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On the impossibility of the phase transitions

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Abstract

Arguments are given for the impossibility of accounting for the phase transitions by statistical mechanics.

With usual notations the grand-partition function is written as

$$Z = \sum e^{\beta(\mu\mathcal{N} - \mathcal{E})} = e^{-\beta\Omega} \quad , \tag{1}$$

where the summation extends over all distinct configurations. The thermodynamic quantities are obtained from the grand-partition potential $\Omega = -pV = F - \mu N$ ($d\Omega = -Vdp = -Nd\mu - SdT$) by

$$E - \mu N = \partial(\beta\Omega)/\partial\beta \ \ , \ \ N = -\partial\Omega/\partial\mu \ . \tag{2}$$

In the thermodynamic limit, the summation over an infinite number of configurations in (1), as well as for an infinite number of contributions to the energies, may lead, at least in principle, to a singularity of Z, and, consequently, to a (logarithmic) singularity in $\beta\Omega$. The same infinite summation may also lead, for some values of β and μ, to a discontinuos Z, in which case its derivatives are singular;[1] one deals in this case with different analytic (real) functions for Z, and if one of them happens to be zero then $\beta\Omega$ has again a logarithmic singularity. This corresponds to what is called condensation phenomena, as, for instance, first-order phase transitions, and Bose-Einstein condensation.[2] Some of thermodynamic quantities may be discontinuos in this case, some others may have singularities, but in all cases the fluctuations are singular, as a consequence of vanishing Z, or of the singular behaviour of its derivatives (as, for instance, the singular entropy).[3]

A particular case is that where a discontinuity with vanishing Z may appear for certain few configurations, which may lead to a continuos $\beta\Omega$ and E, but a singularity in the higher derivatives. This would correspond to what is called cooperative phenomena, and, typically, such a singularity may appear in the specific heat $c = \partial E/\partial T$, as for the second-order phase transitions; since the only type of singularities which may appear are logarithmic singularities (via (1)), one may suppose $c \sim -\ln|t|$, where $t = T - T_c$, T_c being the critical temperature. In this case $E \sim -t\ln|t|$ and $\Omega \sim t^2 \ln|t|$.

On the other hand, the origin of such a singularity in the cooperative phenomena comes from the condensation in the configurational space, *i.e.* from a certain mode of motion which may lead to an ordered state. One may label these modes by wavevectors $\mathbf{k}$, and let the condensing mode in the $\mathbf{k}$-space be $\mathbf{k}$ =0, as for a homogeneous system. Since the $\mathbf{k}$-mode competes with $t=0$ in the singular behaviour one may write the grand-partition potential as

$$\Omega \sim \int_0 dk \cdot k^{d-1} \cdot \ln\left(z + k^m\right) \quad , \tag{3}$$

in a d-dimensional space; where z is a certain function of t (and μ), and the exponent m determines the k-dependence of the mode energy. The quantity z has a series expansion

$$z = z_c + z_c' \cdot t + (1/2)\, z_c'' \cdot t^2 + ..., \tag{4}$$

and for a singular behaviour z_c should vanish, $z_c = 0$. However, z comes from the statistical weights in (1), and, as such, it is always positive. If z vanishes for certain values of T it follows that its first derivative should also vanish there, $z_c' = 0$, *i.e.* z should have a vanishing minimum at the critical temperature. Equation (3) becomes then

$$\Omega \sim -\int_0 dk \cdot k^{d-1} \cdot \ln\left(t^2 + k^m\right) \quad , \tag{5}$$

and leads to $\Omega \sim t^{2d/m} \ln|t|$; on comparing it with $t^2 \ln|t|$ one obtains $m = d$, *i.e.* the only condensing modes that may lead to a phase transition should have the energy $\sim k^d$, where d is the space dimension.[4]

However, the statistical weights for fluctuations appear in this case as $\exp\left(\beta\Omega_{\mathbf{k}}\right) = \exp\left(-\ln\left(t^2 + k^d\right)\right)$, such that they would always imply

$$\int_0 dk \cdot k^{d-1} \cdot \frac{1}{t^2 + k^d} \quad , \tag{6}$$

i.e. a logarithmic singularity. The phase transitions are prevented by fluctuations, and attempting to account for them by statistical mechanics is bound to fail.[5]

Let us assume an ensemble of N particles (or sub-ensembles) described by a set of variables n_i, either continuous or discrete, taking positive values; they may be viewed as corresponding to the mechanical states of the particles, states which are identified by their energy. With usual notations the partition function[6] can be written as

$$\begin{aligned} Z \;&\sim \sum_{n_1, n_2, ...} \exp\left[-\beta\varepsilon\left(n_1, n_2, ...\right) + S\left(n_1, n_2, ...\right)\right] \sim \\ &\sim \int dn_1 dn_2 ... \cdot \exp\left[-\beta\varepsilon\left(n_1, n_2, ...\right) + S\left(n_1, n_2, ...\right)\right] \sim \\ &\sim \int d\mathbf{n} \cdot \exp\left[-\beta\varepsilon\left(\mathbf{n}\right) + S\left(\mathbf{n}\right)\right] \quad , \end{aligned} \tag{7}$$

where $\mathbf{n} = \{n_i\}$. Let us introduce the notations

$$\begin{aligned} \Phi(\mathbf{n}) \;&=\; -\beta\varepsilon\left(\mathbf{n}\right) + S\left(\mathbf{n}\right) \quad , \\ \frac{\partial\Phi(\mathbf{n})}{\partial n_i} \;&=\; \Phi_i(\mathbf{n}) = -\beta\varepsilon_i\left(\mathbf{n}\right) + S_i\left(\mathbf{n}\right) \quad , \\ \frac{\partial^2\Phi(\mathbf{n})}{\partial n_i \partial n_j} \;&=\; \Phi_{ij}(\mathbf{n}) = -\beta\varepsilon_{ij}\left(\mathbf{n}\right) + S_{ij}\left(\mathbf{n}\right) \quad , \end{aligned} \tag{8}$$

and assume that there exists $\mathbf{n}_0$ such that

$$\Phi_i(\mathbf{n}_0) = -\beta\varepsilon_i(\mathbf{n}_0) + S_i(\mathbf{n}_0) = 0 \quad ; \tag{9}$$

denoting $\Phi_0 = \Phi(\mathbf{n}_0)$ and

$$\Phi_{ij}(\mathbf{n}_0) = -\beta\varepsilon_{ij}(\mathbf{n}_0) + S_{ij}(\mathbf{n}_0) = -L_{ij}(\mathbf{n}_0) \tag{10}$$

the partition function can be estimated by steepest descent as

$$Z \sim e^{\Phi_0} \int d\mathbf{n} \cdot \exp\left[-\frac{1}{2}L_{ij}(\mathbf{n}_0)(n_i - n_{i0})(n - n_{j0})\right] \quad . \tag{11}$$

Let us denote by λ_q the eigenvalues of the (non-singular) part of the matrix L_{ij}, and we shall be interested in the singular behaviour of these eigenvalues, *i.e.* $\lambda_q \to \infty$;; then, the relevant part of the partition function[7] reads

$$Z \sim \prod_q (1/\lambda_q)^{1/2} = \prod_q \mu_q^{1/2} \quad , \tag{12}$$

where $\mu_q = 1/\lambda_q \to 0$. Under this circumstance, it is easy to see that the remaining contributions to the integral in (7), in comparison with the integral in (11), *i.e.* those coming from higher-order derivatives of Φ, are vanishing quantities of higher orders, so that the steepest descent gives a highly accurate estimate of the partition function. The relevant part of the free energy F is then given by

$$\beta F \sim -\frac{1}{2}\sum_q \ln \mu_q \quad . \tag{13}$$

Further on, we shall assume that the ensemble of particles is spatial, so that we may identify q with a point, *i.e.* a vector $\mathbf{q}$ in this space; and for a uniform ensemble we may write

$$\beta F \sim -\frac{1}{2}\int dq \cdot q^{d-1} \cdot \ln \mu_q \quad , \tag{14}$$

where d is the space dimension.

The eigenvalues λ_q depend on $\mathbf{n}_0$, $\lambda_q = \lambda_q(\mathbf{n}_0)$, and their singular behaviour should be such that there should exist a point $\mathbf{n}_0 = \mathbf{m}$ for which an integrable set of them, at least, behave like $\mu_q = 1/\lambda_q \sim |\mathbf{n}_0 - \mathbf{m}|^\alpha$, where, obviously, the exponent α ($\alpha > 0$) does not depend essentially on q or β; naturally, the dependence of q and β is to be included in a small term denoted by γ_q, which are going to vanish for that integrable set of singular λ_q. We do not write explicitly the dependence of γ_q on β but we keep in mind the presence of β in γ_q. Therefore, we may take λ_q as being given by

$$\mu_q = 1/\lambda_q \sim |\mathbf{n}_0 - \mathbf{m}|^\alpha + \gamma_q \quad . \tag{15}$$

From $\lambda_q(\mathbf{n}_0)$ given by (15) we can obtain, in principle, $\Phi_{ij}(\mathbf{n}_0)$ given by (10), and hence $\Phi_i(\mathbf{n}_0)$; then, by using $\Phi_i(\mathbf{n}_0) = 0$ as given by (9) we can obtain both the critical temperature, *i.e.* β_c, from $\Phi_i(\mathbf{n}_0 = \mathbf{m}) = 0$, and $|\mathbf{n}_0 - \mathbf{m}|$ as a function of $\beta - \beta_c$; which, finally, will give us μ_q as a function of $\beta - \beta_c$ and γ_q. As one can see the critical temperature is associated with the point $\mathbf{m}$ in the space of the variables $\{n_i\}$.

In order to carry out practically these computations we need further simplifying assumptions. Specifically, we shall assume $\Phi(\mathbf{n}) = \sum_i \Phi(n_i)$, as for an ensemble of independent particles. Under this assumption the matrix $L_{ij} = -\Phi_{ij}$ is diagonal, and preserving the q-labels we may write

$$\lambda_q = -\Phi_{qq}(\mathbf{n}_0) = \left[(n_{0q} - m_q)^\alpha + \gamma_q\right]^{-1} \quad ; \tag{16}$$

whence

$$-\Phi_q(\mathbf{n}_0) = \beta\varepsilon_q(n_{0q}) - S_q(n_{0q}) = = \int_{m_q}^{n_{0q}} dn \cdot \left[(n-m_q)^\alpha + \gamma_q\right]^{-1} + const = = \int_0^{n_{0q}-m_q} dn \cdot \left[n^\alpha + \gamma_q\right]^{-1} + const = 0 \ . \tag{17}$$

From (17) we obtain at once

$$const = \beta_c\varepsilon_q(m_q) - S_q(m_q) = 0 \tag{18}$$

and

$$\beta\varepsilon_q(n_{0q}) - S_q(n_{0q}) = \beta_c\varepsilon_q(m_q) - S_q(m_q) + \int_0^{n_{0q}-m_q} dn \cdot \left[n^\alpha + \gamma_q\right]^{-1} = 0 \ . \tag{19}$$

The integral can be estimates as

$$\int_0^{n_{0q}-m_q} dn \cdot \left[n^\alpha + \gamma_q\right]^{-1} \simeq M/\gamma_q - \frac{M^{1-\alpha}}{1-\alpha} + \frac{(n_{0q}-m_q)^{1-\alpha}}{1-\alpha} \quad , \tag{20}$$

where the cut-off M is chosen such as the integral be independent of M; this means $M = \gamma^{1/\alpha}$ and[8]

$$\int_0^{n_{0q}-m_q} dn \cdot \left[n^\alpha + \gamma_q\right]^{-1} \simeq -\frac{\alpha}{1-\alpha}\gamma_q^{\frac{1}{\alpha}-1} + \frac{1}{1-\alpha}(n_{0q}-m_q)^{1-\alpha} \quad . \tag{21}$$

Using this in (19) we find easily

$$n_{0q} - m_q \simeq \left[(1-\alpha)\varepsilon_q(m_q)\right]^{1/(1-\alpha)}(\beta-\beta_c)^{1/(1-\alpha)} \tag{22}$$

to the first approximation; hence, by using (16),

$$\mu_q = 1/\lambda_q = (n_{0q}-m_q)^\alpha + \gamma_q \simeq \simeq \left[(1-\alpha)\varepsilon_q(m_q)\right]^{\alpha/(1-\alpha)}(\beta-\beta_c)^{\alpha/(1-\alpha)} + \gamma_q \ . \tag{23}$$

In order to get a second-order phase transition one needs[9] $\alpha/(1-\alpha) = 2$ (compare, for instance, (5) and (13)); hence we obtain $\alpha = 2/3$.

Let us turn now to estimating averages of quantities depending on $\{n_i\}$ (or $\{n_q\}$). We can expand such quantities in powers of $n_q - m_q$, so that we are left with estimating averages of the type

$$\int dn_q \cdot (n_q - m_q)^\delta \cdot \exp\left[-\beta\varepsilon(n_q) + S(n_q)\right] \quad , \tag{24}$$

where δ is some positive exponent. We estimate this integral by steepest descent again, and show that it is finite. Indeed, the equation

$$\frac{\delta}{n_{1q}-m_q} - \beta\varepsilon_q(n_{1q}) + S_q(n_{1q}) = 0 \tag{25}$$

can be solved for n_{1q} by using

$$\begin{aligned} \beta\varepsilon_q\left(n_{1q}\right) - S_q\left(n_{1q}\right) &= \beta_c\varepsilon_q(m_q) - S_q(m_q) + \int_0^{n_{1q}-m_q} dn \cdot \left[n^\alpha + \gamma_q\right]^{-1} = \\ &= \int_0^{n_{1q}-m_q} dn \cdot \left[n^\alpha + \gamma_q\right]^{-1} \simeq 3\left(n_{1q} - m_q\right)^{1/3} \end{aligned} \tag{26}$$

from (19) and (21) for $\alpha = 2/3$. We obtain $n_{1q} - m_q = (\delta/3)^{3/4}$, such that the second derivative of (25) becomes

$$-\frac{\delta}{(n_{1q} - m_q)^2} - \left(n_{1q} - m_q\right)^{-2/3} = -4(\delta/3)^{-1/2} \ ; \tag{27}$$

the integral in (24) is therefore $\sim (\delta/3)^{1/4}$. However, the average

$$\overline{\left(n_q - m_q\right)^\delta} \sim (\delta/3)^{1/4}/Z \sim \sqrt{\lambda_q} \tag{28}$$

and it is singular near the critical point, according to (23). Similarly, $\overline{\left(n_q - m_q\right)^{2\delta}} \sim \sqrt{\lambda_q}$, but the fluctuations of these quantities imply $\left[\overline{\left(n_q - m_q\right)^\delta}\right]^2 \sim \lambda_q$, and they are more singular than their averages. The most favourable situation is that where the singularities appear for few configurations q, *i.e.* for $q \sim 0$. In this case the statistical deviations are given by[10]

$$\sum_{q\sim 0} \lambda_q \sim \int_0 dq \cdot q^{d-1} \frac{1}{\left(\beta - \beta_c\right)^2 + \theta(q)} \quad , \tag{29}$$

where d is the space dmension and $\theta(q) \sim \left[3/\varepsilon_q(m_q)\right]^2 \gamma_q$, according to (23). On comparing this with (6) we see that $\theta(q)$ should go like q^d, and the fluctuations exhibit therefore a logarithmic singularity at the critical point.

It is perhaps worth illustrating how the above computations work for some particular cases. Suppose a classical ensemble of free particles in the three-dimensional space; the energy of each particle can be written as

$$\varepsilon(n_1, n_2, n_3) = \varepsilon_0 \left(n_1^2 + n_2^2 + n_3^2\right)/L^2 = \varepsilon_0 n^2/L^2 \quad , \tag{30}$$

where L denotes the linear size of the spatial extension of the ensemble. The number of states available to each particle is $\Gamma \sim n^3$, so that $d\Gamma \sim n^2 dn \sim \exp\left(2\ln n\right) dn$, whence the entropy $S = 2\ln n$. The partition function is therefore given by

$$Z \sim \int dn \cdot \exp\left[-\beta\varepsilon_0 n^2/L^2 + 2\ln n\right] \ ; \tag{31}$$

it can be easily estimated by steepest descent,

$$Z \sim L^3/\left(\beta\varepsilon_0\right)^{3/2} \quad , \tag{32}$$

which is the partition function of a classical ensemble.[11] In particular, (9) has the solution $n_0/L = 1/\sqrt{\beta\varepsilon_0}$. Obviously, there is no phase transition. For quantum gases of free, identical particles we can write the energy as[12]

$$\varepsilon = \sum_i \varepsilon_i n_i \quad , \tag{33}$$

where n_i stand for the average occupancy of the i-th state partition.[13] The entropy can be written as

$$S = \sum_i \left[(1+n_i)\ln(1+n_i) - n_i \ln n_i\right] \tag{34}$$

for bosons, and

$$S = -\sum_i \left[(1-n_i)\ln(1-n_i) + n_i \ln n_i\right] \tag{35}$$

for fermions. The partition function for a state i, as given by (7), is obtained strightforwardly as

$$Z \sim \{1 - \exp\left[-\beta(\varepsilon_i - \mu)\right]\}^{-1} \tag{36}$$

for bosons, and

$$Z \sim 1 + \exp\left[-\beta(\varepsilon_i - \mu)\right] \tag{37}$$

for fermions, where we have introduced the chemical potential μ. The solution n_{0i} to (9) is the statistical occupation number, $\{\exp\left[\beta(\varepsilon_i - \mu)\right] \mp 1\}^{-1}$. We note that the second derivative in the expansion of the integrand exponent in this case is of the order of unity at equilibrium, so that the remaining integral in the steepest descent does not contribute essentially to the partition function. A particular situation occurs for bosons, where the Bose-Einstein condensation appears for an infinite number of occupancy, *i.e.* $m_i \to \infty$ for i corresponding to the zero-energy level. This shows again that a phase transition like the Bose-Einstein condensation can not be tackled by equilibrium statistical mechanics.

References

[1] B. Kahn, PhD thesis, Utrecht 1938; B. Kahn and G. E. Uhlenbeck, Physica **5** 399 (1938); one may visualize this phenomenon by, for instance, $(e^{-\alpha x}+1)^{-1}$ for $\alpha \to \infty$.

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

[3] See, for instance, D. ter Haar, *Elements of Statistical Mechanics*, Rinehart&Co, Inc. (1954).

[4] Note that this is the case of Onsager's solution to the two-dimensional Ising model, L. Onsager, Phys. Rev. **65** 117 (1944).

[5] Compare, for instance, N. D. Mermin and H. Wagner, Phys. Rev. Lett **17** 1133 (1966).

[6] The grand-partition function would not bring an essential change in what follows.

[7] We note that the sign of the quadratic form L_{ij}, as well as the jacobian of the diagonalizing transform are both irrelevant in this context.

[8] We note that by equating (21) to zero we obtain n_{0q} as a function of β, the latter being contained in γ_q.

[9] For a non-vanishing coefficient $\varepsilon_q(m_q)$ in (23).

[10] Compare (6).

[11] $Z_{ens} = (1/N!)Z^N$.

[12] We note the quantum correlations in defining the energy of an ensemble of identical, quantum particles, in contrast to the classical ensemble.

[13] See, for instance, L. Landau and E. Lifshitz, *Statistical Mechanics*, Moscow (1967).