Journal of Statistical Physics, Vol. 78, Nos. 1/2, 1995

Metastable Decay Rates, Asymptotic Expansions, and Analytic Continuation of Thermodynamic Functions

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Received November 4, 1993

The grand potential $P(z)/kT$ of the cluster model at fugacity z, neglecting interactions between clusters, is defined by a power series $\sum_n Q_n z^n$, where Q_n, which depends on the temperature T, is the "partition function" of a cluster of size n. At low temperatures this series has a finite radius of convergence z_s. Some theorems are proved showing that if Q_n, considered as a function of n, is the Laplace transform of a function with suitable properties, then $P(z)$ can be analytically continued into the complex z plane cut along the real axis from z_s to $+\infty$ and that (a) the imaginary part of $P(z)$ on the cut is (apart from a relatively unimportant prefactor) equal to the rate of nucleation of the corresponding metastable state, as given by Becker–Döring theory, and (b) the real part of $P(z)$ on the cut is approximately equal to the metastable grand potential as calculated by truncating the divergent power series at its smallest term.

KEY WORDS: Metastability; asymptotic expansions; analytic continuation; cluster model; complex fugacity plane; lattice gases.

1. INTRODUCTION

Lars Onsager used to tell a story about a glycerine factory somewhere in Canada. One winter it was so cold that the glycerine froze, and from then on no matter how thoroughly the place was cleaned it was impossible to get rid of all the nuclei of solid glycerine. As a result, it was no longer possible to produce glycerine in the usual (metastable) liquid phase. "They had to close the factory," he would say with his impish grin.

One of the approaches that has been tried toward obtaining a theory of metastability uses the idea that the thermodynamic functions of a

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0022-4715/95/0100-0267$07.50/0

metastable state might be obtained by analytic continuation from the neighboring stable state. This idea was already implicit in Maxwell's work on metastability for a substance obeying the van der Waals equation of state.[15] For temperatures below T_c there is a first-order phase transition, but the formulas for the thermodynamic functions, such as free energy and pressure, are not singular at the phase transition point. Maxwell assumed that the thermodynamic functions for metastable phases were represented by the same formula as the stable phases, but with different values for the parameters. This is equivalent (although Maxwell would not have put it in this way) to saying that the thermodynamic functions for metastable phases are analytic continuations of those for the stable phases.

When more powerful methods than the van der Waals equation for studying phase transitions became available, it was found that the thermodynamic functions did have singularities at first-order phase transition points, and therefore the simple extrapolation used by Maxwell was not in fact possible. The strongest result of this nature is that of Isakov,[11] who proved that for an Ising ferromagnet the free energy, considered as a function of the magnetic field H at some fixed temperature T, is infinitely differentiable but nevertheless nonanalytic.

Nevertheless, it may be possible to extrapolate the free energy and other thermodynamic functions into the metastable region of the phase diagram by analytic continuation (or by some other method such as the use of asymptotic expansions). In general the functions obtained by analytic continuation are complex, so that their physical significance, particularly that of their imaginary parts, is not immediately apparent. If the imaginary part is small, then the real part of, say, the analytically continued free energy might reasonably be interpreted as the free energy of the metastable phase, but what can the imaginary part mean? In quantum physics, there is[17,24] a simple connection between the imaginary part of an analytically continued energy and the lifetime of an unstable or metastable state. Indeed, this connection is one of the principal tools for studying quantum dissipative tunneling.[25] Motivated, perhaps, by such results, Langer[12] suggested that the imaginary part of the analytically continued free energy might (apart from unimportant preexponential factors) be equal to the nucleation rate of a metastable state in statistical mechanics. Langer's derivation, however, uses the approximation of replacing an infinite series formula for the free energy of an Ising ferromagnet by the corresponding integral. Since analytic continuation is a form of extrapolation, the uncontrolled errors introduced by this approximation might have a profound effect on the analytically continued free energy.

More recently various authors[16,18,23,22,26] have verified Langer's conjecture for various models, without resolving the question whether the connections they find are restricted to the particular models they study or whether they have some more general validity. Numerical results for the two-dimensional Ising model also confirm the conjecture.[9] Gaveau and Schulman[7] give a class of examples where Langer's conjecture holds in some cases and breaks down in others, showing that the conjecture is not true in general, but the situation for more physically significant examples is still unclear.

The present work concerns a model that has been widely used in the theory of phase transitions, the droplet or cluster model due to Bijl, Frenkel, and Band, whose physical justification is critically reviewed by Fisher.[6] It will be shown that if the "cluster partition functions" characterizing this model at a given temperature can be expressed as the Laplace transform of a suitable function [see Eq. (20) below], then the imaginary part of the analytically continued grand potential does have the suggested relation to the nucleation rate of a metastable state. Moreover, it will be shown that the real part of this analytically continued function corresponds to the corresponding thermodynamic function itself for the metastable state, as calculated from a "restricted ensemble" in which supercritical clusters are forbidden.

Our method is based on a variant of Borel's method for the summation of divergent power series. The analytic continuation can also be done by a direct application of Borel's method, as considered by Borgs.[3]

2. THE CLUSTER MODEL

Consider a dilute lattice gas with nearest-neighbor interactions, or equivalently a ferromagnet with plus boundary conditions in a strong plus magnetic field, so that most of the sites are vacant (plus) and only a few are occupied (minus). Any configuration of the lattice gas can be analyzed into clusters, defined as maximal connected sets of occupied sites. At low densities, the average concentration c_n of n-site clusters is given by

$$c_n = Q_n z^n [1 + O(z)] \tag{1}$$

with the "cluster partition functions" Q_n defined by

$$Q_n = \sum_K y^{b(K)} \tag{2}$$

where the sum goes over all translationally inequivalent n-site clusters, $b(K)$ means the number of bonds (nearest-neighbor pairs) in K, and y is defined by

$$y = e^{\beta U} \tag{3}$$

where $\beta = 1/kT$ and U is minus the interaction energy of a neighboring pair of occupied sites. In the case of a plane square lattice the first few cluster partition functions are

$$\begin{aligned} Q_1 &= 1 \\ Q_2 &= 2y \\ Q_3 &= 6y^2 \\ Q_4 &= 18y^3 + y^4 \\ &\cdots \end{aligned} \tag{4}$$

The approximation $Q_n z^n$ for c_n, implied by (1), is also a rigorous upper bound, but we shall not use this fact.

The grand partition function can be expanded as a sum over cluster configurations. If we make the approximation of neglecting the interaction between clusters which arises because by definition they cannot overlap or even touch, the GPF factorizes (see, for example, ref. 6 or ref. 10):

$$\Xi = \prod_{n \geq 1} \left\{ \sum_{k_n \geq 0} \frac{1}{k_n!} (Q_n z^n)^{k_n} \right\} \tag{5}$$

Its logarithm divided by the number of sites, often called the grand potential, is proportional in the thermodynamic limit to the pressure P (or, for an Ising ferromagnet, the free energy); this thermodynamic function is given by

$$P/kT = \sum_n Q_n z^n \tag{6}$$

A standard thermodynamic formula gives the corresponding approximation for the average density of particles as

$$\rho = z(\partial/\partial z)\, P/kT = \sum_n n Q_n z^n \tag{7}$$

Having regard to (1), we can interpret the sum on the right of (6) as the total number of clusters per lattice site, and the terms of the sum in (7) then have their natural interpretation as the expected number of particles in clusters of each size.

If there is a phase transition at fugacity z_s, we expect the thermodynamic functions, and in particular the above two series, to be singular (though convergent) when $z = z_s$. Since all the coefficients in the series are positive, the singularity nearest to the origin is at the point $z = z_s$ in the complex plane.

As an example of such behavior, consider the case of very low temperature (very large values of y). Then the clusters are approximately square, of side $\sqrt{n}$. Each such square contains (if n is a perfect square) $2n-2\sqrt{n}$ bonds, and so the coefficients Q_n are roughly given by

$$\begin{aligned} Q_n &\simeq \exp \beta[2Un - 2U\sqrt{n}] \\ &= y^{2n-2\sqrt{n}} \end{aligned} \tag{8}$$

where y is given by (3). It can be verified from (4) that (8) gives Q_1 and Q_4 correctly in the large-y limit. If we use the low-temperature approximation (8) for Q_n, the radius of convergence of the series for P/kT and ρ is

$$z_s = y^{-2} \tag{9}$$

and these series both converge when $z = z_s$. Indeed, at very low temperatures, y is large and so both z_s and $\rho(z_s)$ are very small, approximately y^{-2}, so that the approximation we started with, the neglect of interactions between clusters, is likely to be a good one right up to the singularity and even beyond.

The result (9) is compatible with the theorem of Yang and Lee,[13] according to which (in our lattice gas language) the true pressure is analytic for $zy^2 \leqslant 1$, so that the radius of convergence of the exact series for the pressure is at least y^{-2}.

3. METASTABLE STATICS

The cluster model leads to two very different conceptions of metastability, the static and the dynamic; we consider them in turn.

Suppose z is given some value a little bigger than z_s. Then the equilibrium cluster distribution, according to which the number of clusters per site is approximately $Q_n z^n$, no longer makes sense since it gives very large concentrations of large clusters. But if the large clusters are suppressed, then the above formula might still make good sense for small clusters. In fact, if z is only slightly greater than z_s, then the successive terms of the series can decrease to a very small value before increasing again to infinity. By truncating the series at or near the smallest term, we can still use these series to give numerical values for P/kT and ρ even though they diverge. This procedure corresponds to the method of "restricted ensembles"[20] in the statistical mechanics of metastability. For given $z > z_s$ let us define $n^*(z)$ as the value of n that minimizes $Q_n z^n$. Then we can define a "restricted ensemble" by forbidding clusters larger than n^*. In this restricted ensemble the pressure and density are given by the series (6) and (7) truncated at the n^* term, i.e.,

$$P^*(z) := kT \sum_{n \leqslant n^*} Q_n z^n$$
$$\rho^*(z) := \sum_{n \leqslant n^*} nQ_n z^n \tag{10}$$

where the symbol := indicates a definition.

In the low-temperature approximation for the two-dimensional lattice gas which leads to (8), n^* is given by

$$n^* \simeq \left(\frac{\log y}{\log(z/z_s)}\right)^2 = \left(\frac{\beta U}{\log(z/z_s)}\right)^2 \tag{11}$$

which is large if β is large (low temperature) and z is close to z_s (small supersaturation).

These truncated series give the thermodynamic functions for a state of metastable equilibrium in the form of a polynomial of very high order. One expects that they can be used in the usual way to calculate the effects of processes (e.g., temperature changes) which are gentle enough not to destroy the metastable state (e.g., to violate the condition that the smallest term in the series be extremely small).

4. METASTABLE KINETICS

To understand better what it means in the above discussion to say that a disturbance is gentle enough not to upset the metastability, we need to know something about the time evolution of a metastable state. The simplest problem in this area is that of estimating metastable lifetimes.

A useful model for the discussion of cluster kinetics is provided by the Becker–Döring equations[2] for $c_n(t)$, the time-dependent concentration of n-body clusters. These equations come from the assumption that the clusters obey the usual type of chemical reaction kinetics with "reaction"

$$(1\text{-body cluster}) + (n\text{-body cluster}) \rightleftharpoons ((n+1)\text{-body cluster}) \tag{12}$$

The Becker–Döring equations are

$$dc_n(t)/dt = J_n - J_{n-1} \qquad (n = 2, 3, ...)$$
$$dc_1/dt = -2J_1 - \sum_{n=2}^{\infty} J_n \tag{13}$$

where

$$J_n = a_n c_1 c_n - b_{n+1} c_{n+1} \qquad (n = 1, 2,...) \tag{14}$$

and the kinetic coefficients $a_1, a_2,..., b_2, b_3,...$ are constants.

The true equilibrium states are those for which the net reaction rates J_n are all zero; this is compatible with the previously assumed equilibrium distribution $c_n = Q_n z^n$ provided the kinetic coefficients satisfy the relation

$$a_n Q_n = b_{n+1} Q_{n+1} \qquad (n = 1, 2,...) \tag{15}$$

There is an equilibrium state for every value of z up to z_s. For larger values of z_s there are instead metastable (non)equilibrium states, each of which, in the approximation used by Becker and Döring, is characterized by a value of J_n that is independent of n. This value, call it $J(z)$, gives the rate of nucleation, i.e., the rate at which large clusters are being formed. The Becker–Döring formula for $J(z)$ is (see, for example, ref. 20)

$$J(z) = \left[\sum_{m=1}^{\infty} \frac{1}{a_m Q_m z^{m+1}} \right]^{-1} \tag{16}$$

An upper bound on $J(z)$, which also gives a crude approximation (up to a relatively unimportant factor whose order of magnitude is comparable with that of n^*), can be obtained by replacing the series by its smallest term; it is

$$J(z) \sim J^*(z) := a_{n^*} Q_{n^*} z^{n^*+1} \tag{17}$$

In the low-temperature approximation for a two-dimensional lattice gas, Eq. (8), this formula becomes

$$J^*(z) \simeq a_{n^*} \exp\left[-\frac{(\beta U)^2}{\log(z/z_s)} \right] \tag{18}$$

When z is close to z_s this expression is exponentially small, so that the corresponding lifetime can be very long, in conformity with standard ideas about metastability.

5. THREE THEOREMS

In this section we state the main results of the paper, in the form of three theorems. The proofs are given in the next section. The theorems depend on the assumption that Q_n is the Laplace transform of a function $e^{g(u)}$ [Eq. (20) below]. As noted by N. G. van Kampen (cited in ref. 6), this assumption makes it possible to obtain an analytic continuation of the series we are interested in, by a variant of Borel's method[1] for the summation of divergent power series. Some justification for this assumption is provided by the fact that the low-temperature approximation (8) for Q_n is indeed a Laplace transform, by virtue of the formula[5]

$$e^{(2n-2\sqrt{n})\beta U} = \int_{-2\beta U}^{\infty} \frac{\beta U}{[\pi(u+2\beta U)^3]^{1/2}} e^{-nu-(\beta U)^2/(u+2\beta U)}\, du \tag{19}$$

One should be careful with such arguments, however. Bricmont *et al.*[4] have shown that the two series $\sum z^n e^{-\gamma\sqrt{n}}$ and $\sum z^n e^{-\gamma[\sqrt{n}]}$, where $[\sqrt{n}]$ denotes the integral part of $\sqrt{n}$, though apparently very similar, define functions with completely different analytic properties: the former series can be analytically continued into the whole z plane apart from a singularity at $z=1$, while the latter cannot be continued outside the unit circle at all. Thus even an apparently trivial change in the coefficients of the series can drastically change the behavior of its analytic continuation. One would have to prove the Laplace transform property (20) directly before drawing any firm conclusions about the droplet model from the theorems that follow.

Theorem 1 (After Fisher[6]). Suppose that

$$Q_n = \int_{u_0}^{\infty} e^{-nu} e^{g(u)}\, du \qquad (n=1, 2,...) \tag{20}$$

where u_0 is a constant, possibly zero, and g is a Hölder continuous function on (u_0, ∞) such that the integral $\int_{u_0}^{\infty} e^{g(u)}\, du$ converges. Then:

(i) The series (6) has radius of convergence e^{u_0} and its analytic continuation into the entire complex plane, apart from a cut on the real axis from e^{u_0} to $+\infty$, is given by

$$\frac{P(z)}{kT} = \int_{u_0}^{\infty} \frac{ze^{-u}}{1-ze^{-u}} e^{g(u)}\, du \tag{21}$$

(ii) If $z = x \pm i0$ with $x > e^{u_0}$, then

$$\operatorname{Im} P(z)/kT = \pm\pi \exp g(\log x) \tag{22}$$

and

$$\frac{\operatorname{Re} P(z)}{kT} = \mathrm{PV} \int_{u_0}^{\infty} \frac{xe^{-u}}{1-xe^{-u}} e^{g(u)}\, du \tag{23}$$

where PV indicates that the Cauchy principal value of the divergent integral is to be taken.

Theorem 2. If the conditions of Theorem 1 are satisfied and the function g either has a unique maximum at a value $u_2 \in (u_0, +\infty)$ or is monotonically increasing on $(u_0, +\infty)$ (in which case we define $u_2 = +\infty$) and if in addition g has a second derivative g'' which is negative for all $u < u_2$ and is monotonically increasing on (u_0, u_1) for some $u_1 > u_0$, then for large positive n we have

$$\begin{aligned} \log Q_n &< \max_u[-nu + g(u)] + \text{const} \\ \text{and} \quad &> \max_u[-nu + g(u)] - \tfrac{1}{2} - \text{const} \cdot \log |g''(u^*)| \end{aligned} \tag{24}$$

$$\begin{aligned} g(u) &< \min_n[\log Q_n + nu] + \tfrac{1}{2} + \text{const} \cdot \log |g''(u)| \\ &= \log[\min_n(Q_n e^{un})] + \tfrac{1}{2} + \text{const} \cdot \log |g''(u)| \\ \text{and} \quad &> \log[\min_n(Q_n e^{un})] - \text{const} \end{aligned} \tag{25}$$

where u^* in (24) denotes the maximizing value of u, and the minimum in (25) is taken over positive *real* values of n, with Q_n defined for nonintegral values of n by the integral in (20). Further, when $x > e^{u_0}$ we have

$$\operatorname{Im} P(x \pm i0)/kT = \pm\pi \min_n(Q_n x^n)\, e^{O(1 + \log |g''(x)|)} \tag{26}$$

Combining Eq. (26) with (17), we see that the imaginary part of the analytically continued $P(z)/kT$ and the metastable decay rate are indeed proportional up to relatively unimportant factors proportional to powers of n and $g''(x)$. One cannot expect a much more precise correspondence, because the metastable decay rate is not fully determined by the quasi-equilibrium features studied here: it also depends on the kinetics of the model.

Theorem 3. If the conditions of Theorem 2 are satisfied, and if in addition

$$\frac{g'(u)(u-u_0)}{\log |(u-u_0)^{-1} \log \coth((u-u_0)/4)|} \to +\infty \qquad \text{as} \quad u \searrow u_0 \tag{27}$$

and there exists a number A such that

$$|g''(u)/g'(u)| < A/(u-u_0) \qquad \text{as} \quad u \searrow u_0 \tag{28}$$

then we have

$$\operatorname{Re} P(x \pm i0)/kT = \sum_{n=1}^{n^*-1} Q_n x^n + \theta Q_{n^*} x^{n^*} \tag{29}$$

where $0 \leqslant \theta \leqslant 1$ and n^* is a number satisfying

$$n^* = m^*(x)[1 + o(1)] \qquad \text{as} \quad x \searrow z_s \tag{30}$$

where

$$m^*(x) := g'(\log x) \tag{31}$$

and $o(1)$ means a quantity which approaches the limit zero.

By differentiating Eq. (24), it can be seen that the smallest term of the divergent series (6) is about the $m^*(x)$th, and so the result of Theorem 3 has the interpretation that this series gives a good approximation to $\operatorname{Re} P(x \pm i0)/kT$ if it is truncated near its smallest term.

All the conditions of these theorems are satisfied by the low-temperature approximation used in (8).

6. PROOFS OF THE THEOREMS

Proof of Theorem 1. From (20) it follows that $Q_n \leqslant e^{-nu_0} \int_0^\infty e^{g(u)}\, du$ and hence that the series (6) converges absolutely when $|z| < e^{u_0}$. Substituting (20) into (6), we find that

$$\begin{aligned} \frac{P(z)}{kT} &= \sum_{n=1}^{\infty} z^n \int_{u_0}^{\infty} e^{-nu + g(u)}\, du \\ &= \int_{u_0}^{\infty} \sum_{n=1}^{\infty} z^n e^{-nu + g(u)}\, du \\ &= \int_{u_0}^{\infty} \frac{z e^{-u}}{1 - z e^{-u}} e^{g(u)}\, du \end{aligned} \tag{32}$$

The interchange of summation and integration is justified provided that $|z| < e^{u_0}$, and so the formula is valid throughout the circle of convergence of the series in (6). However, the integral on the right defines a function which is analytic in the entire complex z-plane apart from a cut along the real axis from e^{u_0}, i.e., z_s, to $+\infty$. Thus Eq. (32) provides the analytic continuation of $P(z)$ into this cut plane, completing the proof of (21). From now on we take $P(z)/kT$ to stand for this analytically continued function.

The fact that the radius of convergence of the series is precisely e^{u_0} now follows from the fact that the cut begins at $z = e^{u_0}$.

To prove the second part of the theorem, we make the change of variable $w = e^u$ in (21) so that it takes the form

$$\frac{P(z)}{kT} = \int_{e^{u_0}}^{\infty} \frac{z e^{g(\log w)}}{w - z} \frac{dw}{w} \tag{33}$$

Then (22) and (23) follow from the Plemelj formula,[21] which is applicable since g is Hölder continuous, giving in our case

$$\frac{1}{kT} \lim_{y \to 0} P(x \pm i\,|y|) = \mathrm{PV} \int_{e^{u_0}}^{\infty} \frac{x e^{g(\log w)}}{w - x} \frac{dw}{w} \pm i\pi e^{g(\log x)} \tag{34}$$

This completes the proof of Theorem 1. ∎

Proof of Theorem 2. We may without loss of generality assume that $u_1 < u_2$. The conditions on g imply that

$$g'(u) > 0 \quad \text{and} \quad g''(u) < 0 \qquad \text{if} \quad u < u_2 \tag{35}$$

$$g(u) \leqslant g(u_2) \qquad \text{if} \quad u > u_2 \tag{36}$$

Given any positive n, define u^* as the (unique) solution of

$$g'(u^*) = n \tag{37}$$

so that the function $g(u) - nu$ has a unique maximum when $u = u^*$. Moreover, by (35), u^* decreases as n increases, and since we are taking $u_1 < u_2$, the number $n_1 := g'(u_1)$ is positive.

To get an upper bound on Q_n we divide the integral (20) into two parts:

$$Q_n = \int_{u_0}^{u_1} e^{g(u) - nu}\, du + \int_{u_1}^{\infty} e^{g(u) - nu}\, du \tag{38}$$

Since we are interested in large values of n, we may assume that $n > n_1$, so that $u^* < u_1$ and the integrand in the first term of (38) attains its maximum value at u^*. For the second integral we note that (35) and (36) imply

$$\begin{aligned} g(u) &\leqslant g(u_1) + (u - u_1)\, g'(u_1) \\ &= g(u_1) + (u - u_1)\, n_1 \end{aligned} \tag{39}$$

by the definition of n_1. Putting these estimates into (38), we get

$$Q_n \leqslant (u_1 - u_0)\, e^{g(u^*) - nu^*} + e^{g(u_1) - u_1 n_1} \int_{u_1}^{\infty} e^{-(n-n_1)u}\, du$$
$$\leqslant e^{g(u^*) - nu^*}[u_1 - u_0 + 1/(n - n_1)] \tag{40}$$

The last line follows by the definition of n_1 and the fact that the function $g(u) - nu$ is smaller when $u = u_1$ than it is at its maximum, $u = u^*$. This provides the upper bound on Q_n needed for (24).

For the lower bound we start again from (20). Using (37) in the Taylor expansion of $g(u)$ about u^*, we obtain, since g'' is monotonically increasing on (u_0, u_1) and the integrand is nonnegative,

$$Q_n \geqslant \int_{u^*}^{u_1} e^{g(u^*) - nu^* + g''(u^*)(u-u^*)^2/2}\, du \tag{41}$$

Now the integral $\int_0^a e^{-cx^2/2}\, dx$, interpreted as the area under a curve, is (for all positive a and c) bounded below by the area of a rectangle of height $e^{-1/2}$ and width $\min(a, 1/\sqrt{c})$. Using this estimate in (41), we get, since $g''(u^*)$ is negative,

$$Q_n \geqslant e^{g(u^*) - nu^* - 1/2} \min(u_1 - u^*, 1/\sqrt{|g''(u^*)|}) \tag{42}$$

To estimate $u_1 - u^*$, we note that the monotonic increase of g'' implies

$$g'(u_1) \geqslant g'(u^*) + (u_1 - u^*)\, g''(u^*) \tag{43}$$

so that, since $g''(u^*)$ is negative,

$$u_1 - u^* \geqslant (g'(u^*) - g'(u_1))/|g''(u^*)|$$
$$= (n - n_1)/|g''(u^*)| \tag{44}$$

Combining (42) and (44), we get the lower bound on Q_n necessary to complete the proof of (24).

To prove (25), let $\bar{g}(u)$ be any function that is concave on the whole of (u_0, ∞) and coincides with $g(u)$ in all the places where we are requiring g to be concave, i.e., on (u_0, u_2):

$$\bar{g}(u) = g(u) \qquad (u \in (u_0, u_2)) \tag{45}$$

Let h and $\bar{h}$ be the Legendre transforms of g and $\bar{g}$, defined by

$$h(x) := \max_u [-xu + g(u)] \tag{46}$$

$$\bar{h}(x) := \max_u [-xu + \bar{g}(u)] \tag{47}$$

These two functions coincide for those values of x where the maximizing values of u in the two defining formulas are less than u_2, that is, for $x>0$. Since $\bar{g}$ is concave, we have, by the duality theorem for convex functions,[14,8]

$$\bar{g}(u)=\min_x[xu+\bar{h}(x)] \tag{48}$$

This formula is true for all $u\in(u_0,\infty)$. For $u\in(u_0,u_2)$ we know also that $g(u)=\bar{g}(u)$, and hence, since the minimizing value of x is positive, that $h(x)=\bar{h}(x)$ at the minimum; thus we obtain

$$g(u)=\min_x[xu+h(x)] \qquad (u\in(u_0,u_2)) \tag{49}$$

Combining (49), (46), and (24), we complete the proof of (25). Then Eq. (26) follows immediately from (25) and (22). ▌

Proof of Theorem 3. The error in replacing $P(x\pm i0)$, as given by (23), by the first m terms of the series (6), with Q_n given by (20), is

$$\begin{aligned}P(x\pm i0)-\sum_{n=1}^{m}\frac{Q_n}{kT}&=\mathrm{PV}\int_{u_0}^{\infty}\frac{(xe^{-u})^{m+1}}{1-xe^{-u}}e^{g(u)}\,du\\&=\mathrm{PV}\int_{-\infty}^{\infty}\frac{e^{-(m+1/2)v}}{e^{v/2}-e^{-v/2}}e^{g(u^*+v)}\,dv\end{aligned} \tag{50}$$

where $u^*:=\log x$, $v:=u-u^*$, and $e^{g(u)}$ is defined to be 0 for $u<u_0$. The integral is a monotonic decreasing function of m; we shall estimate the value of m at which this function passes through the value zero.

We first convert to a normal integral by subtracting from both sides $e^{g(u^*)}$ times the integral $\mathrm{PV}\int dv/(e^{v/2}-e^{-v/2})$, which is zero by symmetry. Denoting the right side of (50) by $I(m)$, this gives

$$I(m)=\int_{-\infty}^{\infty}\frac{e^{g(u^*+v)-(m+1/2)v}-e^{g(u^*)}}{e^{v/2}-e^{-v/2}}\,dv \tag{51}$$

We can write this integral in the form $I_+ + I_-$, as the sum of the contributions of positive and negative values of v.

To obtain upper and lower bounds on these integrals, let the numbers u_+, u_- satisfy

$$u_0<u_-<u^*<u_+<u_1 \tag{52}$$

and define

$$m_-:=g'(u_-), \qquad m^*:=g'(u^*), \qquad m_+:=g'(u_+) \tag{53}$$

where the prime denotes a derivative. By the concavity of the function g, the ordering of these numbers is

$$m_+ \leqslant m^* \leqslant m_- \tag{54}$$

The concavity of g also implies

$$\begin{aligned} g(u^*+v) &\leqslant g(u^*)+m^*v \qquad (-\infty<v<\infty) \\ g(u^*+v) &\geqslant g(u^*)+g'(u^*+v)\,v \\ &\geqslant g(u_*)+m_+v \qquad (0\leqslant v\leqslant v_+) \\ g(u^*+v) &\geqslant g(u_*)+m_-v \qquad (v_-\leqslant v\leqslant 0) \end{aligned} \tag{55}$$

where $v_\pm := u_\pm - u^*$. Using this last set of inequalities in the integrals I_+ and I_-, we obtain the following estimates:

$$\begin{aligned} I_+ &< e^{g(u^*)}\int_0^\infty \frac{e^{(m^*-m-1/2)v}-1}{e^{v/2}-e^{-v/2}}\,dv \qquad \text{if} \quad m^*-m-1<0 \\ &\leqslant e^{g(u^*)}\int_0^\infty \frac{e^{-v}-1}{e^{v/2}-e^{-v/2}}\,dv \qquad \text{if} \quad m^*-m-\frac{1}{2}<-1 \\ &= -2e^{g(u^*)} \end{aligned} \tag{56}$$

$$\begin{aligned} I_+ &> e^{g(u^*)}\left[\int_0^{v_+} \frac{e^{(m_+-m-1/2)v}-1}{e^{v/2}-e^{-v/2}}\,dv-\int_{v_+}^\infty \frac{dv}{e^{v/2}-e^{-v/2}}\right] \\ &> e^{g(u^*)}\left[\int_0^{v_+}(e^{(m_+-m-1)v}-e^{-v/2})\,dv-\int_{v_+}^\infty \frac{dv}{e^{v/2}-e^{-v/2}}\right] \\ &\qquad \left(m_+-m-\frac{1}{2}>0\right) \\ &> e^{g(u^*)}\left[v_+e^{(m_+-m-1)v_+/2}-2(1-e^{-v_+/2})-\log\coth\frac{v_+}{4}\right] \end{aligned} \tag{57}$$

since $\int_0^X e^{\alpha x}\,dx > Xe^{\alpha X/2}$ for all positive α, X. By analogous methods, we also obtain

$$I_- > \int_{-\infty}^0 \frac{e^{(m^*-m-1/2)v}-1}{e^{v/2}-e^{-v/2}}\,dv > 2e^{g(u^*)} \qquad \left(m^*-m-\frac{1}{2}>1\right) \tag{58}$$

$$I_- < e^{g(u^*)}\left[-|v_-|\,e^{(m-m_-)|v_-|/2}+2(1-e^{-|v_-|/2})+\log\coth\frac{|v_-|}{4}\right] \tag{59}$$

Combining (56) and (59) gives the upper bound, valid when $m > \max(m_- - 1/2, m^* + 1/2)$,

$$I(m) < e^{g(u^*)}\left[-|v_-|\, e^{(m-m_-)|v_-|/2} - 2e^{-|v_-|/2} + \log\coth\frac{|v_-|}{4}\right] \tag{60}$$

while (57) and (58) give a lower bound, valid when $m < \min(m_+ - 1/2, m^* - 3/2)$,

$$I(m) > e^{g(u^*)}\left[v_+\, e^{(m_+ - m - 1)v_+/2} + 2e^{-v_+/2} - \log\coth\frac{v_+}{4}\right] \tag{61}$$

Condition (27) of the theorem can be written

$$\lim_{u \searrow u_0} g'(u)\, f(u-u_0) = +\infty \tag{62}$$

where

$$f(u-u_0) := \frac{u-u_0}{\log|(u-u_0)^{-1}\log\coth((u-u_0)/4)|} \tag{63}$$

By virtue of (62) and the fact that $g'(u) \to \infty$ and $f(u) \to 0$ as $u - u_0 \to 0$ it is possible to find positive numbers M, V depending on u in such a way that

$$M(u)/g'(u) \to 0 \qquad \text{as} \quad u \searrow u_0 \tag{64}$$

$$V(u)/(u-u_0) \to 0 \tag{65}$$

$$M(u)\, f(V(u)) \to +\infty \tag{66}$$

For example, we could choose M, V so that $M(u) := [g'(u)]^{2/3} [f(u-u_0)]^{-1/3}$ and $f(V(u)) := [f(u-u_0)]^{2/3} [g'(u)]^{-1/3}$.

In the upper bounds (60) and (61), take

$$v_+ = V(u^*), \qquad v_- = -V(u^*) \tag{67}$$

and $m_\pm = g'(u_0 + v_\pm)$ as in (53). This gives, with the help of (66),

$$\begin{aligned} I(m_- + M(u^*) + 1) &< e^{g(u^*)}[-V(u^*)\, e^{M(u^*)\, V(u^*)} + \log\coth(V(u^*)/4)] \\ &< 0 \qquad \text{for small enough} \quad (u^* - u_0) \end{aligned} \tag{68}$$

In a similar way, we also obtain

$$I(m_+ - M(u^*) + 1) > 0 \qquad \text{for small enough} \quad (u^* - u_0) \tag{69}$$

Since I is a decreasing function of m, it has at most one zero; the above inequalities show that this zero lies between $m_+ - M(u^*) + 1$ and $m_- + M(u^*) + 1$. We take the n^* in the statement of the theorem to be the next integer after this zero; then the error in replacing $P(x \pm i0)$ by the series (6) truncated at the n^*th term is positive and is at most equal to the last term included, as stated in the theorem.

It remains to prove (30), i.e., that $(m_- + M(u^*) + 1) - m^*$ and $m^* - (m_+ - M(u^*) + 1)$ are $o(m^*)$. From (64) we known that $M(u^*) = o(m^*)$. To show that $m_- - m^*$ and $m^* - m_+$ are $o(m^*)$, we can argue as follows:

$$\begin{aligned} 0 < m_- - m_+ &= \int_{u_-}^{u_+} [-g''(u)]\, du \\ &< \int_{u_-}^{u_+} \frac{Ag'(u)}{u - u_0}\, du && \text{by (28), since } g'' < 0,\ g' > 0 \\ &< \frac{Ag'(u_-)(u_+ - u_-)}{u_- - u_0} && \text{by concavity} \\ &= \frac{2Am_- V(u^*)}{u^* - u_0 - V(u^*)} && \text{by (53) and (67)} \end{aligned} \tag{70}$$

This can be rearranged to give

$$\frac{m_-}{m_+} - 1 < \frac{2AV(u^*)}{u^* - u_0 - (1 + 2A)\, V(u^*)} \tag{71}$$

The left side is nonnegative, by (54), and the right side tends to zero as $x \searrow z_s$, by (65); it follows, again using (54), that

$$m_- - m_+ = o(m^*) \quad \text{so that} \quad m_- - m^* = o(m^*), \quad m^* - m_+ = o(m^*) \tag{72}$$

Combining this result with (64), we obtain the desired results

$$\begin{aligned} (m_- + M(u^*) + 1) - m^* &= (m_- - m^*) + M(u^*) + 1 = o(m^*) \\ m^* - (m_+ - M(u^*) + 1) &= (m^* - m_+) + M(u^*) + 1 = o(m^*) \end{aligned} \tag{73}$$

This completes the proof of Theorem 3. ∎

ACKNOWLEDGMENTS

I am grateful for C. Borgs, J. Bricmont, M. E. Fisher, R. Kotecki, and P. A. Rikvold for helpful information, and to the referees for useful suggestions for improving the paper.

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