Gibbs vs. Non-Gibbs in the Equilibrium Ensemble Approach to Disordered Systems

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Abstract. We describe the salient ideas of the equilibrium ensemble approach to disordered systems, paying due attention to the appearance of non-Gibbsian measures. A canonical scheme of approximations — constrained annealing — is described and characterised in terms of a Gibbs' variational principle for the free energy functional. It provides a family of increasing exact lower bounds of the quenched free energy of disordered systems, and is shown to avoid the use of non-Gibbsian measures. The connection between the equilibrium ensemble approach and conventional low-concentration expansions or perturbation expansions about ordered reference systems is also explained. Finally applications of the scheme to a number of disordered Ising models and to protein folding are briefly reviewed.

1. Introduction

The statistical physics of systems with quenched disorder [1] continues to pose challenging problems, and is being put to work in an ever widening range of disciplines. Applications have not been confined to the study of conventional disordered solids, but rather proceeded to investigations of hard combinatorial optimisation, of neural networks, error-correcting codes, financial markets, the protein-folding problem, and more (for overviews describing some of these applications, see e.g. [2, 3]).

Systems with quenched disorder are notoriously difficult to analyse and generally much less well-understood than their ordered counterparts. Thus for instance, relatively few exact solutions of finite-dimensional systems with quenched disorder are known. Moreover, conventional approximation methods, such as perturbation or other series expansions, renormalisation group or Monte Carlo calculations, have in several cases produced conflicting, and sometimes even spurious results, when applied to disordered systems. This being so, having a broad range of alternative methods for the investigation of disordered systems at hand is always desirable, in particular, as it is well known that disorder is responsible for a range of interesting and potentially useful phenomena which have no counterpart in ordered systems — electron-localisation [4], Griffiths' singularities [5], or the universal glassy low-temperature anomalies originating from two-level tunnelling excitations [6] to name but a few.

The present contribution is devoted to the description of a method for investigating the statistical physics of systems with quenched disorder, which is originally due to Morita [7]. Morita's method proposes to treat disorder degrees of freedom of a quenched disordered system and dynamical variables proper on the same footing, and to introduce a disorder potential — i.e., an extensive interaction energy depending solely on the disorder degrees of freedom — which is added to the Hamiltonian of the disordered system, and chosen in such a way that disorder averaging becomes part of a thermal Gibbs averaging procedure in an enlarged phase space. The method is not widely known, but natural enough to have been considered, used or reinvented several times, and existing applications of it reveal considerable potential [8–15]. Recently the method has aroused some renewed interest [16, 17], when it was realized that the joint distributions of spin and disorder variables in systems with quenched randomness, in terms of which the method is initially formulated, are quite often non-Gibbsian, which created some concern about the validity of the method (see [18, 19]).

In the present paper we review some general aspects of the method, paying due attention to the possible appearance of non-Gibbsian measures, and we also describe some of the applications of the method, thereby trying to assess its strengths and weaknesses. Many, though not all, results presented below have appeared elsewhere in the literature before. For a detailed description of general aspects of the equilibrium ensemble approach, we refer in particular to [20].

The remainder of this paper is organised as follows. In Section 2 we shall give a brief outline of the general ideas underlying Morita's equilibrium ensemble approach to disordered systems. Section 3 describes constrained annealing as a canonical approximation scheme within the general approach. It is formulated in terms of a Gibbs' variational principle for the free energy functional, and is demonstrated to provide a family of increasing exact lower bounds of the quenched free energy of the disordered system, while avoiding the use of non-Gibbsian measures at any 'finite' level within the approximation scheme.

A complementary formulation of the variational approach, based on Jensen's inequality and without explicit reference to Gibbs' variational principle is also briefly described. Section 4 describes formal relations between Morita's approach and conventional low-concentration expansions or perturbation expansions about ordered reference systems. Section 5 finally reviews a number of applications of the scheme (i) spin diluted Ising models in one and 2 dimensions, (ii) mean-field systems with site disorder, such as the van Hemmen model, and the Curie–Weiss version of the random field ferromagnet, and (iii) an application to protein folding. We end with a summary and outlook in Section 6.

2. General theory

Systems with quenched disorder are characterised by two types of variable, the dynamical variables proper — to be collectively denoted by σ in the present paper — and the so-called configurational or disorder degrees of freedom, to be denoted by κ. Whereas the former attain thermal equilibrium on typical experimental time scales, the latter typically do not. Hence thermal equilibrium is incomplete, equilibrium of the dynamical degrees of freedom proper, being *conditioned* on the frozen disorder configuration κ.

The proper thermodynamic potential for the description of such systems is the so-called quenched free energy [1], i.e. the average of the configuration dependent free energy over the distribution describing the disorder

$$f_\Lambda^q = -(\beta|\Lambda|)^{-1}\langle\ln Z_\Lambda(\kappa)\rangle_{q_\Lambda}. \qquad (2.1)$$

We will typically be considering lattice systems, with Λ denoting a finite subset of a regular D-dimensional lattice, containing $|\Lambda|$ vertices. In (2.1), $q_\Lambda(\kappa)$ denotes the distribution describing the disorder, which is determined through the process of initial fabrication of the system, and thereafter considered independent of temperature or the fields the system might be exposed to.

The evaluation of the quenched free energy (2.1) is difficult, as it requires averaging the logarithm of the partition function, which usually precludes any useful factorisation of the averaging process even in situations where such factorisation is possible when considering the average of $Z_\Lambda(\kappa)$ itself. The presence of two kinds of variable in the problem that need to be treated on different footing is, among other things, responsible for the fact that the statistical physics of disordered systems is less well developed than that of their ordered counterparts.

In order to circumvent the complications associated with the evaluation of quenched disorder average (2.1), Morita [7] suggested to introduce an equivalent equilibrium ensemble in which configurational averaging, as embodied in (2.1), becomes part of a thermal averaging procedure in an enlarged phase space that is defined over both, the configurational degrees of freedom κ, and the dynamical variables proper. This is achieved by introducing a 'fictitious' disorder potential

$\phi_\Lambda(\kappa)$ which is added to the system Hamiltonian

$$\mathcal{H}_\Lambda(\sigma|\kappa) \rightarrow \mathcal{H}_\Lambda^\phi(\sigma, \kappa) = \mathcal{H}_\Lambda(\sigma|\kappa) + \phi_\Lambda(\kappa) \tag{2.2}$$

in such a way that the system described by $\mathcal{H}_\Lambda^\phi$ will have thermodynamic equilibrium properties identical to the non-equilibrium properties of the quenched system. This is achieved by demanding equality over the enlarged phase space of the Gibbs distribution $p_\Lambda^\phi(\sigma, \kappa)$ generated by $\mathcal{H}_\Lambda^\phi$, and the quenched joint distribution of dynamical and disorder degrees of freedom, $p_\Lambda^q(\sigma, \kappa)$,

$$p_\Lambda^q(\sigma, \kappa) \equiv \frac{q_\Lambda(\kappa)}{Z_\Lambda(\kappa)} \exp\left[-\beta \mathcal{H}_\Lambda(\sigma|\kappa)\right] = \frac{1}{Z_\Lambda^\phi} \exp\left[-\beta \mathcal{H}_\Lambda^\phi(\sigma, \kappa)\right] \equiv p_\Lambda^\phi(\sigma, \kappa). \tag{2.3}$$

This condition is easily solved for $\phi_\Lambda(\kappa)$, giving

$$\beta \phi_\Lambda(\kappa) = -\ln\left[q_\Lambda(\kappa)/Z_\Lambda(\kappa)\right] - \ln Z_\Lambda^\phi, \tag{2.4}$$

an equation to which we shall refer to as the Morita equation.

Normalising ϕ_Λ in such a way that its average over the quenched disorder distribution vanishes, $\langle \phi_\Lambda(\kappa) \rangle_{q_\Lambda} = 0$, one obtains

$$-\beta F_\Lambda^\phi = \ln Z_\Lambda^\phi = \langle \ln Z_\Lambda(\kappa) \rangle_{q_\Lambda} - \langle \ln q_\Lambda(\kappa) \rangle_{q_\Lambda}, \tag{2.5}$$

rendering the free energy of equilibrium ensemble in this normalization equal to free energy of system with quenched disorder — up to a temperature and field-independent contribution that is readily identified as an entropy of mixing (or a complexity). At first sight, therefore, these results appear sufficient to demonstrate that an equivalent Gibbs equilibrium ensemble for the description of systems with quenched disorder *exists*.

However, note the following. The full specification of the disorder potential using (2.4) and (2.5),

$$\beta \phi_\Lambda(\kappa) = -\left[\ln \frac{q_\Lambda(\kappa)}{Z_\Lambda(\kappa)} - \left\langle \ln \frac{q_\Lambda(\kappa)}{Z_\Lambda(\kappa)} \right\rangle_{q_\Lambda}\right] \tag{2.6}$$

requires the evaluation of free energies for *every* disorder configuration, over and above that of its configuration average, not to speak of the difficulties of solving or analysing models with a contribution to the interaction potential as complicated as (2.6).

Moreover, as the thermodynamic limit $|\Lambda| \rightarrow \infty$ is taken, the *potential ϕ_Λ inherits all singularities of the quenched free energy of the system* under investigation. E.g., for spin- or bond-diluted Ising ferromagnets it will, for all levels of dilution, exhibit Griffiths' singularities at all temperatures below the transition temperature of the pure system [5]. This is related to another observation that

was recently made [16, 17], namely that joint distributions of spin and disorder variables in systems with quenched randomness are quite often non-Gibbsian. That is, the joint distribution p_Λ^ϕ with its *formally* Gibbsian specification in terms of $\mathcal{H}_\Lambda^\phi$ may turn out to be *non-Gibbsian* in the thermodynamic limit due to non-localities appearing in ϕ_Λ. Thus Morita's equilibrium ensemble approach seems to be entirely formal: despite appearances, the Gibbs measure p_Λ^ϕ may turn out to be non-Gibbsian after all, as the thermodynamic limit is taken.

The fact that similar occurrences of non-Gibbsian measures are responsible for some of the pathologies of real-space renormalisation group transformations [21], led van Enter et al. to raising concerns [18] that the equilibrium ensemble approach applied to the spin-diluted 2-D Ising model in [13] was ill defined for the model under consideration.

In what follows, a canonical approximation scheme for the equilibrium ensemble will be described which provides a family of increasing exact variational lower bounds of the quenched free energy of disordered systems, and which is shown to avoid the use of non-Gibbsian measures and thus appears to be perfectly well defined.

3. Constrained annealing — generalised grand ensembles

Scepticism concerning fundamental properties of the equilibrium ensemble approach aside — the general formulation of the method as described above is clearly not very useful in practice. It appears to *require* the very quantities it was originally *meant to deliver*.

The present section demonstrates that this is not quite the case. It also uses a formulation of the equilibrium ensemble idea that readily lends itself to a systematic scheme of approximations — more precisely perhaps — a formulation that is conceived as providing approximate descriptions of quenched disorder from the outset. This scheme of approximations can, at least in principle, proceed all the way to exact solutions, and avoids the use of non-Gibbsian measures all along.

3.1. Gibbs' variational principle with constraints

Morita's equilibrium ensemble approach is here introduced in terms of Gibbs' variational principle supplemented by a set of constraints arising from the description of quenched disorder. In order to simplify reasoning (and notation), we initially restrict ourselves to the description of systems with bimodal bond or site-disorder; for a more general outline of these ideas, see [20].

We assume that the disorder configurations can be specified in terms of occupation numbers $\{k_a\}$, with $k_a \in \{0, 1\}$, as

$$\kappa = \{k_a;\ a \in \Lambda\} \equiv \{a \in \Lambda;\ k_a = 1\}, \tag{3.1}$$

where Λ either denotes the set of vertices of a regular lattice (in the case of site-disorder), or the set of edges (in the case of bond-disorder). The k_a take the values 0 or 1, according to whether a site is occupied by one sort of particle or the other, or according to whether a bond-strength takes one or the other of two possible values.

For *independent* occupancy of vertices/bonds, the distribution of disorder configurations can be characterised in terms of independent distributions of Bernoulli trials at density ρ, as

$$q_\Lambda(\kappa) = \prod_{a \in \Lambda} \rho^{k_a}(1-\rho)^{1-k_a} = \rho^{|\kappa|}(1-\rho)^{|\Lambda|-|\kappa|}, \qquad (3.2)$$

or equivalently in terms of its complete set of moments

$$\left\langle \prod_{a \in \omega} k_a \right\rangle_{q_\Lambda} = \langle k_\omega \rangle_{q_\Lambda} = \rho^{|\omega|} = f_\omega, \quad \omega \in \mathcal{P}(\Lambda), \qquad (3.3)$$

where $\mathcal{P}(\Lambda)$ is the power-set of the set of sites/bonds of the system.

The equilibrium ensemble's joint distribution of disorder degrees of freedom and dynamical variables proper is now introduced in terms of a Gibbs variational principle for the free energy functional

$$F_\Lambda[p_\Lambda] = \sum_{\sigma,\kappa} p_\Lambda(\sigma,\kappa) \mathcal{H}_\Lambda(\sigma|\kappa) + \beta^{-1} \sum_{\sigma,\kappa} p_\Lambda(\sigma,\kappa) \ln p_\Lambda(\sigma,\kappa) \qquad (3.4)$$

subject to constraints given by the moments of quenched disorder distribution.

That is, the distribution $p_\Lambda^{\mathcal{Q}}$ is defined as the (unique!) minimiser of $F_\Lambda[p_\Lambda]$ subject to constraints as follows,

$$F_\Lambda[p_\Lambda^{\mathcal{Q}}] = \min_{p_\Lambda} \left\{ F_\Lambda[p_\Lambda]; \ \langle k_\omega \rangle_{p_\Lambda} = f_\omega \ , \ \omega \in \mathcal{Q} \subseteq \mathcal{P}(\Lambda) \right\}. \qquad (3.5)$$

Here $\mathcal{Q}$ may — but need not — be a proper subset of $\mathcal{P}(\Lambda)$; if it *is*, $p_\Lambda^{\mathcal{Q}}$ provides only a variational *approximation* to the full joint distribution of disorder degrees of freedom and dynamical variables proper of the system with quenched disorder. Note that $\omega = \emptyset$ must always be contained in $\mathcal{Q}$, as the corresponding constraint defines the normalisation condition for $p_\Lambda^{\mathcal{Q}}$. Note also that treating disorder distributions other than independent Bernoulli trials appears to be a straightforward exercise within the present formulation, requiring just an appropriate modification of the f_ω.

Introducing Lagrange multipliers $\{\lambda_\omega\}_{\omega \in \mathcal{Q}}$ to take constraints into account, one may express the minimiser $p_\Lambda^{\mathcal{Q}}$ as

$$p_\Lambda^{\mathcal{Q}}(\sigma,\kappa) = \frac{1}{\mathcal{Z}_\Lambda^{\mathcal{Q}}} \exp\left[-\beta \mathcal{H}_\Lambda(\sigma|\kappa) + \sum_{\omega \in \mathcal{Q}_\emptyset} \lambda_\omega k_\omega(\kappa) \right]. \qquad (3.6)$$

In (3.6), the Lagrange multiplier $\lambda_\emptyset$ was treated as special and re-expressed in terms of the equilibrium ensemble's partition sum $\mathcal{Z}_\Lambda^\mathcal{Q}$, so $\mathcal{Q}_\emptyset = \mathcal{Q} \setminus \emptyset$. The λ_ω must be determined as functions of temperature and fields in such a way that $p_\Lambda^\mathcal{Q}$ shares the specified moments with the quenched disorder distribution.

Note that the λ_ω are like generalised chemical potentials in terms of which average set-occupancies $\langle k_\omega \rangle_{p_\Lambda}$ are controlled. In this sense the equilibrium ensemble constitutes nothing but a generalisation of the idea of grand-canonical ensembles.

From the generalised grand potential

$$\Omega_\Lambda^\mathcal{Q} = -\beta^{-1} \ln \mathcal{Z}_\Lambda^\mathcal{Q} \tag{3.7}$$

the corresponding free energy is obtained via a Legendre transform

$$F_\Lambda^\mathcal{Q} = \Omega_\Lambda^\mathcal{Q} + \beta^{-1} \sum_{\omega \in \mathcal{Q}_\emptyset} \lambda_\omega f_\omega = \Omega_\Lambda^\mathcal{Q} - \sum_{\omega \in \mathcal{Q}_\emptyset} \lambda_\omega \frac{\partial \Omega_\Lambda^\mathcal{Q}}{\partial \lambda_\omega}. \tag{3.8}$$

This may be interpreted as a redefinition of the Morita potential according to

$$-\beta \phi_\Lambda^\mathcal{Q}(\kappa) = \sum_{\omega \in \mathcal{Q}_\emptyset} \lambda_\omega k_\omega(\kappa) \quad \rightarrow \quad \sum_{\omega \in \mathcal{Q}_\emptyset} \lambda_\omega \big(k_\omega(\kappa) - f_\omega \big), \tag{3.9}$$

which ensures that its configuration average *vanishes*.

Note the following features: (i) If $\mathcal{Q}$ is a proper subset of $\mathcal{P}(\Lambda)$, the description of disorder is approximate. (ii) In this case the values of the Lagrange multipliers λ_ω depend on the level of approximation, i.e. on the choice of $\mathcal{Q}$, hence $\lambda_\omega = \lambda_\omega^\mathcal{Q}$. (iii) The scheme provides a *variational family of increasing exact lower bounds* for the free energy of systems with quenched randomness in the sense that

$$F_\Lambda^\mathcal{Q} \leq F_\Lambda^{\mathcal{Q}'} \leq F_\Lambda^\phi, \quad \text{if} \quad \mathcal{Q} \subseteq \mathcal{Q}' \subseteq \mathcal{P}(\Lambda). \tag{3.10}$$

(iv) As long as the maximum diameter of the sets ω in $\mathcal{Q}$ is kept finite, the approximating scheme furnishes approximate descriptions of the system *in terms of Gibbs measures* on the joint space of dynamical and disorder degrees of freedom. These measures agree on an increasing set of moments with the measure characterising the quenched disorder, as the size of $\mathcal{Q}$ is increased.

In this sense, the approximation scheme defined by (3.5) is perfectly well defined [19, 20]. A major issue from a pragmatic point of view then is that of the *efficiency* of the method in analysing unsolved problems in the physics of systems with quenched randomness.

Before turning to that issue, we shall briefly describe another line of reasoning, which highlights the variational content of the equilibrium ensemble approach, and which is better suited to cases where the disorder is not of the bimodal type.

3.2. Variational bounding of free energies using convexity

From what has been said above, it transpires that the equilibrium ensemble approach could have been formulated as a variational problem right from the outset. This variational point of view was taken by Georges et al. [10] in their computation of phase-boundaries of bond-disordered 2-D Ising models — without, however, connecting it to the equilibrium ensemble idea and to the heuristics associated with it, and apparently without the awareness that it allows proceeding to exact descriptions of quenched disorder.

To see the variational content of the approach, it is useful to interpret the equilibrium ensemble's partition function as a *functional* of ϕ_Λ,

$$
\begin{aligned}
Z_\Lambda^\phi = Z_\Lambda[\phi_\Lambda] &= \sum_{\sigma,\kappa} \exp\left[-\beta\mathcal{H}_\Lambda(\sigma|\kappa) - \beta\phi_\Lambda(\kappa)\right] \\
&= \sum_\kappa Z_\Lambda(\kappa)\exp\left[-\beta\phi_\Lambda(\kappa)\right],
\end{aligned} \tag{3.11}
$$

and rewrite it as an average over the disorder

$$
Z_\Lambda[\phi_\Lambda] = \left\langle Z_\Lambda(\kappa)\exp\left[-\beta\phi_\Lambda(\kappa) - \ln q_\Lambda(\kappa)\right]\right\rangle_{q_\Lambda}. \tag{3.12}
$$

In case of continuous disorder distributions, the κ-sums above are to be read as integrals. By Jensen's inequality (for *arbitrary* ϕ_Λ with $\langle\phi_\Lambda(\kappa)\rangle_{q_\Lambda} = 0$)

$$
\ln Z_\Lambda[\phi_\Lambda] \geq \left\langle \ln Z_\Lambda(\kappa)\right\rangle_{q_\Lambda} - \left\langle \ln q_\Lambda(\kappa)\right\rangle_{q_\Lambda}, \tag{3.13}
$$

with equality *iff*

$$
\ln Z_\Lambda(\kappa) - \beta\phi_\Lambda(\kappa) - \ln q_\Lambda(\kappa) = \text{const.} = \ln Z_\Lambda^\phi. \tag{3.14}
$$

This is nothing but Morita's equation (2.4). It is the formal solution of the variational problem

$$
\frac{\delta \ln Z_\Lambda[\phi_\Lambda]}{\delta\phi_\Lambda(\kappa)} = 0, \tag{3.15}
$$

constrained to ϕ's of zero mean. As before, this procedure will generate non-Gibbsian measures, *unless* one turns to approximations by restricting domain of definition of $Z_\Lambda[\phi_\Lambda]$, e.g. to functions ϕ_Λ of finite range, or to functions defining summable interactions potentials. In so doing, one would restore Gibbsianness within the approximation scheme. Again, it is easily seen that the scheme provides a family of exact lower bounds to the quenched free energy of the system — bounds which increase when the domain of definition of the functional $Z_\Lambda[\phi_\Lambda]$ is enlarged.

4. Low-concentration expansions and perturbation theory

Another connection that we are going to explain here is the relation between the equilibrium ensemble approach and low concentration expansions and perturbative expansions about pure reference systems. For simplicity we restrict ourselves once more to systems with bimodal bond/site-disorder as specified in (3.1)–(3.3). The ideas are more thoroughly explained in [20].

For systems with bimodal bond or site disorder, the relation with low-concentration expansions is established by considering Morita's equation (2.4),

$$\beta\phi_\Lambda(\kappa) = -\ln\left[q_\Lambda(\kappa)/Z_\Lambda(\kappa)\right] - \ln Z_\Lambda^\phi$$

with the representation

$$\beta\phi_\Lambda(\kappa) = -\sum_{\emptyset\neq\omega\subseteq\Lambda} \lambda_\omega\left(k_\omega(\kappa) - \rho^{|\omega|}\right), \tag{4.1}$$

and by solving it iteratively for a suitably chosen sequence of disorder configurations κ.

Combining the cases (i) $\kappa = \emptyset$, and (ii) $\kappa \neq \emptyset$ gives

$$\sum_{\emptyset\neq\omega\subseteq\kappa} \lambda_\omega = -|\kappa|\ln\left[\frac{1-\rho}{\rho}\right] - \ln Z_\Lambda(\kappa) + \ln Z_\Lambda(\emptyset), \quad \forall\, \kappa \neq \emptyset. \tag{4.2}$$

Define x_ω recursively via

$$\ln Z_\Lambda(\kappa) = \sum_{\omega\subseteq\kappa} \ln x_\omega, \tag{4.3}$$

which can be inverted to give

$$\ln x_\omega = \sum_{\kappa\subseteq\omega} (-)^{|\omega|-|\kappa|} \ln Z_\Lambda(\kappa). \tag{4.4}$$

Inserting these relations into the $\kappa = \emptyset$-version of the Morita equation one obtains

$$\ln Z_\Lambda^\phi = -|\Lambda|\left[\rho\ln\rho + (1-\rho)\ln(1-\rho)\right] + \sum_{\omega\subseteq\Lambda} \rho^{|\omega|}\ln x_\omega, \tag{4.5}$$

which is nothing but a low concentration expansion of the free energy of the quenched system (including the contribution of the entropy of mixing). With (4.4) it can be recast into

$$\ln Z_\Lambda^\phi = -|\Lambda|\left[\rho\ln\rho + (1-\rho)\ln(1-\rho)\right] + \sum_{\kappa\subseteq\Lambda} \rho^{|\kappa|}(1-\rho)^{|\Lambda|-|\kappa|}\ln Z_\Lambda(\kappa), \tag{4.6}$$

which makes the Brout configuration average of the free energy explicit.

Note that we have not specified the *meaning* of the $\kappa = \emptyset$ configuration — for a diluted spin-system it could either mean the system without spins or the system without vacancies. Thus, the above expressions, if combined with the appropriate definitions of the x_ω, could formally be interpreted either as low concentration expansions, or as expansions about the pure reference system.

5. Applications

Having explained the general and formal aspects of the equilibrium ensemble approach, we now turn to briefly reviewing some applications, so as to illustrate the strengths and weaknesses of the method.

5.1. The 1-*D* spin-diluted Ising chain

This application is mainly chosen, because it provides a simple, yet non-trivial system where approximate solutions obtained via the equilibrium ensemble approach can be compared with exact results, allowing to get an impression about the efficiency of the method. The results of this section have not previously appeared in the literature.

The Hamiltonian of the system is

$$\mathcal{H}_\Lambda(\sigma|\kappa) = -J \sum_{i=1}^{N} k_i \sigma_i k_{i+1} \sigma_{i+1} - h \sum_{i=1}^{N} k_i \sigma_i. \tag{5.1}$$

Periodic boundary conditions are assumed, and $|\Lambda| = N$.

In Figure 1, we compare the zero-temperature magnetisation of the exact solution [23] with that of the first sensible approximation that may be formulated within the equilibrium ensemble approach. It consists in introducing two chemical potentials to control the constraints of average occupancy of lattice sites, as well as nearest neighbour occupancy. Thus, for a quenched system at density ρ of magnetic impurities, one introduces

$$-\beta\phi_\Lambda(\kappa) = \lambda_1 \sum_{i=1}^{N} (k_i - \rho) + \lambda_2 \sum_{i=1}^{N} (k_i k_{i+1} - \rho^2), \tag{5.2}$$

and determines λ_1 and λ_2 so as to enforce

$$\langle k_i \rangle_{p_\Lambda} = \rho,$$
$$\langle k_i k_{i+1} \rangle_{p_\Lambda} = \rho^2.$$

The following features deserve mention [22]. On the positive side: (i) It can be shown that, whereas the present approximation is exact at $B = 0$ and
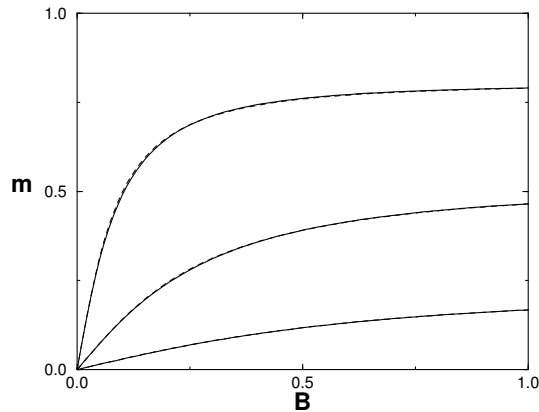
Figure 1. Zero temperature magnetisation of the spin-diluted Ising chain as a function of $B = \beta h$, for various spin-densities ρ. From top to bottom the curves correspond to $\rho = 0.8$, $\rho = 0.5$, and $\rho = 0.2$. Full lines represent the exact solution, dashed lines the first sensible approximation within the equilibrium ensemble approach, as described in the main text.

in the limit $B \to \infty$, an infinite number of constraints need to be taken into account for all finite nonzero B to arrive at the exact solution. Still the first sensible approximation is very close to the exact solution at all B. (ii) The present approximation reproduces the exact scaling forms of thermodynamic functions in the vicinity of the multi-critical point at $T = B = 0$, $\rho = 1$. On the negative side: (iii) No finite approximation within the scheme will exhibit Griffiths' singularities of the exact solution [23] at $T = B = 0$.

5.2. The 2-D spin-diluted Ising model

The rather impressive performance of the method in the case of the 1-D chain naturally prompted attempts to use it for studying properties of the phase transition to magnetic order in 2-D [13, 14].

Ad hoc variants of the grand-ensemble approach had been used earlier to obtain fairly accurate approximations for transition lines in 2-D bond-disordered systems [8–10]. These calculations are usually facilitated by the fact that the equilibrium ensemble's free energy for simple approximations of bond-disorder may be mapped onto that of the pure system at renormalised values of bond strengths.

In [13, 14], the equilibrium ensemble approach is combined with Nightingale's phenomenological renormalisation group scheme [24] to investigate criti-
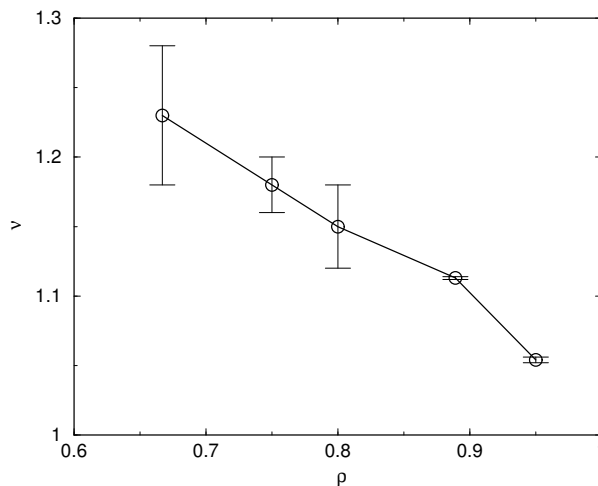
Figure 2. Critical exponent ν of the correlation length obtained by extrapolations of finite-size scaling approximants $\nu_{eff}(L)$ using strip-widths up to $L = 13$. Data taken from [14]. The connecting line is merely a guide to the eye. Error bars refer to the insecurity of the extrapolation. They are set by comparing results from several extrapolation methods [14].

cal behaviour of the 2-D spin-diluted Ising model. The phase-digram obtained in [13, 14] is very accurate if measured by the exactly known results about the transition line of the system, which are all reproduced to within small fractions of a percent. As far as critical exponents are concerned, the scenario appears to be of 'weak-universality' type, that is, the critical exponent ν was found to vary continuously with ρ as shown in Figure 2, whereas η and the ratio γ/ν were found to be independent of the degree of dilution and equal to the pure system values to within $\mathcal{O}(10^{-4})$ [13, 14]. The usual scaling relations imply that other exponents such as α, β, or γ would individually also vary with disorder, while δ and ratios such as α/ν and β/ν would remain constant just like γ/ν. The results are in quantitative and qualitative accord with those of an independent Monte Carlo simulation [25].

These findings are in contrast to expectations derived from field-theoretical investigations of systems with infinitesimally weak disorder [26, 27], which predicted critical behaviour as in the pure system modified only by logarithmic corrections. There are a number of Monte Carlo and transfer-matrix strip-scaling [28], as well as series expansion [29] investigations devoted to testing the validity of the field-theoretical results. They are mostly concerned with bond-disorder (as that case offers a simple way to locate the transition point using

duality) and need to depart from the infinitesimal disorder limit, in order to see effects of disorder on critical behaviour at all. In their majority these investigations claim to confirm the logarithmic corrections scenario of [26, 27]. However, as carefully discussed in [14], these studies may perhaps not be as decisive on this matter as their authors have tended to believe. Thus, it is perhaps fair to say that the issue concerning the correct description of the critical behaviour of 2-D disordered ferromagnetic Ising models is still unresolved.

5.3. Random-site mean-field models

The equilibrium ensemble approach has been used to solve simple mean-field models with site-randomness, such as the van Hemmen spin-glass model [30] solved in [11] and the mean-field version of the random field Ising model (RFIM) [12]. Both provide cases where simple approximations within the constrained annealing scheme described in Section 3 already provide *exact* solutions to the model with quenched disorder. Technically the two cases are treated in a similar fashion, the RFIM being even simpler than the spin-glass model.

For the lattice version of the RFIM in $D \geq 3$, joint measures on the space of spin and disorder variables were recently demonstrated to be almost surely non-Gibbsian in the multi-phase region [17], a property which was thereafter demonstrated to persist in the mean-field limit in the form of almost sure discontinuity of conditional probabilities as functions of the conditioning [31].

In the light of these findings, and also, because the mean-field version of the RFIM is technically very simple to solve, both directly and via the equilibrium ensemble approach, we will review these solutions in what follows, demonstrating their equivalence at the level of equations of state.

The Hamiltonian of the mean-field RFIM containing $|\Lambda| = N$ spins takes the form

$$\mathcal{H}_\Lambda(\sigma|\kappa) = -\frac{J}{2N} \sum_{i,j} \sigma_i \sigma_j - h \sum_i k_i \sigma_i. \tag{5.3}$$

A bimodal field distribution is assumed, i.e. $k_i = \pm 1$ with probability $1/2$, and the k_i are taken to be independent. The solution of this model follows standard reasoning.

The partition sum at a given configuration of the disorder variables, is

$$Z_\Lambda(\kappa) = \sum_\sigma \exp\left\{\frac{\beta J}{2N}\left(\sum_i \sigma_i\right)^2 + \beta h \sum_i k_i \sigma_i\right\}. \tag{5.4}$$

A Gauss–Hubbard–Stratonovich transformation is invoked to decouple spins and do the single-site partition functions

$$Z_\Lambda(\kappa) = \int \frac{dm}{\sqrt{2\pi/(\beta J N)}} \exp\left\{N\left[-\frac{\beta J}{2}m^2 + \frac{1}{N}\sum_i \ln 2\cosh[\beta(Jm + hk_i)]\right]\right\}. \tag{5.5}$$

As $N \to \infty$, the m integral is evaluated by the Laplace method, being dominated by $m = m_\Lambda(\kappa)$ which solves the fixed point equation

$$m = \frac{1}{N} \sum_i \tanh\left[\beta(Jm + hk_i)\right]. \tag{5.6}$$

In the large-system limit the right-hand side of (5.6) is almost surely given by the average over the disorder distribution,

$$\frac{1}{N} \sum_i \tanh\left[\beta(Jm+hk_i)\right] \longrightarrow \frac{1}{2}\tanh\left[\beta(Jm+h)\right] + \frac{1}{2}\tanh\left[\beta(Jm-h)\right]. \tag{5.7}$$

So we have

$$m = \frac{1}{2}\tanh\left[\beta(Jm + h)\right] + \frac{1}{2}\tanh\left[\beta(Jm - h)\right] \tag{5.8}$$

as the equation of state of the system.

The same equation of state is readily obtained within the equilibrium ensemble formalism by taking only a single constraint into account, thereby avoiding the introduction of additional non-local interactions over and above those used to define the mean-field limit. Indeed, as the system is of mean-field type, it suffices to control the average $N^{-1}\sum_i k_i$ via a suitable chemical potential in an approach that treats the σ_i and the k_i on the same footing in the spirit of the equilibrium ensemble approach [12]. So the modified Hamiltonian is

$$\mathcal{H}_\Lambda^\phi(\sigma, \kappa) = -\frac{J}{2N} \sum_{i,j} \sigma_i \sigma_j - h \sum_i k_i \sigma_i - \mu \sum_i k_i, \tag{5.9}$$

and the grand ensemble's partition function

$$Z_\Lambda^\phi = \sum_{\sigma,\kappa} \exp\left\{ \frac{\beta J}{2N} \left(\sum_i \sigma_i\right)^2 + \beta h \sum_i k_i \sigma_i + \beta\mu \sum_i k_i \right\}. \tag{5.10}$$

As before, a Gauss–Hubbard–Stratonovich transformation is used to decouple spins to give

$$Z_\Lambda^\phi = \int \frac{dm}{\sqrt{2\pi/(\beta JN)}} \exp\left\{ N\left[-\frac{\beta J}{2}m^2 + \ln \sum_{k=\pm 1} 2\cosh[\beta(Jm + hk)]\, e^{\lambda k} \right] \right\}, \tag{5.11}$$

where we abbreviated $\lambda = \beta\mu$. Again, the Laplace method is used to evaluate the integral; this gives a fixed point equation for m of the form

$$m = \frac{\sum_{k=\pm 1} \sinh[\beta(Jm + hk)]\, e^{\lambda k}}{\sum_{k=\pm 1} \cosh[\beta(Jm + hk)]\, e^{\lambda k}}. \tag{5.12}$$

The Lagrange parameter λ must be determined to give

$$\langle k \rangle_{p_\Lambda^\phi} = N^{-1} \partial \ln Z_\Lambda^\phi / \partial \lambda = 0,$$

$$\langle k \rangle_{p_\Lambda^\phi} = \frac{\sum_{k=\pm 1} k \cosh[\beta(Jm + hk)] \, e^{\lambda k}}{\sum_{k=\pm 1} \cosh[\beta(Jm + hk)] \, e^{\lambda k}} = 0. \tag{5.13}$$

This requires

$$\cosh[\beta(Jm + h)] \, e^\lambda = \cosh[\beta(Jm - h)] \, e^{-\lambda}. \tag{5.14}$$

Upon inserting this into the fixed point equation (5.12) for m, one obtains

$$m = \frac{1}{2} \tanh\left[\beta(Jm + h)\right] + \frac{1}{2} \tanh\left[\beta(Jm - h)\right] \tag{5.15}$$

for the equation of state, i.e. the same equation as when using the direct way.

This result [12] — simple and reassuring as it is — must be regarded as remarkable in the light of concerns raised about the appearance of non-Gibbsian measures within the equilibrium ensemble approach [16–18] and the identification of the RFIM as providing a realization of a system exhibiting almost surely non-Gibbsian joint measures [17, 31].[1]

5.4. An application to protein folding

The application of the equilibrium ensemble approach to a problem in the theory of protein folding finally provides a case, where neither conventional approaches nor the equilibrium ensemble approach have as yet produced fully plausible results, but where the investigation based on the equilibrium ensemble idea appears to have produced some improvement over conventional approaches.

The model is a lattice version of the random hydrophilic-hydrophobic model originally introduced by Obukhov [32] in which the monomers along a heteropolymer chain are randomly either hydrophilic or hydrophobic, and interact with the solvent through a short range two-body interaction. The energetics of the chain conformation is supposed to be negligible, apart from the self-avoidance constraint. The conformational statistics of this system were investigated in a continuum formulation by Garel et al. [33]. A 2-D lattice version was investigated via the equilibrium ensemble approach by Trovato et al. [15]. The Hamiltonian for a chain of length $|\Lambda| = N$ is

$$\mathcal{H}_\Lambda(z|\kappa) = -\sum_{i=0}^{N} k_i z_i, \tag{5.16}$$

where the sum is over the $N + 1$ sites of the lattice visited by a self-avoiding N-step walk, the z_i is the number of nearest neighbour contacts of monomer i

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[1] See the Note Added at the end of this paper.

with solvent molecules, i.e. the number of nearest neighbour sites of monomer i *not* visited by the walk.[2] The hydrophilicities k_i are taken to be independent identically distributed random variables with a Gaussian probability density

$$q(k_i) = \frac{1}{\sqrt{2\pi\sigma_k^2}} \exp\Big[-\frac{(k_i - \overline{k})^2}{2\sigma_k^2} \Big]. \tag{5.17}$$

The canonical partition function of the system is

$$Z_\Lambda(\kappa) = \sum_{W_N} \exp\Big[\beta \sum_{i=0}^{N} k_i z_i \Big], \tag{5.18}$$

where the sum is over all self-avoiding walks of N steps.

Trovato et al. [15] consider 3 approximations, (i) the annealed approximation, obtained by performing a simple average of the partition function

$$Z_\Lambda^a = \langle Z_\Lambda(\kappa) \rangle_{q_\Lambda} = \sum_{W_N} \exp\Big[\beta\overline{k} \sum_{i=0}^{N} z_i + \frac{\beta^2\sigma_k^2}{2} \sum_{i=0}^{N} z_i^2 \Big] \tag{5.19}$$

and two constrained annealed approximations, in which (ii) the average hydrophilicity is fixed at its quenched value $\overline{k}$

$$\frac{1}{N}\Big\langle \sum_i k_i \Big\rangle_{p_\Lambda} = \overline{k}, \tag{5.20}$$

and (iii) both average hydrophilicity (5.20), and its global variance

$$\frac{1}{N}\Big\langle \sum_i (k_i - \overline{k})^2 \Big\rangle_{p_\Lambda} = \sigma_k^2 \tag{5.21}$$

are fixed at their quenched values. This is achieved by introducing disorder potentials à la Morita of the form

$$-\beta\phi_\Lambda(\kappa) = \sum_i \ln q(k_i) + \lambda_1 \sum_i (k_i - \overline{k}) + \lambda_2 \sum_i \big(k_i^2 - (\overline{k}^2 + \sigma_k^2) \big), \tag{5.22}$$

which includes the (logarithm of the) quenched distribution as an offset. It describes the annealed approximation and the constrained annealed system in which only the average hydrophilicity is fixed as special cases for $\lambda_1 = \lambda_2 \equiv 0$, and $\lambda_2 \equiv 0$, respectively. In all cases a partial partition function — the

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[2]For the sake of readability, we have in our review of the results of Trovato et al. adapted some of their notation to that used in the present paper.

integrals over the hydrophlicities k_i — can be performed, leading to an effective
homopolymer-model described by the remaining effective partition sum

$$Z_\Lambda^{eff} = \sum_{W_N} \exp\left[N\beta_0 + \beta_1 \sum_{i=0}^{N} z_i + \beta_2 \sum_{i=0}^{N} z_i^2\right], \qquad (5.23)$$

in which the β_i are functions of temperature which depend on the average
hydrophilicity $\overline{k}$ and its variance σ_k^2, and on the level of approximation chosen
to describe the disorder.

In (5.23), β_0 is an irrelevant constant and $\beta_2 \geq 0$ by construction. The phase
diagram of the model in the (β_1, β_2)-plane exhibits the following salient features.
For $\beta_2 = 0$ there is a critical value $\beta_1^* < 0$ at which the chain undergoes a 2nd
order (tri-critical) θ-transition from a swollen phase at $\beta_1 > \beta_1^*$ to a collapsed
phase at $\beta_1 < \beta_1^*$. The tri-critical θ-point extends as a tri-critical line into
the region $\beta_2 > 0$, but eventually ends in a tetra-critical point (β_1^m, β_2^m), from
where — on further increase of β_2 — it continues as a coexistence line between
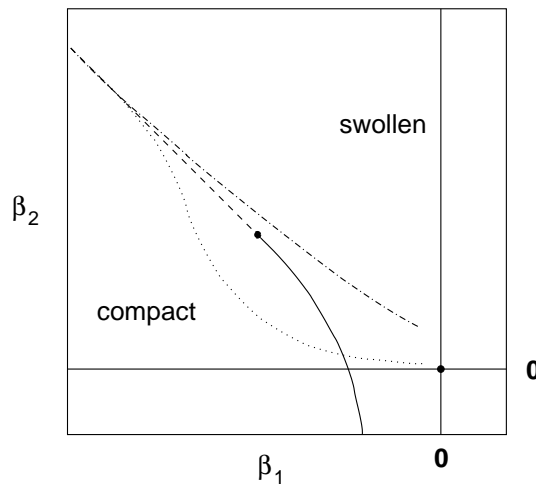swollen and compact phase (see Figure 3).

Figure 3. Generic phase diagram in the (β_1, β_2)-plane. The solid line is the
tricritical θ-line; it ends in a multicritical point and continues as a (dashed)
coexistence line. The two other lines describe generic trajectories in constrained
annealed systems of either type (ii) or (iii), as described in the main text, for
$\overline{k}_{eff} < \overline{k}_m$ (dotted) and for $\overline{k}_{eff} > \overline{k}_m$ (dot-dashed), respectively (after [15]).

The strategy of [15] then is to follow the (β_1, β_2) trajectory in the various
approximations, as temperature of the system is varied. A transfer-matrix tech-

nique is used to study the system on $n \times \infty$-strips of finite width n, and the trend of the data with increasing strip-widths is extracted.

Their results are as follows. The decisive system parameter is the ratio of average hydrophilicity and its variance, $\overline{k}_{eff} = \overline{k}/\sigma_k$.

(i) In the annealed approximation, chains which in the quenched version are on average hydrophilic, $\overline{k}_{eff} > 0$, are always found to be in a swollen phase. Chains that are on average hydrophobic, $\overline{k}_{eff} < 0$, are (for entropic reasons) in a swollen phase at high-temperatures, and undergo a 2nd order swollen-to-collapsed θ-transition as the temperature is lowered. Remarkably there is another 1st order reentrant transition into the swollen phase at still lower temperatures. The latter transition must be regarded as an artifact of the annealed approximation. The corresponding annealed version of the continuum theory [33] produces a result which is less plausible, in that even strongly hydrophilic chains are predicted to be in a collapsed phase at low temperatures, a feature which according to [33] persists in their quenched calculation.

(ii) In a constrained annealed system which fixes the average hydrophilicity at its quenched value, there is a particular value $\overline{k}_m < 0$, such that systems which are on average less hydrophobic, $\overline{k}_{eff} > \overline{k}_m$, are in their swollen phase at high temperatures, but hit the two-phase coexistence line at sufficiently low temperatures, whereas systems which are on average more hydrophobic, $\overline{k}_{eff} < \overline{k}_m$, first undergo a swollen-to-collapsed θ-transition, and then hit the coexistence line as the temperature is lowered further. In both cases, the swollen and collapsed fractions in coexistence become equal in the $T \to 0$-limit.

(iii) In a constrained annealed system which fixes both the average hydrophilicity and its variance at their quenched values, the qualitative behaviour is similar, the main difference being that the asymptotic fractions of collapsed and swollen phases at low-temperature coexistence, now depend on $\overline{k}_{eff}$, the collapsed fraction approaching 1, as $\overline{k}_{eff} \to -\infty$, and 0, as $\overline{k}_{eff} \to +\infty$.

While approximations (ii) and (iii) do constitute improvements over the annealed results, and the improvement of (iii) upon (ii) concerning asymptotic fractions of swollen and collapsed phases goes into the right direction, the very phenomenon of low-temperature phase-separation is most likely still unphysical. To improve upon it, one would — as correctly remarked in [15] — have to control *local* correlations $\langle k_i k_{i+s} \rangle$ of hydrophilicities along the chain. As this was hardly feasible with the numerical methods used in [15], this possibility has been left unexplored so far. However, it is conceivable that such refined approximations could be successfully implemented by returning to a continuum version of the theory.

Remarkably, the expression for the free energy in approximation (ii) [15] coincides, in fact, with that obtained in the continuum calculation [33] for the fully quenched system, although the conclusions drawn in [33] where quite different (namely that behaviour of the quenched system would not qualitatively differ from that of the annealed system). This could be traced back [15] to a

sub-optimal variational ansatz being used for evaluating the free energy in [33]. It would also have to imply that the results so far obtained in the continuum approximation are not yet the end of the story.

6. Summary and outlook

We have described the key ideas of Morita's equilibrium ensemble approach to disordered systems. A canonical scheme of approximations — constrained annealing — has been described and introduced in terms of a Gibbs' variational principle for a free energy functional defined in a natural way as a functional over joint distributions of disorder degrees of freedom and dynamical variables proper of systems with quenched disorder. The scheme was demonstrated to provide a family of increasing exact lower bounds for the quenched free energy of the disordered system, and was shown to avoid the use of non-Gibbsian measures at all finite levels of approximation. The connection between Morita's approach and conventional low-concentration expansions or perturbation expansions about ordered reference systems was also explained. Finally, applications of the scheme to a number of disordered Ising models and to protein folding were reviewed. For other applications, see the literature cited in [20].

In the context of the theory of non-Gibbsian measures and weaker forms of Gibbsianness, we recall, in particular the simple solution of the Curie – Weiss version of the RFIM within the equilibrium ensemble approach. It reproduces the exact solution at the cost of introducing a just single 'chemical potential' to fix the average value of the random field, which creates a term in the modified Hamiltonian that introduces no non-locality into the model over and above that already contained in the definition of the Curie – Weiss limit. This is a remarkable result in the light of concerns raised about the appearance of non-Gibbsian measures within the equilibrium ensemble approach [16–18] and the identification of the RFIM as providing a realization of a kind of 'worst-case scenario' in the non-Gibbsian world, viz., a system exhibiting almost surely non-Gibbsian joint probabilities of spin and disorder degrees of freedom [17,31].

The power of constrained annealing as a method for treating systems with quenched disorder has only begun to be explored. One aspect, for instance, that we have not seen discussed or exploited in the literature is that of *consistency relations* required to hold between coupling constants of disorder potentials such as introduced in Subsection 3.1. Consider a generalised ensemble with partition sum

$$\mathcal{Z}_\Lambda^\mathcal{Q} = \sum_{\sigma,\kappa} \exp\left[-\beta\mathcal{H}_\Lambda(\sigma|\kappa) + \sum_{\omega\in\mathcal{Q}_\emptyset} \lambda_\omega k_\omega(\kappa) \right], \qquad (6.1)$$

as introduced in (3.6). Then for any pair of disjoint sets ω_1 and ω_2 in $\mathcal{Q}$ for which their union $\omega_{12} = \omega_1 \cup \omega_2$ is also in $\mathcal{Q}$ the following relation must hold

$$\frac{\partial^2}{\partial \lambda_{\omega_1} \partial \lambda_{\omega_1}} \ln \mathcal{Z}_\Lambda^{\mathcal{Q}} = \frac{\partial}{\partial \lambda_{\omega_{12}}} \ln \mathcal{Z}_\Lambda^{\mathcal{Q}} - \frac{\partial}{\partial \lambda_{\omega_1}} \ln \mathcal{Z}_\Lambda^{\mathcal{Q}} \frac{\partial}{\partial \lambda_{\omega_2}} \ln \mathcal{Z}_\Lambda^{\mathcal{Q}}. \qquad (6.2)$$

It is conceivable that such relations may be exploited to constrain (or even fix) some of the coupling constants λ_ω of the disorder potential. In the context of field theory, for instance, similar relations are known to facilitate the effective summation of large classes of Feynman diagrams; see, e.g. [34].

Another direction which seems worth pursuing is the combination of the equilibrium ensemble approach with other approximation methods or with renormalisation group ideas. We have started to look into one such case ourselves, namely the combination of equilibrium ensemble approach and the density matrix renormalisation group (DMRG) [35]. It would allow to apply the DMRG to genuinely 2-D disordered systems and would allow to boost strip-scaling for such systems considerably. Preliminary results for strip-widths up to $L = 96$ (!) for the 2-D spin diluted Ising model — almost an order of magnitude larger than what has been reached before — have been obtained [36], showing that specific heat data taken do still not allow to disentangle the two conflicting scenarios that exist for the description of critical behaviour in that system. Stability of the algorithms is, however, still an issue here.

Note Added: After completion of this paper we learnt that Christof Külske [37] (this volume), prompted by the apparent absence of traces of non-Gibbsianness in the Morita approach to the RFIM, took a closer look at that solution, and pointed out that the derivation reported above is not entirely unproblematic, relying as it does on a metastable minimizer of the Morita free energy to obtain the equation of state. While arguments in favour of the validity of the self-consistency equations (5.12), (5.14) derived *within* the Morita approach to the problem can be advanced (see [37]), they remain non-rigorous as of now. Remarkably however, Külske [37] goes on to show that the same equations appear in a different way as rigorous consistency equations for the single-site conditional probabilities of the true joint measures, and that the validity of their solutions is in fact intimately related to their almost surely discontinuous behavior, i.e. to the non-Gibbsianness of the joint measure. For details we refer to [37].

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