

AN "AVERAGED" PHASE TRANSITION

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An example of averaging of the singularities of thermodynamic quantities at phase transition points with respect to the interaction Hamiltonian is considered. The example is equivalent to the replacement of the density of zeroes of the partition function by the density of zeroes of random polynomials with positive coefficients. Such an averaged system will always be subject to a first-order phase transition.

1. AVERAGING OVER THE INTERACTION

DURING the past few years, intensive investigations of the singularities of thermodynamic functions at phase transition points have been carried out. However, until now the question whether the singularity at a phase transition point is universal, as required by Landau's theory, or whether the singularity depends on the specific form of the interaction, at short distances between the particles, as apparently follows from numerical solutions, has remained unsolved. If there is universality, then there must without doubt exist a method of averaging "over all systems" (i.e., with respect to the Hamiltonians) which conserves the form of the singularity of the thermodynamic functions. In other words, there exists one or several distributions with respect to the Hamiltonians, replacing the Gibbs distribution, and satisfying all the necessary requirements. Of course the "thermodynamic potentials" corresponding to such distributions (ensembles) do not have the usual meaning of energy, free energy, etc.; the same refers to the variables T, V, P, ... since it is obvious that if we wish to conserve in some form the singularity with respect to T, say, then for each of the systems it is necessary to take its own temperature, which is close to the phase transition temperature. In other words, the "averaged" thermodynamic potential will be a function of the modulus of the appropriate distribution, and we hope that the singularity with respect to that modulus will be the same as for real systems.

Unfortunately we were unable even to come close to the ideal achieved in the brilliant papers of Wigner and Dyson (cf., e.g.,^[1]) on the correlations between the nuclear levels for which all possible invariant measures have been constructed. We present here simply an attempt to guess at the real properties of such distributions by making some simple assumptions. It will be shown, in particular, that the universal character of the singularity at a first-order phase transition point is related to the universal character of the distribution of zeroes of random polynomials.

Let us first consider how an averaged singularity might look. Let us assume that we are able to carry out the averaging at a given transition temperature T_c , or, what amounts to the same, at an unchanged relative distance to the transition point $\tau = (T - T_c)/T_c$. This

means that we know the distribution $f(\alpha)$ of the exponent α of the singularity, say, of the free energy

$$F_{\text{sing}} = A |\tau|^\alpha. \tag{1}$$

If α does not depend on the form of the interaction, the averaged potential F_{sing} exhibits the same singularity. Otherwise, we have

$$\langle F_{\text{sing}} \rangle = \int A(\alpha) |\tau|^{\alpha} f(\alpha) d\alpha \approx A(\alpha_{\text{min}}) f(\alpha_{\text{min}}) \frac{|\tau|^{\alpha_{\text{min}}}}{|\ln \tau|}.$$

If $A(\alpha)$ or $f(\alpha)$ vanish or become infinite at $\alpha = \alpha_{\text{min}}$, the answer will contain also other powers of $\ln \tau$.

Neglecting slowly varying functions one can always write

$$\langle F_{\text{sing}} \rangle \sim |\tau|^{\alpha_{\text{min}}}. \tag{2}$$

In the case of a first order phase transition $\alpha_{\text{min}} = 1$. For a second-order transition there are three possibilities: 1) the singularity is universal, i.e., there exists one or several discrete values of α each of which corresponds to its own universal distribution over the Hamiltonians; 2) the singularity is not universal, but $\alpha_{\text{min}} > 1$. Then this value is, so-to-speak a "law of nature," and corresponds also to some universal distribution; 3) the case corresponding to "absolute non-universality." Here α takes on all values between 1 and 2. Of course, the selection of the reduced temperature τ as a quantity which is conserved in the averaging process is not compulsory.

We describe below a method of averaging which yields $\alpha_{\text{min}} = 1$. We shall average the grand partition function Z and the corresponding thermodynamic potential $\Omega(T, V, \mu)$ for fixed values of the fugacity $u = e^{\mu/T}$. Since the averaging over "all systems" (i.e., all Hamiltonians) includes in a natural manner an averaging over the volume, neither of the variables T, V, μ is conserved separately. Thus

$$\omega = \frac{\Omega}{T} = - \ln \sum_{N=0}^{\infty} z_N u^N, \tag{3}$$

where z_N is the ("petit") partition function for a system consisting of N particles. Accordingly

$$\langle \omega \rangle = - \left\langle \ln \sum z_N u^N \right\rangle. \tag{4}$$

As we already said at the beginning, we are not aware of universal distributions over "all systems."

Therefore we can only guess at such distributions making some simple assumptions about the distributions of the (canonical) partition functions. Our first assumption is that the partition functions for systems with different particle numbers are uncorrelated under our averaging process:

$$\langle (z_N - \langle z_N \rangle) (z_{N'} - \langle z_{N'} \rangle) \rangle = 0.$$

This is a sufficiently natural assumption, since in principle systems with different numbers of particles have different Hamiltonians.

The second assumption is that the expectation values $\langle z_N \rangle$ and all the correlation functions depend on N only exponentially

$$\langle z_N \rangle = a_0^N f_0(N), \quad \langle (z_N - \langle z_N \rangle)^2 \rangle = a_1^N f_1(N), \dots; \quad (5)$$

where f_0, f_1, \dots are power functions of N and a_0, a_1, \dots do not depend on N at all. This assumption also seems natural, since factorial dependences on N occur only for fixed volume; the averaging over Hamiltonians corresponds more closely to an averaging over densities.

Introducing the new notations

$$z_N = \xi_N a_0^N, \quad v = u a_0,$$

we have

$$\langle \omega \rangle = - \left\langle \ln \sum \xi_N v^N \right\rangle; \quad (6)$$

$$\langle \xi_N \rangle = f_0(N), \quad \langle (\xi_N - \langle \xi_N \rangle)^2 \rangle = (a_1/a_0)^N f_1(N), \dots$$

We now note the following circumstance. The coefficients of the grand partition function decrease, before averaging, in a factorial manner as N increases.

Therefore the grand partition function can be computed by the saddle-point method, leading to a proportionality of ω to the volume V . After our averaging the factorial behavior disappears, and this means that $\langle \omega \rangle$ will be proportional to some actually infinite quantity. Physical meaning can now be attributed to a potential γ which is the potential $\langle \omega \rangle$ ‘‘referred to one particle’’:

$$\gamma(v) = \lim_{N \rightarrow \infty} \frac{\langle \omega_{N_0} \rangle}{N_0} = - \lim_{N \rightarrow \infty} \frac{1}{N_0} \left\langle \ln \sum \xi_N v^N \right\rangle. \quad (7)$$

The definition (7) means that we change the order of letting the volume and particle number in the system approach infinity. Whereas before the averaging we in fact first express $\langle N \rangle$ in terms of V , and then let the latter tend to infinity, we now do not restrict the volume from the very beginning.

For the computation of γ we use the method proposed by Yang and Lee for the calculation of the grand partition function^[2], and represent (7) in the form

$$\gamma = - \lim_{N \rightarrow \infty} \frac{1}{2N} \iint dx dy \rho_N(x, y) \ln [(v-x)^2 + y^2], \quad (8)$$

where ρ_N is the average density of zeros of a positive random polynomial P_N of degree N :

$$P_N = \sum_{n=0}^N \xi_N v^n, \quad \xi_N > 0,$$

with ξ_N determined from (6).

It is intuitively clear that as N increases the roots of an arbitrary random polynomial will be concentrated on a circle of radius one with uniform density, i.e.,

$$\rho \rightarrow \frac{N}{2\pi} \delta(\sqrt{x^2 + y^2} - 1) \text{ as } N \rightarrow \infty. \quad (9)$$

In the next section it will be shown that the same holds for the zeroes of random polynomials with positive coefficients. Substituting (9) into (8) we obtain an expression for the singular part of γ :

$$\begin{aligned} \gamma_{\text{sing}} &= \gamma(v) - \gamma(1) = - \frac{1}{4\pi} \int_{-\pi}^{\pi} d\varphi \ln \frac{(v - \cos \varphi)^2 + \sin^2 \varphi}{(1 - \cos \varphi)^2 + \sin^2 \varphi} \\ &\approx - \frac{1}{4\pi} \int_{-\infty}^{\infty} d\varphi \ln \frac{(v-1)^2 + \varphi^2}{\varphi^2} = - \frac{|v-1|}{2}, \end{aligned} \quad (10)$$

i.e., an expression corresponding to a phase transition of the first kind.

2. THE ZEROES OF RANDOM POLYNOMIALS

We have seen that the universal nature of the singularity at a first-order phase transition point is closely related to the universal character of the limiting distribution of zeroes of random polynomials. We are not aware of a general proof of Eq. (9), and therefore we shall verify it for a sufficiently large class of distributions of the coefficients of the polynomials.

We start with the simplest case of a polynomial for which the coefficients may have both signs. Assume that the coefficients of the polynomial are normally distributed with unit variance:

$$w(\xi) = \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{\xi^2}{2}\right).$$

The density of roots of the polynomials $P_N(x + iy)$ is given by¹⁾:

$$\rho_N(x, y) = \frac{1}{8\pi} \Delta \ln |P_N|^2, \quad (11)$$

where Δ is the Laplacian. However, the distribution of zeroes of polynomials of finite order oscillate rapidly with the angles (over distances $\varphi \sim 1/N$), therefore it is more convenient to compute the expectation value of the smoother quantity $\ln |P_N|^2$. Then, if the limiting distribution has the form (9):

$$\lim_{N \rightarrow \infty} \langle \ln |P_N|^2 \rangle = N|r-1| \quad (12)$$

and conversely. It is also clear that we can restrict our attention to real values of the variable ($y = 0$).

Thus, we have to calculate

$$\langle \ln P_N^2 \rangle, \quad P_N = \sum_{n=0}^N \xi_n x^n.$$

It is known²⁾ that if the quantities ξ_n are normally distributed, any of their linear combinations, i.e., the polynomial P_N itself, also has a Gaussian distribution,

$$W(P) = (2\pi\sigma)^{-1/2} \exp(-P^2/2\sigma),$$

with variance σ , defined by

$$\sigma = \langle P_N^2 \rangle.$$

In our case

$$\sigma = \langle P_N^2 \rangle = \sum_{n,m} x^{n+m} \langle \xi_n \xi_m \rangle = \sum_{n=0}^N x^{2n} = \frac{1-x^{2N+2}}{1-x^2}.$$

Hence

$$\langle \ln P^2 \rangle = \frac{1}{\sqrt{2\pi\sigma}} \int_{-\infty}^{\infty} dP \exp\left(-\frac{P^2}{2\sigma}\right) \ln P^2$$

¹⁾One can verify the validity of this formula by noting that $\Delta \ln(x^2 + y^2) = 8\delta(x)\delta(y)$.

²⁾We owe this proof to V. I. Matsaev.

$$= \ln 2\sigma + \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} dP e^{-P^2} \ln P^2.$$

In the right-hand side one can omit all terms except $\ln \sigma$, since they remain finite for $N \rightarrow \infty$. Thus

$$\langle \ln P^2 \rangle \approx \ln \sigma.$$

For $|x| < 1$ the quantity

$$\ln \sigma = \ln \frac{1 - x^{2N+2}}{1 - x^2}$$

vanishes for $N \rightarrow \infty$, so that

$$\langle \ln P^2 \rangle \approx 0, \quad |x| < 1.$$

For $|x| > 1$ we have

$$\langle \ln P^2 \rangle \approx \ln |x|^{2N} \approx 2N(|x| - 1),$$

which up to a smooth function of x coincides with (12).

We now pass on to the case of positive polynomials in which we are interested. We first consider the simple distribution for ξ :

$$w(\xi) = e^{-\xi}, \quad \xi > 0.$$

This corresponds to having all a_0, a_1, \dots equal in Eqs. (6), and all f constant. In place of $\langle \ln P \rangle$ it is more convenient to compute the derivative with respect to x of this quantity.

$$\frac{P'}{P} = -\frac{d}{dx} \int_0^{\infty} \frac{ds}{s + i\delta} e^{-sP(x)}, \quad \delta \rightarrow 0$$

We use the equation and compute the average of the integral. We have

$$\begin{aligned} \langle e^{-sP} \rangle &= \prod_{n=0}^N \int_0^{\infty} d\xi_n \exp(-s\xi_n x^n - \xi_n) \\ &= \prod_{n=0}^N \frac{1}{1 + sx^n} = \exp\left[-\sum_{n=0}^N \ln(1 + sx^n)\right]. \end{aligned}$$

For $x < 1$ only small values of $s = 1 - x$ are essential in the integral over $\langle e^{-sP} \rangle$. Therefore

$$\sum_{n=0}^{\infty} \ln(1 + sx^n) \approx s \sum_{n=0}^{\infty} x^n \approx \frac{s}{1-x}.$$

Hence

$$\int_0^{\infty} \frac{ds}{s + i\delta} \langle e^{-sP} \rangle = \int_0^{\infty} \frac{ds}{s + i\delta} \exp\left(-\frac{s}{1-x}\right)$$

and

$$\left\langle \frac{P'}{P} \right\rangle = \frac{1}{(1-x)^2} \int_0^{\infty} ds \exp\left(-\frac{s}{1-x}\right) = \frac{1}{1-x}.$$

This quantity must be discarded, since it is not proportional to the degree N of the polynomial. (By assumption $x^N \ll 1$, hence $1 - x \gg 1/N$.) Consequently

$$\langle \ln P \rangle = 0, \quad x < 1. \tag{13}$$

For $x > 1$ in the sum

$$\sum_{n=0}^N \ln(1 + sx^n)$$

large values of $n \approx N$ become important. Replacing it by an integral we have

$$\begin{aligned} \int_0^N \ln(1 + sx^n) dn &\approx \int_0^{\infty} \ln(1 + sx^{N-n}) dn \\ &\approx \frac{1}{x-1} \Phi(se^{N(x-1)}), \end{aligned}$$

where

$$\Phi(y) = \int_0^{\infty} \ln(1 + ye^{-n}) dn.$$

In the integration the values $se^{N(x-1)} \approx x - 1$. Therefore $\Phi(y) \approx y$ and

$$\sum \ln(1 + sx^n) \approx \frac{se^{N(x-1)}}{x-1}.$$

Making use of this expression, we find

$$\begin{aligned} \left\langle \frac{P'}{P} \right\rangle &= \int_0^{\infty} ds \left(\frac{N}{x-1} - \frac{1}{(x-1)^2} \right) e^{N(x-1)s} \exp\left(-\frac{se^{N(x-1)}}{x-1}\right) \\ &= N - \frac{1}{x-1}. \end{aligned}$$

Omitting the N -independent part, we obtain

$$\langle \ln P \rangle = N(x-1), \quad x > 1, \tag{14}$$

which, as in the preceding case coincides with (12).

The result will not change if one takes other forms of the distribution of the coefficients of the polynomial, e.g., a step function

$$w(\xi) = \begin{cases} 1, & 0 < \xi < 1 \\ 0, & \xi > 1 \end{cases}.$$

or setting $\xi = \eta^2$ and assuming η to be normally distributed. The same answer is obtained from distributions in which the expectation value of the coefficients ξ_N and their dispersions are exponential functions of N , e.g., arbitrary distributions of the form:

$$w(\xi_N) = \lambda_N \exp(-\lambda_N \xi_N), \quad \lambda_N = a^N N^b,$$

where a and b are constants. (In this latter case the transition point will be shifted: $v_c = 1$ moves to $v_c = 1/a$.) This all forces us to think that the limiting distribution (9) does correctly describe the distribution of zeroes of polynomials of high degrees.

We also note that a stronger dependence than exponential (e.g., of the type $N!$ or $\exp(N^a)$, $a > 1$) for the expectation values and correlations will in general destroy the phase transition.

3. CONCLUSION

The results of this averaging represent essentially a derivation of the thermodynamic equations near a first-order phase transition point, and the relation to the distribution of zeroes of random polynomials allows one to hope that there is a genuine distribution "over all systems" describing this transition. At the same time, the latter circumstance leads to the idea that phase transitions of the second kind can hardly be universal. Indeed, making use of the formula of Yang and Lee^[2] for the potential

$$\Omega = -\frac{1}{2} T \int \int dx dy \rho(x, y) \ln[(u-x)^2 + y^2],$$

where ρ is the distribution of zeroes of the grand partition function, it can be seen that the singularity at second-order transition point is determined by more subtle properties of the function ρ , which determine the vanishing of this function on the real axis. For example, a singularity of the form

$$\Omega_{\text{sing}} \sim |u - u_c|^\alpha$$

is given by a function of the form (near the real axis)

$$\rho \sim \delta(x - u_c) |y|^{\alpha-1}.$$

It seems to us improbable that such subtle nuances in the distribution of zeroes of entire functions (which are

not polynomials) would be preserved in any averaging over interactions.

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Porter, Ed., Academic Press, N. Y. 1965.

²C. N. Yang and T. D. Lee, Phys. Rev. 87, 404, 410 (1952).

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¹Statistical Theory of Spectra; Fluctuations, C.