of ferroelectricity, ferromagnetism, and nematic liquid crystals.

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<sup>a)</sup>Electronic mail: mpalfy@cpip.kent.edu

<sup>1</sup>M. Plischke and B. Bergersen, *Equilibrium Statistical Physics* (World Scientific, Singapore, 1994).

<sup>2</sup>F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, New York, 1965).

<sup>3</sup>R. Brout, *Phase Transitions* (Benjamin, New York, 1965).

<sup>4</sup>E. S. R. Gopal, *Statistical Mechanics and Properties of Matter* (Halsted, New York, 1974).

<sup>5</sup>A. F. Devonshire, "Theory of ferroelectrics," *Adv. Phys.* **3**, 85–130 (1954).

<sup>6</sup>C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1996).

<sup>7</sup>H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Clarendon, Oxford, 1971).

<sup>8</sup>A. Sommerfeld, *Thermodynamics and Statistical Mechanics* (Academic, New York, 1964).

<sup>9</sup>D. Tabor, *Gases, Liquids and Solids and Other States of Matter* (Cambridge U.P., Cambridge, 1979).

<sup>10</sup>R. Baierlein, *Atoms and Information Theory* (Freeman, San Francisco, 1971).

<sup>11</sup>S.-K. Ma, *Modern Theory of Critical Phenomena* (Benjamin, Reading, MA, 1976).

<sup>12</sup>N. Goldenfeld, *Lectures on Phase Transitions and the Renormalization Group* (Addison-Wesley, Reading, MA, 1992).

<sup>13</sup>L. P. Kadanoff, *Statistical Physics* (World Scientific, Singapore, 1999).

<sup>14</sup>J. M. Yeomans, *Statistical Mechanics of Phase Transitions* (Clarendon, Oxford, 1992).

<sup>15</sup>D. L. Goodstein, *States of Matter* (Dover, New York, 1975).

<sup>16</sup>R. Feynman, R. B. Leighton, and M. Sands, *The Feynman Lectures on Physics, Vol. II* (Addison-Wesley, Reading, MA, 1964).

<sup>17</sup>W. Maier and A. Saupe, "Eine einfache molekular-statistische theorie der nematischen kristallinflussigen phase. Teil I," *Z. Naturforsch. A* **14A**, 882–889 (1959); "Eine einfache molekular-statistische theorie der nematischen kristallinflussigen phase. Teil II," *ibid.* **15A**, 287–292 (1960).

<sup>18</sup>G. R. Luckhurst, "Molecular field theories of mematics," in *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic, London, 1979).

<sup>19</sup>S. Chandrasekhar, *Liquid Crystals* (Cambridge U.P., Cambridge, 1977).

<sup>20</sup>P. Palfy-Muhoray, D. A. Dunmur, W. H. Miller, and D. A. Balzarini, "Orientational order in binary mixtures of nematic liquid crystals," in *Liquid Crystals and Ordered Fluids*, edited by A. C. Griffin and J. F. Johnson (Plenum, New York, 1984), Vol. 4.

<sup>21</sup>P. D. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974).