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Statistical mechanics and thermodynamics of magnetic and dielectric systems based on magnetization and polarization fluctuations: Application of the quasi-Gaussian entropy theory

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The quasi-Gaussian entropy (QGE) theory employs the fact that a free-energy change can be written as the moment-generating function of the appropriate probability distribution function of macroscopic fluctuations of an extensive property. In this article we derive the relation between the free energy of a system in an external magnetic or electric field and the distribution of the ''instantaneous'' magnetization or polarization at zero field. The physical-mathematical conditions of these distributions are discussed, and for several continuous and discrete model distributions the corresponding thermodynamics, or ''statistical state,'' is derived. Some of these statistical states correspond to well-known descriptions, such as the Langevin and Brillouin models. All statistical states have been tested on several magnetic and dielectric systems: antiferromagnetic $MnCl_2$, the two-dimensional Ising spin model, and the simulated extended simple point charge (SPC/E) water under an electric field. The results indicate that discrete modeling of magnetization and polarization is rather essential for all systems. For the Ising model the ''discrete uniform'' state (corresponding to a Brillouin function) gives the best description. $MnCl_2$ is best described by a ''symmetrized binomial state,'' which reflects the two opposing magnetic sublattices. For simulated water it is found that the polarization, as well as the type of distribution of the fluctuations, is strongly affected by the shape of the system. [DOI: 10.1063/1.1448290]

I. INTRODUCTION

In recent articles we demonstrated that it is actually rather fruitful to approach statistical mechanics from the point of view of macroscopic fluctuations, as initiated by Einstein[1–3] and further developed by Landau and Lifshitz[4] and by Greene and Callen,[5] instead of the usual microscopic Hamiltonian point of view, as proposed by Gibbs.[6]

It is well known that many free energy changes with respect to a proper reference state can be written in terms of the moment-generating function[7–9] of some macroscopic probability distribution $\rho(\mathcal{X})$, where $\mathcal{X}$ corresponds to some fluctuating macroscopic extensive property, e.g., the internal energy, enthalpy, volume, or number of particles.[10] All information to evaluate the free-energy difference as a function of the intensive parameter, e.g., temperature or pressure, is contained in $\rho(\mathcal{X})$. So, instead of modeling the molecular Hamiltonian and trying to evaluate by some means the partition function which is usually only possible with severe approximations, we can directly model the distribution $\rho(\mathcal{X})$, using all available physical-mathematical constraints and requirements on the distribution. Each model distribution yields a unique and complete set of thermodynamic functions, the ''statistical state'' of the system. It must be stressed that, except for simplified model systems, it is (very) difficult to obtain from ''first principles'' the exact distribution. However, because of the macroscopic character of thermodynamic systems, the central limit theorem[7] can be invoked to show that $\rho(\mathcal{X})$ is close to a Gaussian distribution, at least in the vicinity of the mode. In the ''quasi-Gaussian entropy'' (QGE) theory we therefore simply assume that $\rho(\mathcal{X})$ is ''quasi-Gaussian,'' i.e., it can be described by the convolution of distributions corresponding to identical, statistically independent subsystems. These subsystem distributions may be unimodal-like and are likely to be of relatively low mathematical complexity. In general, the information available on a macroscopic system provides several requirements or restrictions that are essential in modeling the distribution function. Unfortunately, such restrictions are insufficient to provide a unique choice of the model distribution, but the investigation on many different systems is clearly showing that it is possible to identify a typical distribution for each

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instantaneous property $\mathcal{X}$ that is a good model for a very large class of systems.

Using this formalism for fluctuations of the "potential" energy of the system, we were able to derive a relatively simple and general, yet very accurate model, the confined gamma state, for describing the temperature dependence of thermodynamic properties at constant density.[11,12] It also forms the basis of complete equations of state for the Lennard-Jones fluid[13] and water.[14,15] The potential power of the method is indicated by the fact the same model is applicable to systems that differ so much in polarity.

In this article we will use the QGE theory to describe the statistical mechanics and thermodynamics of macroscopic systems as a function of an external magnetic or electric field. The effect of an external magnetic field is not only interesting by itself. Because of the strong analogy between magnetization and density fluctuations (see, for instance, the isomorphism between the Ising magnet and the lattice gas[16,17]) this effect may also point to new ways of obtaining improved descriptions of the density dependence of thermodynamic properties.[18] In the following paper[19] we will investigate in more detail the construction of complete equations of state as a function of external field and temperature, based on the QGE models derived in this article. Another interesting point of magnetic and electric systems is the effect of the shape of the sample on thermodynamics and statistical mechanics, especially on the spontaneous fluctuations that are of central interest in the QGE theory.

II. THEORY

A. General electromagnetic definitions

In this article we will use the SI formulation of the electromagnetic relations.[20–22] We consider a macroscopic system on which a constant and uniform external magnetic (H_0) or electric field (E_0) is applied. The system is assumed to have an ellipsoidal shape (including limiting cases like a needle, sphere, and disk), so that the resulting electromagnetic (em) moment $M_m=IV$ or $M_e=PV$ (with V the sample volume and I and P the magnetization and polarization, respectively) inside the system is also homogeneous.[22–24] For simplicity, and without loss of generality, we align the external field along the z axis, which coincides with one of the ellipsoidal axes. We also assume, for mathematical convenience, that the system reacts isotropically; often this is a good approximation,[24] and the general tensorial relations become the scalar equations that we use in this paper. We explicitly exclude systems that exhibit hysteresis effects (e.g., ferromagnets and ferroelectrics) where the em moment is not a single-valued function of the external field.[21,24–27]

The external field (H_0 or E_0) creates a homogeneous field (H or E) inside the sample, which are related via[20–24,28] $H=H_0-f_dI$ or $E=E_0-f_d(P/\epsilon_0)$, where f_dI and f_dP/ϵ_0 are the *demagnetizing* and *depolarizing* fields, respectively, ϵ_0 is the vacuum permittivity, and f_d is a factor depending on the shape of the sample: for a thin needle aligned with the field $f_d=0$, for a spherical sample $f_d=\frac{1}{3}$, and for a flat disk perpendicular to the field $f_d=1$ (see Refs. 23 and 29 for general formulas of f_d). The magnetic or electric susceptibility (χ_m or χ_e) is defined via $I=\chi_mH$ or $P/\epsilon_0=\chi_eE$ with $\chi_m=\mu_r-1$ and $\chi_e=\epsilon_r-1$, where μ_r and ϵ_r are the relative permeability and dielectric constant of the sample. The susceptibility is independent of the volume and shape of the sample.[30,31] From this follows that $I=\chi_m/(1+f_d\chi_m)H_0$, $P/\epsilon_0=\chi_e/(1+f_d\chi_e)E_0$, $H=H_0/(1+f_d\chi_m)$, and $E=E_0/(1+f_d\chi_e)$. To express the magnetic energy in the SI system, it is actually more convenient to use $B_0=\mu_0H_0$ as the external field, where μ_0 is the vacuum permeability.

We introduce at this stage a general notation for both magnetic and electric systems, with $\mathfrak{F}_0=\{B_0,E_0\}$ the external field, $M=\{M_m,M_e\}$ the total em moment, $\chi=\{\chi_m,\chi_e\}$ the susceptibility, and $\zeta_0=\{\mu_0,1/\epsilon_0\}$. Hence, the total moment is given by

$$M(\mathfrak{F}_0)=\frac{V}{\zeta_0}\left(\frac{\chi}{1+f_d\chi}\right)\mathfrak{F}_0, \tag{1}$$

or vice versa

$$\chi(\mathfrak{F}_0)=\frac{\zeta_0M/(V\mathfrak{F}_0)}{1-f_d\zeta_0M/(V\mathfrak{F}_0)}. \tag{2}$$

Note that for small χ (where $\zeta_0M/V\ll\mathfrak{F}_0$) we have approximately[20]

$$\chi(\mathfrak{F}_0)\approx\frac{\zeta_0}{V}\frac{M}{\mathfrak{F}_0}. \tag{3}$$

Since the susceptibility is shape independent, it follows that by reversibly deforming the sample at constant external field from a shape with factor ${}^0f_d$ and magnetization or polarization ${}^0M$ to a shape with factor f_d, we obtain

$$M(\mathfrak{F}_0,f_d)=\frac{{}^0M(\mathfrak{F}_0)}{1+(f_d-{}^0f_d)\zeta_0\,{}^0M(\mathfrak{F}_0)/(V\mathfrak{F}_0)}, \tag{4}$$

i.e., the total em moment is a function of the shape of the sample, which in fact must be considered a state variable. This suggests that also higher-order moments of fluctuations of the instantaneous em moment are a function of the shape. Since the em moment is given by the field derivative of the Helmholtz free energy $A(N,V,T,\mathfrak{F}_0)$,

$$M(\mathfrak{F}_0)=-\left(\frac{\partial A}{\partial\mathfrak{F}_0}\right)_{N,V,T}, \tag{5}$$

it follows that free-energy difference with respect to a reference system with the same volume, temperature, and number of particles at zero external field is thus given as a general function of the shape by

$$\Delta A(\mathfrak{F}_0,f_d)\equiv A(N,V,T,\mathfrak{F}_0,f_d)-A(N,V,T,0,f_d)=-\int_0^{\mathfrak{F}_0}\frac{{}^0M(\mathfrak{F}_0')}{1+(f_d-{}^0f_d)\zeta_0\,{}^0M(\mathfrak{F}_0')/(V\mathfrak{F}_0')}\,d\mathfrak{F}_0'. \tag{6}$$

Clearly, only for very special functional relationships between the moment ${}^0M(\mathfrak{F}_0)$ and the field $\mathfrak{F}_0$, such as a linear one (i.e., linear response in the weak-field limit), the free energy expression $\Delta A(\mathfrak{F}_0,f_d)$ has the same functional form for each value of f_d, see, e.g., the expressions of the Gaussian statistical state [Eqs. (29)–(31)].

B. Free energy

Following Davidson,[20] the Helmholtz free energy $A(N,V,T,\mathfrak{F}_0)$ of the total system is statistical-mechanically defined as

$$A(N,V,T,\mathfrak{F}_0) = -kT \ln Q(N,V,T,\mathfrak{F}_0), \tag{7}$$

where the quantum-mechanical partition function is given by

$$Q(N,V,T,\mathfrak{F}_0) = \sum_n e^{-\beta \mathcal{E}_n(\mathfrak{F}_0)}. \tag{8}$$

The summation runs over all the Hamiltonian eigenstates, and $\mathcal{E}_n(\mathfrak{F}_0)$ is the total energy of the system in state n as a function of the external field. It is important to note that the field used in these expressions is the external field, not the internal one.[20,30]

For the energy as a function of $\mathfrak{F}_0$ we use an expansion of the energy to second order in the external field, based on second-order quantum perturbation theory, giving[24,32–37]

$$\mathcal{E}_n(\mathfrak{F}_0) = \mathcal{E}_n^{(0)} - \mathcal{M}_n' \mathfrak{F}_0 + \tfrac{1}{2}\mathcal{A}\mathfrak{F}_0^2. \tag{9}$$

Here, the first term is the unperturbed energy (i.e., at zero external field), including all possible ''internal'' interactions, like spin–orbit coupling, electron correlations, and exchange interactions. The second term is the linear Zeeman or Stark effect, and the third term the quadratic Zeeman or Stark effect. The coefficient $\mathcal{A}$ is customarily considered to be a constant, independent of the quantum state (and hence of temperature).[24,34,38] In the magnetic case, for example, $\mathcal{A}$ represents both the diamagnetic and temperature-independent paramagnetic effect,[34] which is usually positive (except when there are low-lying energy levels, in which case $\mathcal{A}$ might be negative). In the dielectric case, $\mathcal{A}$ is negative and can be related to the optical refractive index n_{opt} via $\mathcal{A} = -V\epsilon_0(n_{\text{opt}}^2 - 1)/[1 + f_d(n_{\text{opt}}^2 - 1)]$; see also Ref. 19.

Hence the free energy and total moment are given by

$$A(\mathfrak{F}_0) = \tfrac{1}{2}\mathcal{A}\mathfrak{F}_0^2 - kT \ln \sum_n e^{-\beta[\mathcal{E}_n^{(0)} - \mathcal{M}_n'\mathfrak{F}_0]}, \tag{10}$$

$$M(\mathfrak{F}_0) = -\mathcal{A}\mathfrak{F}_0 + M'(\mathfrak{F}_0), \tag{11}$$

where the ''reduced'' moment M' (excluding the second-order field effect) is

$$M'(\mathfrak{F}_0) = \langle \mathcal{M}' \rangle = \frac{\Sigma_n \mathcal{M}_n' e^{-\beta[\mathcal{E}_n^{(0)} - \mathcal{M}_n'\mathfrak{F}_0]}}{\Sigma_n e^{-\beta[\mathcal{E}_n^{(0)} - \mathcal{M}_n'\mathfrak{F}_0]}}. \tag{12}$$

Using Eq. (10), the free energy difference $\Delta A(\mathfrak{F}_0)$ [see Eq. (6)] is thus given by

$$\Delta A(\mathfrak{F}_0) = A(\mathfrak{F}_0) - A(0) = \tfrac{1}{2}\mathcal{A}\mathfrak{F}_0^2 - kT \ln G^0_{\mathcal{M}'}(\beta\mathfrak{F}_0), \tag{13}$$

where $G^0_{\mathcal{M}'}(\beta\mathfrak{F}_0) = \langle e^{\beta\mathcal{M}_n'\mathfrak{F}_0}\rangle_{\mathfrak{F}_0=0}$ is the moment generating function[7–9] (MGF) of the probability distribution function at zero external field of the em moment $\mathcal{M}'$ evaluated at $\beta\mathfrak{F}_0$. The zero superscript denotes that the MGF is to be evaluated at zero external field. In general, the MGF of the distribution of a random variable $\mathcal{X}$ is the expectation value $G_{\mathcal{X}}(t) = \langle e^{t\mathcal{X}}\rangle$. The change in Helmholtz free energy ΔA when applying an external field is via Eq. (13) completely determined by the distribution of the (instantaneous) magnetization or polarization $\mathcal{M}'$ at zero field. Hence modeling of this distribution directly provides an (analytical) expression of the free energy and related thermodynamic functions: the ''statistical state'' of the system.

C. Double-state model

Instead of modeling the distribution of $\mathcal{M}'$ at zero field within the total available configurational space to obtain expressions for ΔA, we may think of configurational space to be ''naturally'' divided into two subspaces. At zero external field there must be some symmetry in phase space, because of the symmetry of magnetization or polarization when changing (for nonferromagnetic or nonferroelectric systems) the direction of the field 180°, and because of the symmetry breaking of ferromagnetic or ferroelectric systems: i.e., without a small external field, the remanent moment has no preference for the positive or negative direction.[17,24,39] Using such a division, which is by definition independent of the external field, we obtain a double-state model[40,41] as follows.

Both the actual and reference partition functions can be written as the sum of subspaces 1 and 2, and hence

$$\Delta A(\mathfrak{F}_0) = -kT \ln\{\epsilon_1(T) e^{-\beta\Delta A_1(\mathfrak{F}_0)} + [1 - \epsilon_1(T)] e^{-\beta\Delta A_2(\mathfrak{F}_0)}\}, \tag{14}$$

where

$$\epsilon_1(T) = \frac{Q_1(0)}{Q(0)} = \frac{\Sigma_{n\in 1} e^{-\beta\mathcal{E}_n^{(0)}}}{\Sigma_n e^{-\beta\mathcal{E}_n^{(0)}}} \tag{15}$$

and

$$e^{-\beta\Delta A_i(\mathfrak{F}_0)} = \frac{Q_i(\mathfrak{F}_0)}{Q_i(0)} = e^{-(1/2)\beta\mathcal{A}\mathfrak{F}_0^2}\langle e^{\beta\mathcal{M}'\mathfrak{F}_0}\rangle_{i,\mathfrak{F}_0=0}. \tag{16}$$

Since $\beta\Delta A_i(\mathfrak{F}_0)$ is of the order $O(N\sim 10^{23})$, with ΔA_i the free energy difference (with respect to zero external field) of the *whole* system in subspace i, we find that $e^{-\beta\Delta A_i(\mathfrak{F}_0)}$ will therefore for any macroscopic system behave like a step function. Already a small difference in $\Delta\Delta A(\mathfrak{F}_0) = \Delta A_1(\mathfrak{F}_0) - \Delta A_2(\mathfrak{F}_0)$ is very large with respect to kT; so if $\Delta\Delta A(\mathfrak{F}_0) < 0$ for $\mathfrak{F}_0 < 0$, say, subspace 1 is virtually the only populated part, and vice versa. Moreover, if we require that at zero external field both subspaces have identical thermodynamics as a function of T, and, because of symmetry, the distributions of $\mathcal{M}'$ in both subspaces are therefore each other's mirror images, we find simply that $\epsilon_1(T) = \epsilon_2(T) = \frac{1}{2}$ independent of temperature. Hence, the free energy and total moment are

$$\Delta A(\mathfrak{F}_0) = \tfrac{1}{2}\mathcal{A}\mathfrak{F}_0^2 - \begin{cases} kT \ln G^0_{\mathcal{M}',1}(\beta\mathfrak{F}_0) & (\mathfrak{F}_0 < 0) \\ kT \ln G^0_{\mathcal{M}',2}(\beta\mathfrak{F}_0) & (\mathfrak{F}_0 > 0), \end{cases} \tag{17}$$

$$M(\mathfrak{F}_0) = -\mathcal{A}\mathfrak{F}_0 + \begin{cases} M_1'(\mathfrak{F}_0) & (\mathfrak{F}_0 < 0) \\ M_2'(\mathfrak{F}_0) & (\mathfrak{F}_0 > 0), \end{cases} \tag{18}$$

with, obviously, $M_i'(\mathfrak{F}_0) = \langle \mathcal{M}' \rangle_i$ the average ''reduced'' magnetization or polarization of subspace i.

D. Model distribution functions

There are several general remarks to make about model distributions $\rho(\mathfrak{F}_0)$.

First, because of the macroscopic nature, the system can be subdivided into a large number $\mathbb{N}_e$ of identical and independent thermodynamic subsystems, where such subsystems can never be smaller than the elementary systems[12] (the minimal independent thermodynamic subsystems). Note that since the magnetization and polarization are a function of the sample shape [Sec. II A, Eq. (4)], the elementary systems, as well as the subsystems, must have the same shape as the overall sample, i.e., an ellipsoid. Since the subsystems are statistically independent, with the total moment $\mathcal{M}'$ equal to the sum of the moments per subsystem, the distribution of $\mathcal{M}'$ is the $\mathbb{N}_e$-fold convolution of the distribution of the subsystem moment, and the MGF $G^0_{\mathcal{M}'}(t)$ is simply the product of the corresponding subsystem moment generating functions.[7–9] As we did for the quantum energy distribution of solids,[42] we assume that the distribution of each of the $\mathbb{N}_e$ subsystems can be mathematically decomposed into $\mathbb{N}_s$ simple ''basic'' distributions of ''basic'' moments m', with corresponding MGF $\tilde{g}^0_{m'}(t)$. Hence the total MGF is given by

$$G^0_{\mathcal{M}'}(\beta\mathfrak{F}_0)=[\{\tilde{g}^0_{m'}(\beta\mathfrak{F}_0)\}^{\mathbb{N}_s}]^{\mathbb{N}_e}=\{\tilde{g}^0_{m'}(\beta\mathfrak{F}_0)\}^{\mathbb{N}}, \tag{19}$$

with $\mathbb{N}=\mathbb{N}_e\mathbb{N}_s$ the total number of ''basic'' distributions and MGF's used to model the system. Note that for distributions that are closed under convolution[43] (i.e., the distribution after convolution is of the same type as the original distributions, which is the case for a Gaussian, gamma, or binomial distribution, to mention a few), it is the same to model the distribution of m' or directly that of $\mathcal{M}'$, and $\mathbb{N}$ is a redundant quantity. Because of the central limit theorem,[7,44] it also follows from Eq. (19) that the overall distribution of $\mathcal{M}'$ must be very close to a Gaussian, at least in the vicinity of its mode (maximum). In the QGE theory we model such macroscopic fluctuation distributions as ''quasi-Gaussian'' distributions, i.e., via the convolution of relatively simple analytical ''basic'' distributions which may be unimodal-like.

Second, if at zero field the distribution of $\mathcal{M}'$ or m' is symmetric around zero, there is no spontaneous magnetization or polarization, which is the case for the systems under consideration.

Third, since the free energy $\Delta A(\mathfrak{F}_0)$ is finite for any finite external field, the moment generating function $G^0_{\mathcal{M}'}(t)$ or $\tilde{g}^0_{m'}(t)$ of any suitable model distribution must converge for any finite $t=\beta\mathfrak{F}_0$.

Fourth, it is very reasonable to assume that the domain of $\mathcal{M}'$ or m' is finite and is symmetric around zero. However, if the mode of the distribution is very far from one of the borders of the domain, the distribution on that side may be well approximated by a distribution that is analytically defined up to infinity. This may be the case with the double state model, Eq. (17), where for physical reasons the distribution of subspace 1 ($\mathfrak{F}_0<0$) has necessarily a lower limit, but may be formally defined up to infinity (since this limit is only important for $\mathfrak{F}_0\gg 0$, where in any case $\Delta A_1>\Delta A_2$), and likewise the distribution of subspace 2 must have an upper limit but may be formally defined from minus infinity.

Finally, because of the quantum-mechanical origen of magnetism, the magnetization is also quantized, and we should in principle use a discrete distribution. However, for macroscopic systems the separation of magnetization or polarization levels may be so small that one could use a continuous model distribution.[20,35]

We will focus in general on the description of the ''basic'' distribution of the moment m'. A *continuous* distribution $\rho^0(m')$ is thus defined on the interval $[-m'_0,+m'_0]$, and so

$$\tilde{g}^0_{m'}(\beta\mathfrak{F}_0)=\int_{-m'_0}^{+m'_0} e^{\beta m'\mathfrak{F}_0}\rho^0(m')dm'. \tag{20}$$

For *discrete* magnetization or polarization levels within the same interval $[-m'_0,+m'_0]$, the simplest assumption we can make is to express the moment in the lth level as

$$m'_l=-m'_0+l\Delta m', \quad l=0,1,...,n, \quad n=2m'_0/\Delta m', \tag{21}$$

with $\Delta m'$ the separation between two magnetization or polarization levels. Hence

$$\begin{aligned}\tilde{g}^0_{m'}(\beta\mathfrak{F}_0)&=e^{-\beta m'_0\mathfrak{F}_0}\tilde{g}^0_l(\beta\Delta m'\mathfrak{F}_0)\\&=e^{-\beta m'_0\mathfrak{F}_0}\sum_{l=0}^{n} e^{\beta\Delta m'\mathfrak{F}_0 l}p^0_l,\end{aligned} \tag{22}$$

where p^0_l is the ''basic'' discrete probability distribution of the magnetization or polarization level l at zero external field.

Finally, note that an elegant method to obtain symmetric distributions is described by Feller.[43] Let $\mathcal{X}_1$ and $\mathcal{X}_2$ be two identical and independent random variables from a distribution with MGF $G_{\mathcal{X}}(t)$. The new variable $\mathcal{X}_1-\mathcal{X}_2$ has a symmetric distribution around zero with MGF $G^{\mathrm{sym}}_{\mathcal{X}}(t)\equiv G_{\mathcal{X}_1-\mathcal{X}_2}(t)=G_{\mathcal{X}}(t)G_{\mathcal{X}}(-t)$, which is called the ''symmetrized'' distribution of $\mathcal{X}$. This procedure can be used for any suitable continuous or discrete distribution. Note that for an already symmetric distribution, the procedure basically yields the same statistical state. Also note that if $\mathcal{X}_i$ is a discrete variable defined on $[0,n]$, obviously $\mathcal{X}_1-\mathcal{X}_2$ is defined on $[-n,n]$. When we apply this to the distribution of the index l, since in that case $m'_l=l\Delta m'$, we should therefore slightly adapt Eq. (22) to

$$\begin{aligned}\tilde{g}^0_{m'}(\beta\mathfrak{F}_0)&=\tilde{g}^{\mathrm{sym},0}_l(\beta\Delta m'\mathfrak{F}_0)\\&=\tilde{g}^0_l(\beta\Delta m'\mathfrak{F}_0)\tilde{g}^0_l(-\beta\Delta m'\mathfrak{F}_0).\end{aligned} \tag{23}$$

The appropriate continuous or discrete model distributions $\rho^0(m')$ or p^0_l may be taken from any suitable system or family of distributions. For continuous distributions, we can use the Pearson[45–48] or generalized Pearson[11,49] system; for discrete distributions we can invoke the Katz,[50] Ord,[47] Kemp's generalized hypergeometric probability distributions (GHPD) or generalized hypergeometric factorial moment distributions (GHFD)[9,42,51,52] families. The use of a system or family of distributions allows one to increase the complexity of the model distribution in a rather systematic way.

E. Parameter estimation

Via Eqs. (13) and (19) the free energy ΔA is expressed in terms of the parameters $\boldsymbol{a}^0$ of the ''basic'' model distribution of the instantaneous moment m' at zero field, $\mathbb{N}$, and for discrete distributions also m_0' and $\Delta m'$. To obtain the values of these parameters, we can use the ''method of moments,'' [7,42,53] i.e., equating the first few theoretical moments (or cumulants) of the model distribution (expressed in terms of the parameters $\boldsymbol{a}^0$), and the corresponding ''experimental'' or sample moments (cumulants) of the total magnetization or polarization $\mathcal{M}'$ (which via statistical mechanics can be expressed in terms of derivatives of the magnetization or polarization with respect to the external field). This is equivalent to equating the first few derivatives of the theoretical free energy expression in the external field (as a function of the parameters $\boldsymbol{a}^0$, $\mathbb{N}$, m_0', and $\Delta m'$) at zero field to the corresponding experimental values. Note that the experimental cumulants depend on the shape of the sample (see Sec. II A).

However, we find it more useful to express the parameters of the model distributions (and the corresponding thermodynamic models) in terms of the saturation magnetization/polarization,[21,25]

$$M_s' = \lim_{\mathfrak{F}_0 \to +\infty} M(\mathfrak{F}_0) + \mathcal{A}\mathfrak{F}_0 = \lim_{\mathfrak{F}_0 \to +\infty} M'(\mathfrak{F}_0) \tag{24}$$

and the domain quantities m_0' and $\Delta m'$.

F. Statistical states

In this section we will derive several statistical states, based both on continuous and discrete magnetization or polarization distributions, which fulfill the general requirements discussed in Sec. II D. Throughout, we will model the ''basic'' distribution of the moment m'. After evaluating the moment generating function of the model distribution,[7–9,54,55] Eq. (20) or (22), we obtain the free energy via Eqs. (13) [or for the double-state model Eq. (17)] and (19). To relate parameters via the method of moments to thermodynamic derivatives, we will also provide the limit $\lim_{\mathfrak{F}_0 \to 0} \partial M/\partial \mathfrak{F}_0 = \partial M^0/\partial \mathfrak{F}_0$. For all statistical states $M(0)=0$, and, except for the Gaussian state, the limit of the reduced moment at infinite field is M_s', i.e., the magnetization and polarization saturate because of the finite domain of m'.

1. Gaussian state

The Gaussian or normal distribution,[7,8,54]

$$\rho(m') = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left\{ -\frac{m'^2}{2\sigma^2} \right\} \tag{25}$$

with zero average and σ^2 the variance, is closed under convolution and is defined from $-\infty$ to ∞; hence it is not strictly a physically acceptable distribution. However, as it is the prototypical example of a fluctuation distribution and is often used to model fluctuations within a mean-field description, we include it here. The thermodynamics is given by

$$\Delta A(\mathfrak{F}_0) = \tfrac{1}{2}\mathcal{A}\mathfrak{F}_0^2 - \tfrac{1}{2}\beta K^0 \mathfrak{F}_0^2, \tag{26}$$

$$M(\mathfrak{F}_0) = -\mathcal{A}\mathfrak{F}_0 + \beta K^0 \mathfrak{F}_0, \tag{27}$$

$$\frac{\partial M^0}{\partial \mathfrak{F}_0} = -\mathcal{A} + \beta K^0, \tag{28}$$

with $K^0 = \mathbb{N}\sigma^2$. Note that for $\mathfrak{F}_0 \to \pm\infty$ no saturation occurs. The Gaussian state actually corresponds to a second-order Taylor expansion of the free energy in $\mathfrak{F}_0$ around zero, yielding a linear relation between magnetization or polarization and external field. The Gaussian state is the weak-field limit of all statistical states. If K^0 is a temperature-independent constant, we obtain Curie's law for the usual paramagnetic susceptibility,[21,26,38] $\chi_m = C/T$ with $C = \mu_0 K^0/kV$ the Curie constant; see also Ref. 19.

From Eq. (6) it follows that if for a certain shape (${}^0f_d$) the system is described by a Gaussian state, this is actually true for *all* shapes (i.e., values of f_d), since

$$\Delta A(\mathfrak{F}_0, f_d) = \tfrac{1}{2}\mathcal{A}(f_d)\mathfrak{F}_0^2 - \tfrac{1}{2}\beta K^0(f_d)\mathfrak{F}_0^2, \tag{29}$$

with

$$\mathcal{A}(f_d) = \frac{{}^0\mathcal{A}}{1 + (f_d - {}^0f_d)(-{}^0\mathcal{A} + \beta\,{}^0K^0)\zeta_0/V}, \tag{30}$$

$$K^0(f_d) = \frac{{}^0K^0}{1 + (f_d - {}^0f_d)(-{}^0\mathcal{A} + \beta\,{}^0K^0)\zeta_0/V}. \tag{31}$$

It can be easily derived [cf. Eq. (A1) of Ref. 19] that $K^0 = \kappa_2^0[\mathcal{M}']$ is the variance of the instantaneous ''reduced'' moment $\mathcal{M}'$ at zero field. Hence for the systems under consideration where $|\beta\,{}^0K^0| \gg |{}^0\mathcal{A}|$, the variance and so the magnitude of fluctuations are largest for $f_d = 0$ (a thin needle) and least for $f_d = 1$ (a flat disk). Since for small fields all statistical states converge to the Gaussian one, this is a general feature of all states: fluctuations are suppressed by the demagnetizing/depolarizing field.

2. Beta state

The simplest symmetric continuous Pearson distribution on a finite domain is the beta distribution,[7,55]

$$\rho(m') = \frac{(2m_0')^{1-2a}}{B(a,a)} (m' + m_0')^{a-1} (m_0' - m')^{a-1} \qquad (a \geqslant 0) \tag{32}$$

with $B(a,a)$ the beta function.[56] The thermodynamics is given by

$$\Delta A(\mathfrak{F}_0) = \tfrac{1}{2}\mathcal{A}\mathfrak{F}_0^2 + M_s'\mathfrak{F}_0 - \frac{M_s'}{\beta m_0'} \times \ln\left\{ \Gamma(a + \tfrac{1}{2}) \times \left(\frac{\beta m_0' \mathfrak{F}_0}{2} \right)^{-a+1/2} e^{\beta m_0' \mathfrak{F}_0} I_{a-1/2}(\beta m_0' \mathfrak{F}_0) \right\}, \tag{33}$$

$$M(\mathfrak{F}_0) = -\mathcal{A}\mathfrak{F}_0 + M_s' \left[\frac{I_{a+1/2}(\beta m_0' \mathfrak{F}_0)}{I_{a-1/2}(\beta m_0' \mathfrak{F}_0)} \right], \tag{34}$$

$$\frac{\partial M^0}{\partial \mathfrak{F}_0} = -\mathcal{A} + M_s' \frac{\beta m_0'}{2a+1}, \tag{35}$$

with $M_s'=\mathbb{N}m_0'$; $I_\nu(x)$ and $\Gamma(x)$ are the modified Bessel function of the first kind of order ν and the gamma function, respectively.[56] Note that for some specific values of a, the beta state reduces to the following well-known models:

For $a=1$ the beta distribution degenerates to a continuous uniform distribution, $\rho(m')=1/2m_0'$, yielding the *continuous uniform state*:

$$\Delta A(\mathfrak{F}_0)=\tfrac{1}{2}\mathcal{A}\mathfrak{F}_0^2-\frac{M_s'}{\beta m_0'}\ln\left\{\frac{\sinh(\beta m_0'\mathfrak{F}_0)}{\beta m_0'\mathfrak{F}_0}\right\}, \tag{36}$$

$$M(\mathfrak{F}_0)=-\mathcal{A}\mathfrak{F}_0+M_s'\mathcal{L}(\beta m_0'\mathfrak{F}_0), \tag{37}$$

$$\frac{\partial M^0}{\partial\mathfrak{F}_0}=-\mathcal{A}+M_s'\frac{\beta m_0'}{3}, \tag{38}$$

with $M_s'=\mathbb{N}m_0'$ and $\mathcal{L}(x)=\coth(x)-1/x$ the Langevin function. Interestingly, the continuous uniform state corresponds to the Langevin model[23,26,35,57] of an independent "classical" magnetic or electric dipole moment μ that can assume any orientation in space and interacts with an external field $\mathfrak{F}_0$. For $\mathbb{N}$ independent moments, we have $m_0'=\mu$ and $M_s'=\mathbb{N}\mu$. Feller[58] shows that the projection of a three-dimensional random vector on a line is uniformly distributed (see also Amadei, Ceruso, and Di Nola[59]), so this is an example where, based on a very simple Hamiltonian, one can determine the distribution $\rho(\mathcal{M}')$ and hence the free energy from first principles.

For $a\to 0$ the beta distribution tends to a two-state discrete uniform distribution [Eq. (39), $n=1$] or a (symmetrized) binomial distribution [Eq. (44), $p=\frac{1}{2}$, $n=1$]. The corresponding thermodynamics is given by Eqs. (45)–(47).

3. Discrete uniform state

The simplest symmetric discrete distribution on a finite domain is the (discrete) uniform distribution,[7,9]

$$p_l=\frac{1}{n+1}\quad(l=0,1,\ldots,n) \tag{39}$$

and is the discrete counterpart of the continuous uniform distribution (Sec. II F 2). The thermodynamics is given by

$$\Delta A(\mathfrak{F}_0)=\tfrac{1}{2}\mathcal{A}\mathfrak{F}_0^2-\frac{M_s'}{(n/2)\beta\Delta m'}\times\ln\left\{\frac{\sinh\{[\frac{1}{2}(n+1)]\beta\Delta m'\mathfrak{F}_0\}}{(n+1)\sinh\{\frac{1}{2}\beta\Delta m'\mathfrak{F}_0\}}\right\}, \tag{40}$$

$$M(\mathfrak{F}_0)=-\mathcal{A}\mathfrak{F}_0+M_s'\mathcal{B}_{n/2}\left(\frac{n}{2}\beta\Delta m'\mathfrak{F}_0\right), \tag{41}$$

$$\frac{\partial M^0}{\partial\mathfrak{F}_0}=-\mathcal{A}+M_s'\frac{(n+2)\beta\Delta m'}{6}, \tag{42}$$

where $M_s'=\mathbb{N}m_0'=\mathbb{N}n\Delta m'/2$ and

$$\mathcal{B}_J(x)=\left(\frac{2J+1}{2J}\right)\coth\left(\frac{2J+1}{2J}x\right)-\frac{1}{2J}\coth\left(\frac{x}{2J}\right) \tag{43}$$

is the Brillouin function.[26,33] This is the exact description[20] of a system of $\mathbb{N}$ ideal (i.e., noninteracting) paramagnetic atoms with spin $J=n/2$ where $M_s'=\mathbb{N}g\mu_B J$ and $\Delta m'=g\mu_B$ with g the Landé g factor. Since in the absence of an external field all quantum states with quantum numbers $-J,\ldots,J$ are equally probable, the distribution of J and hence of l is discrete uniform. This is the second example where, for a very simple system, the distribution can be known from first principles. Note that for $n\to\infty$ and $\Delta m'\to 0$ with $n\Delta m'/2=m_0'$, Eqs. (40)–(42) transform into Eqs. (36)–(38), i.e., the continuous uniform state. This is the well-known classical limit of the Brillouin function:[35] $\lim_{J\to\infty}\mathcal{B}_J(x)=\mathcal{L}(x)$, corresponding to the discrete uniform distribution tending to a continuous uniform distribution. For $n=1$ we have $\mathcal{B}_{1/2}(x)=\tanh(x)$, and the distribution converges to a binomial; see the next subsection.

4. Binomial state

The simplest discrete unimodal distribution on a finite domain is the binomial distribution,[7–9]

$$p_l=\binom{n}{l}p^l(1-p)^{n-l}\quad(l=0,1,\ldots,n,\quad 0\leqslant p\leqslant 1). \tag{44}$$

It is the simplest acceptable member of the Katz family and generalized hypergeometric probability family of discrete distributions[9,42] and is closed under convolution. To obtain a symmetric distribution, we must use $p=\frac{1}{2}$. The thermodynamics is then given by

$$\Delta A(\mathfrak{F}_0)=\tfrac{1}{2}\mathcal{A}\mathfrak{F}_0^2-2\frac{M_s'}{\beta\Delta m'}\ln\cosh(\tfrac{1}{2}\beta\Delta m'\mathfrak{F}_0), \tag{45}$$

$$M(\mathfrak{F}_0)=-\mathcal{A}\mathfrak{F}_0+M_s'\tanh(\tfrac{1}{2}\beta\Delta m'\mathfrak{F}_0), \tag{46}$$

$$\frac{\partial M^0}{\partial\mathfrak{F}_0}=-\mathcal{A}+M_s'\frac{\beta\Delta m'}{2}, \tag{47}$$

where $M_s'=\mathbb{N}m_0'=\mathbb{N}n\Delta m'/2$.

5. Symmetrized binomial state

As described in Sec. II D, the MGF of a "symmetrized" binomial distribution is given by Eq. (23) with $g_l^0(t)$ the MGF of the binomial distribution, Eq. (44). The distribution is defined from $-n$ to $+n$, and is closed under convolution. The thermodynamics is given by

$$\Delta A(\mathfrak{F}_0)=\tfrac{1}{2}\mathcal{A}\mathfrak{F}_0^2-\frac{M_s'}{\beta\Delta m'}\ln\{p^2+(1-p)^2+2p(1-p)\cosh(\beta\Delta m'\mathfrak{F}_0)\}, \tag{48}$$

$$M(\mathfrak{F}_0)=-\mathcal{A}\mathfrak{F}_0+M_s'\times\left[\frac{2p(1-p)\sinh(\beta\Delta m'\mathfrak{F}_0)}{p^2+(1-p)^2+2p(1-p)\cosh(\beta\Delta m'\mathfrak{F}_0)}\right], \tag{49}$$

$$\frac{\partial M^0}{\partial\mathfrak{F}_0}=-\mathcal{A}+2M_s'p(1-p)\beta\Delta m', \tag{50}$$

with $M_s' = \mathbb{N} m_0' = \mathbb{N} n \Delta m'$. Note that for $p = \frac{1}{2}$ we retrieve the binomial state, Eqs. (45)–(47). Also observe that Eqs. (48)–(50) are symmetric in p and $(1-p)$, so we can restrict the range of p to $[0, \frac{1}{2}]$.

6. Double binomial state

Using for each subspace a binomial distribution, Eq. (44), we can obtain a double-state model, where for subspace 1 ($\mathfrak{F}_0 < 0$) we have m_0', $\Delta m' > 0$ and m_0', $\Delta m' < 0$ for subspace 2. The resulting thermodynamics is given by

$$\Delta A(\mathfrak{F}_0) = \tfrac{1}{2}\mathcal{A}\mathfrak{F}_0^2 - M_s'|\mathfrak{F}_0| - \frac{M_s'}{p\beta\Delta m'} \ln\{1-p + pe^{-\beta\Delta m'|\mathfrak{F}_0|}\}, \tag{51}$$

$$M(\mathfrak{F}_0) = -\mathcal{A}\mathfrak{F}_0 + \mathrm{sgn}(\mathfrak{F}_0) M_s' \left[\frac{(1-p)(1-e^{-\beta\Delta m'|\mathfrak{F}_0|})}{1-p+pe^{-\beta\Delta m'|\mathfrak{F}_0|}}\right], \tag{52}$$

$$\frac{\partial M^0}{\partial \mathfrak{F}_0} = -\mathcal{A} + M_s'(1-p)\beta\Delta m', \tag{53}$$

with $M_s' = \mathbb{N} m_0' = \mathbb{N} n \Delta m' p$ and $\mathrm{sgn}(x) = -1$, 0, or $+1$ for x negative, zero, or positive, respectively. Note that in these expressions, m_0' and $\Delta m'$ are defined to be positive. In the limit $p \to 0$ and $n \to \infty$ with $pn = \theta$ a constant, the binomial distribution tends to the Poisson distribution,[8] $p_l = (e^{-\theta}\theta^l / l!)$, so for any nonzero M_s' Eqs. (51)–(53) tend for $p \to 0$ to the *double Poisson state*, with $M_s' = \mathbb{N} m_0' = \mathbb{N}\theta\Delta m'$, and where

$$\Delta A(\mathfrak{F}_0) = \tfrac{1}{2}\mathcal{A}\mathfrak{F}_0^2 - M_s'|\mathfrak{F}_0| - \frac{M_s'}{\beta\Delta m'}(e^{-\beta\Delta m'|\mathfrak{F}_0|} - 1) \tag{54}$$

is the corresponding nontrivial limit of Eq. (51).

III. RESULTS AND DISCUSSION

In this section we will present results of three different systems: experimental measurements on antiferromagnetic $MnCl_2$, Monte Carlo results of the paramagnetic two-dimensional (2D) Ising model above the Curie temperature, and molecular dynamics results of the extended simple point charge (SPC/E) water model in the presence of an electric field.

Since for all systems the remanent magnetization or polarization M_r' is zero, and the value of $\mathcal{A}$ is known beforehand, the knowledge of M_s' and $\partial M^0/\partial \mathfrak{F}_0$ is for many statistical states (Gaussian, continuous uniform, binomial) sufficient to obtain all parameters. In other cases (beta, symmetrized binomial, double binomial, and discrete uniform) we used a nonlinear fit to obtain the third parameter. In doing that the parameters were restricted to physically meaningful values, in order to retain physically consistent models.

A. $MnCl_2$

Giauque *et al.*[60,61] have measured the magnetic moment of a spherical sample of $MnCl_2$ at low temperature (1.3–4.2 K) in an external homogeneous magnetic field, up to values of 10 T, aligned along the *b* magnetic axis (or *a* crystallographic axis). $MnCl_2$ is a classical example of an antiferromagnetic substance, showing no hysteresis effects within that temperature range. We analyzed data at $T = 1.33$ K in the experimental setup ($f_d = \frac{1}{3}$).

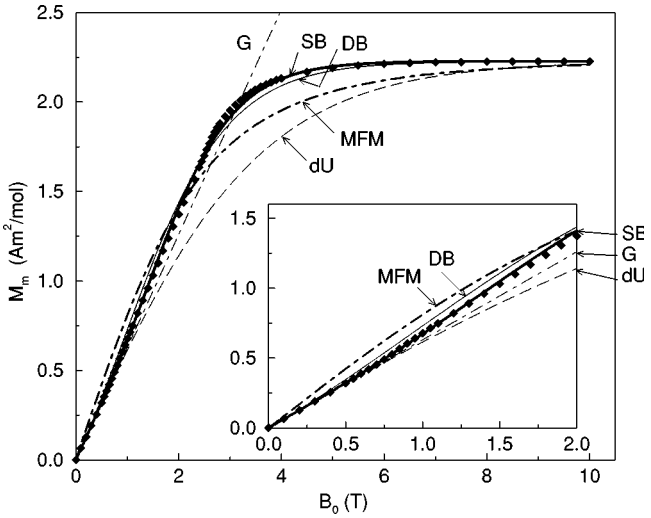

FIG. 1. Magnetization M_m of $MnCl_2$ vs external magnetic field B_0 at $T = 1.33$ K; experimental data (♦) and some QGE statistical states: Gaussian (G, -·-·), discrete uniform (dU, ---), double binomial (DB, —), and symmetrized binomial (SB, —). Also included is the mean-field model, Eq. (55) (MFM, -·--·).

For this sample, the value of $\mathcal{A}$ was smaller than the experimental noise[61] and hence could be set to zero. The maximum moment M_s' was measured (being 2.227 A m^2/mol), as well as the initial slope $\partial M_m^0/\partial B_0$. The zero-field susceptibility $\chi_m = 1.88 \times 10^{-2}$ differs only ~0.6% from the estimate using Eq. (3). Hence the effect of shape (i.e., f_d) on the magnetization curve is in this case negligible.

In Fig. 1 we present the experimental data, along with the results of some statistical states. Clearly visible is the sigmoidal behavior of the experimental curve, which is characteristic of an antiferromagnetic system.[62] In Table I we give the root mean square deviation (RMSD) values of the various models, normalized by M_s', i.e.,

$$\mathrm{RMSD}/M_s' = \frac{1}{M_s'}\sqrt{\frac{1}{N_{\mathrm{data}}}\sum_i^{N_{\mathrm{data}}}\{M_i(B_0) - M_{\mathrm{expt},i}\}^2}.$$

The Gaussian state (one parameter) is only applicable over a limited range ($B_0 \lesssim 0.5$ T), where linear magnetization is present. From the graph and the table it is clear that the best models are the double binomial and, especially, the symmetrized binomial states (each with three parameters). For an antiferromagnetic system this latter fact might be physically explained by supposing that the magnetization of each of the two magnetic sublattices is approximately described by a binomial state, and hence the total magnetization, being the difference between the two sublattice magnetizations, by a symmetrized binomial state. The symmetrized binomial state also gives the correct sigmoidal behavior. Interestingly, the optimal beta state has $a = 0$ and is therefore identical to the binomial state. This indicates that the magnetization distribution is discretelike instead of continuous.

TABLE I. Root mean square deviations (RMSD) normalized by M_s' for different statistical states and various systems.

Statistical state	No. par.	$MnCl_2$	2D Ising
Gaussian [Eq. (27)]	1	0.512	1.60
Cont. uniform [Eq. (37)]	2	0.168	0.043
Beta [Eq. (34)]	3	0.109 ($a=0.0$)	0.019 ($a=0.28$)
Binomial [Eq. (46)]	2	0.109	0.048
Symm. binomial [Eq. (49)]	3	0.008 ($p=0.130$)	0.048 ($p=0.5$)
Double binomial [Eq. (52)]	3	0.021 ($p=0.719$)	0.014 ($p=0.282$)
Discrete uniform [Eq. (41)]	3	0.109 ($n=1$)	0.008 ($n=8$)
N_{data}		62	15
f_d		$\frac{1}{3}$	0

For comparison, in Fig. 1 also an antiferromagnetic Weiss-like mean-field model[22,24,63] is presented,

$$M_A' = \tfrac{1}{2} M_s' \mathcal{B}_J(\beta g \mu_B [B_0 - \lambda M_B']),$$
$$M_B' = \tfrac{1}{2} M_s' \mathcal{B}_J(\beta g \mu_B [B_0 - \lambda M_A']), \tag{55}$$

where M_A' and M_B' are the sublattice magnetizations, $M' = M_A' + M_B'$, and[60] $g=2.004$, $J=5/2$. The least-square fitted value of the exchange coupling parameter $\lambda = 0.44$ yields RMSD/$M_s' = 0.056$; the mean-field model is clearly worse than the symmetrized binomial state.

B. Two-dimensional Ising magnet

The next system is an idealized model, the two-dimensional Ising spin system[64] with only nearest-neighbor interactions. Since there is no analytical solution for the partition function in the presence of an external field, we used standard Metropolis Monte Carlo (MC) simulations[39,65] to obtain values of the magnetization as a function of external field. Since as usual in these simulations periodic boundary conditions were employed, no demagnetizing field can build up, so $f_d = 0$ and $H_0 = H$ is the field used in the Hamiltonian description. In reduced units, the Hamiltonian is

$$\mathcal{E}^*(B_0^*) = -\sum_{\langle i,j \rangle} \sigma_i \sigma_j - B_0^* \sum_i \sigma_i, \tag{56}$$

with $\mathcal{E}^* = \mathcal{E}/J$ and $B_0^* = g\mu_B B_0/J$, where J is the exchange coupling constant between neighboring spins σ_i and $\sigma_j = \pm 1$. The reduced temperature, free energy, and magnetic moment are $T^* = kT/J$, $A^* = A/NJ$, and $M_m^* = M_m/Ng\mu_B$ with N the number of spins in the system. From this follows that $\chi_m = [\rho_N \mu_0 (g\mu_B)^2/J]\chi_m^*$ with ρ_N the spin density and $\chi_m^* = M_m^*/B_0^*$. Clearly, to analyze the system at a geometry different from $f_d = 0$, the values of g, J, and ρ_N are required. Therefore, the simulation geometry $f_d = 0$ was used.

For each state point we used a square lattice of 32×32 spins with periodic boundary conditions, and production runs of 10^6 MC cycles. The temperature was set to $T^* = 6.0$, which is well above the critical (Curie) temperature[16] $T_c^* = 2.269$, and hence the system is in the paramagnetic regime.

Obviously, $M_s'^* = 1.0$ and $\mathcal{A} = 0$, and the numerical slope $\partial M_m^{0*}/\partial B_0^* = 0.381$ matched within the accuracy of the simulations the value obtained from the second moment of the magnetization fluctuations at zero external field, $\kappa_2^0[N\mathcal{M}'^*]/(NT^*)$.

Results are given in Fig. 2 and Table I. Again, the Gaussian state is only applicable for small fields ($B_0^* \lesssim 0.7$). The best model is the discrete uniform state with $n=8$. Note that if there would be no interactions between the spins ($J=0$) and hence no correlation, the magnetization would be given by an "ideal gas" model based on elementary systems containing only one spin, described by a two-state ($n=1$) discrete uniform distribution, giving

$$M^*(B_0') = \mathcal{B}_{1/2}\left(\frac{B_0^*}{2T^*}\right). \tag{57}$$

However, from Fig. 2 it is clear that such a model is not appropriate, even at such a relatively high temperature. Furthermore, of the other QGE models the double binomial and beta states also provide a good description of the magnetization.

For the beta state the parameter $a = 0.28$ is rather close to zero, suggesting that there is some discretelike clustering in the magnetization distribution. From the Hamiltonian it is clear that the distribution must be discrete. Note also that the number $\mathbb{N}$ of "basic" distributions connected to the discrete uniform and beta state may be (very) different; in fact, we

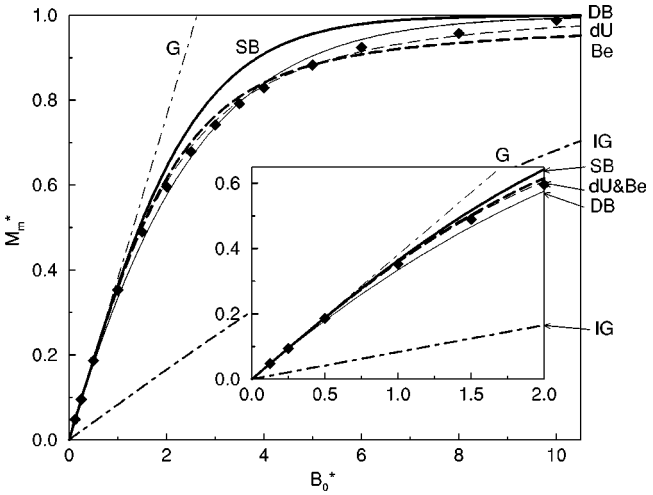

FIG. 2. Magnetization M_m^* of the 2D Ising system vs external magnetic field B_0^* at $T^* = 6.0$; MC data (◆) and some QGE statistical states: Gaussian (G, -·-·-), beta (Be, ---), discrete uniform (dU, ---), double binomial (DB, —) and symmetrized binomial (SB, —). Also included is the "ideal-gas" model, Eq. (57) (IG, -·-·-).

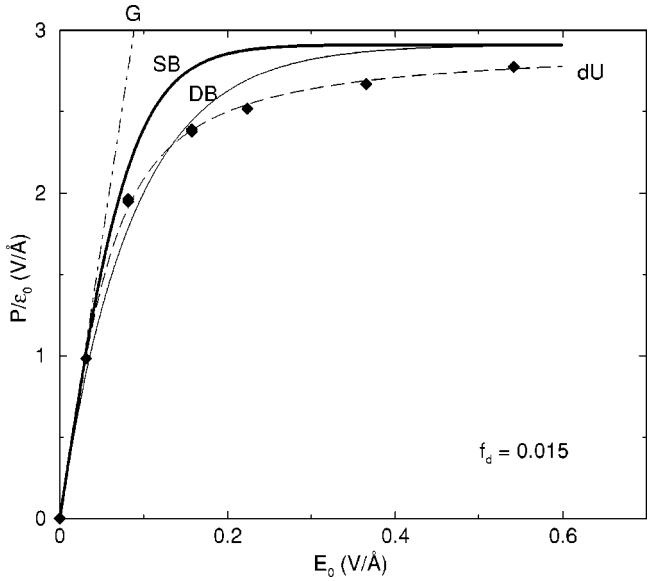

FIG. 3. Polarization P/ϵ_0 of SPC/E water vs external electric field E_0 at $T=300$ K and geometry $f_d=0.015$; simulation data (◆) and some QGE statistical states: Gaussian (G, -·-·-), discrete uniform (dU, ---), double binomial (DB, —), and symmetrized binomial (SB, —).

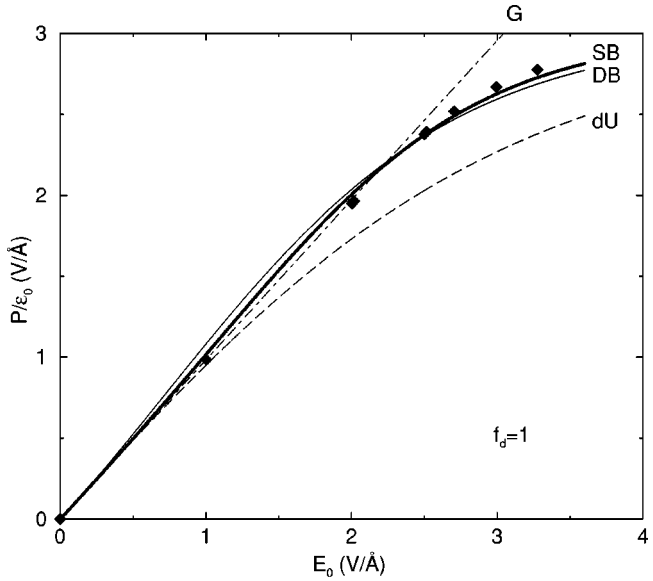

FIG. 4. Polarization P/ϵ_0 of SPC/E water vs external electric field E_0 at $T=300$ K and geometry $f_d=1$; simulation data (◆) and some QGE statistical states: Gaussian (G, -·-·-), discrete uniform (dU, ---), double binomial (DB, —), and symmetrized binomial (SB, —).

find that a discrete uniform ''basic'' distribution corresponds to approximately 5.5 spins, whereas a beta distribution to about 3.6 spins.

C. SPC/E water

The last example consists of a system of SPC/E water molecules[66] in the presence of an external electric field E_0. Yeh and Berkowitz[31] performed molecular dynamics simulations of this system at 300 K using Ewald summation in two different setups: a water layer between explicit charged solid Pt walls, and 3D periodic bulk water in the presence of a field. Both methods gave identical results for the dielectric constant ϵ_r as a function of the field. Since for water $\chi_e=\epsilon_r-1\sim O(10^1-10^2)$ is very large, there is a significant effect of the shape of the sample on the polarization curve. Hence the system has been analyzed for three different geometries: $f_d=0.015$ (a thin cigar with length to width ratio $\sim$12), $f_d=\frac{1}{3}$ (a sphere), and $f_d=1$ (a flat disk, perpendicular to the field).

Yeh and Berkowitz used water with a density of 1.0 g/cm^3, which together with the permanent molecular dipole $\mu=2.39$ D gives a maximum possible polarization $M_s'/(V\epsilon_0)=P_s'/\epsilon_0=3.01$ V/Å. Note, however, that for very large external fields a phase transition to an icelike structure has been observed; this phase transition likely depends on the geometry, so in fact we can only say that $P_s'/\epsilon_0 \leqslant 3.01$ V/Å. Moreover, since the SPC/E molecules have no molecular polarizability, it follows that for this classical system by definition $\mathcal{A}=0$. For a given geometry f_d, the slope $\partial[P^0/\epsilon_0]/\partial E_0$ with $P^0=P(\mathfrak{F}_0=0)$ can be obtained from the zero-field estimate of $\epsilon_r\cong 69.6\pm 1.5$ by Svishchev and Kusalik[67] and Eq. (1).

Results are given in Figs. 3 and 4 and Table II. For different geometries we observed that the optimal value of P_s'/ϵ_0 changed slightly from 2.91 ($f_d\approx 0$) to 3.01 V/Å ($f_d=1$), which may be connected to the phase transition.

For small f_d ($f_d=0.015$), where the depolarizing field is relatively small, the best description is given by the beta and continuous and discrete uniform states. Since for the latter $n=356$, it is basically a continuous uniform state; for the beta state $a=0.89$ is very close to 1 and hence also approximately a continuous uniform state. The Gaussian description is only applicable up to $E_0\sim 0.05$ V/Å.

For larger f_d values ($f_d=\frac{1}{3}$ and 1) with large depolarizing fields, the Gaussian state is applicable up to much larger external fields, e.g., $E_0\lesssim 2$ V/Å; see Fig. 4. Also the type of optimal statistical state changes rather dramatically to the double binomial and especially symmetrized binomial states, indicating that the polarization becomes more discretelike. This is also supported by the fact that $a=0$ for the beta state (i.e., equal to the binomial state). The discretelike character of the polarization distribution can be interpreted as a ''grouping'' of the possible polarizations, which physically may be caused, for example, by collective reorientations of the hydrogen-bonding network relative to the external field.

In Fig. 5 we present ϵ_r as a function of internal field E, independent of shape. As can be seen, the continuous uniform state ($f_d=0.015$) perfectly describes the simulation data. The Gaussian state provides a constant value of ϵ_r. For comparison, also an ''ideal gas'' model[57,68]

$$\epsilon_r(E)=1+\frac{\rho_N\mu}{\epsilon_0 E}\mathcal{L}(\beta\mu E) \tag{58}$$

and the nonpolarizable Onsager model[68,69]

$$\epsilon_r(E)=1+\frac{\rho_N\mu}{\epsilon_0 E}\mathcal{L}\left(\beta\mu\frac{3\epsilon_r}{2\epsilon_r+1}E\right) \tag{59}$$

are shown, which clearly fail to describe the data.

TABLE II. Root mean square deviations (RMSD) normalized by M_s' for different statistical states applied to SPC/E data at various geometries (f_d values).

Statistical state	$f_d=0.015$	$f_d=1/3$	$f_d=1$
Gaussian	2.367	0.198	0.067
Cont. uniform	0.009	0.152	0.172
Beta	0.008 ($a=0.89$)	0.075 ($a=0.0$)	0.106 ($a=0.0$)
Binomial	0.092	0.075	0.106
Symm. binomial	0.092 ($p=0.5$)	0.007 ($p=0.187$)	0.013 ($p=0.162$)
Double binomial	0.049 ($p=0.0$)	0.012 ($p=0.640$)	0.024 ($p=0.672$)
Discrete uniform	0.009 ($n=356$)	0.075 ($n=1$)	0.106 ($n=1$)
N_{data}	8	8	8
M_s'	2.91	2.95	3.01

IV. CONCLUSIONS

In this paper we used the quasi-Gaussian entropy (QGE) theory to derive statistical-mechanical models of the effect of an external electric or magnetic field $\mathfrak{F}_0$ on the thermodynamics of macroscopic systems. General electromagnetic (em) theory shows that the em moment, its higher-order central moments, and the free energy are in general a function of the (ellipsoidal) shape of the sample in the form of the geometry factor f_d.

Using second-order quantum perturbation theory, the Helmholtz free energy is related to the moment generating function of the probability distribution $\rho(\mathcal{M}')$ of the total ''reduced'' em moment $\mathcal{M}'$ (the total moment minus the second-order field effect). By modeling this distribution at zero external field as the many fold convolution of ''basic'' distributions $\rho(m')$ that are supposed to be rather ''simple,'' one obtains exact expressions of the free energy and related thermodynamics (''statistical state'') as a function of field. The physical requirements of these ''basic'' distributions are discussed, and various continuous and discrete models with corresponding statistical states have been derived. Also an additional two-state model is presented. Apart from the Gaussian model, which just yields the usual linear response of the system to the external field, all models describe saturation effects. Some correspond to well-known models: the continuous uniform distribution yields a Langevin model, the discrete uniform distribution yields a Brillouin model.

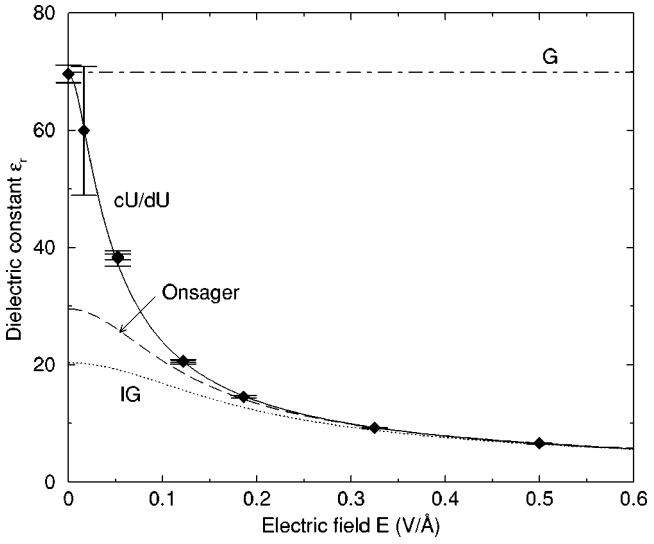

FIG. 5. Dielectric constant of SPC/E water vs electric field E at $T=300$ K; simulation data (♦) and some QGE statistical states: Gaussian (G, -·-·), continuous/discrete uniform at $f_d=0.015$ (cU/dU, —). Also included are the ''ideal-gas'' model, Eq. (58) (IG, ···) and the Onsager model, Eq. (59) (Onsager, ---).

The models have been applied to three different test systems: antiferromagnetic $MnCl_2$, the two-dimensional Ising spin model in the paramagnetic regime, and the SPC/E water model with an external electric field. In general, discrete model distributions $\rho(m')$ provide the best description of these systems; in particular, the discrete uniform distribution is a rather good and general model for systems in the ''needle'' or ''cigar'' geometry, i.e., $f_d\approx 0$. Interestingly, the (sigmoidal) field dependence of the magnetization of $MnCl_2$ is best described by the symmetrized binomial distribution, which may reflect the fact that the magnetization fluctuations of each of the two opposing magnetic sublattices are well described by a binomial distribution. In the case of SPC/E water, since the sample shape is important because of the large susceptibility, the system was analyzed using three geometries (needle, sphere, and disk). It was found that in the first case the best model distributions are more continuouslike (beta), whereas in the other cases the distribution becomes more discretelike (symmetrized binomial). Hence, apart from the magnitude, also the type of fluctuations changes as a function of sample shape. For all systems the indicated QGE statistical states give a significantly better description of the data than other common mean-field expressions, such as the antiferromagnetic Weiss model, the ''ideal gas'' model, and the Onsager model.

In the following paper[19] we will describe a method of combining the field models, as derived in this paper, with a general QGE temperature model, to obtain a complete equation of state in temperature and external field for fluid systems.

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