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Riemannian geometry and stability of thermodynamical equilibrium systems

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Abstract. A geometrical approach to statistical thermodynamics is proposed. It is shown that any r-parameter generalised Gibbs distribution leads to a Riemannian metric of parameter space. The components of the metric tensor are represented by second moments of stochastic variables. The scalar curvature R, as a geometrical invariant, is a function of the second and third moments, so is strictly connected with fluctuations of the system. In the case of a real gas, R is positive and tends to infinity as the system approaches the critical point. In the case of an ideal gas, $R=0$. The obtained results, and the results of our previous papers, suggest that for a wide class of models R tends to $+\infty$ near the critical point. We treat R as a measure of the stability of the system. We propose some sort of statistical principle: only such models may be accepted for which R tends to infinity if the system is approaching the critical point. It is shown that, if this criterion is adopted for a class of models for which the scaling hypothesis holds, then we obtain the new inequalities for the critical indices. These inequalities are in good agreement with model calculations and experiment.

1. Introduction

Recently many authors [1-5] investigated the structure of the space of thermodynamic parameters in the geometrical framework. These investigations were mainly concerned with an analysis of the Riemannian metric. In our previous papers [6, 7] we investigated magnetic systems and quantum gases from this point of view. It turned out that the Riemann scalar curvature R is especially important. Statistically R depends on the second and third moments of fluctuations (variances and covariances of the respective stochastic variables). In the case of the simplest magnetic models, R is positive and tends to infinity, if the critical point is approached. Also in the case of an ideal bosonic gas R is positive and tends to infinity if the Bose-Einstein condensation region is approached. In these papers the general formulae for the scalar curvature R in various representations have been derived. The scalar curvature has been interpreted as a measure of the stability of the system. Statistically R accounts for global part fluctuations caused by the interactions of particles. The system is less stable if R is larger and vice versa.

This paper is a continuation of those investigations. We investigate ideal and real classical gases described by Boguslavski (P-T distribution [8]). The behaviour of R in the vicinity of the critical point is similar as in the previously investigated cases. We propose that the property $R \to +\infty$ in the vicinity of the critical points may be used

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as the criterion for the appropriate choice of the statistical description of a thermodynamical system. We assert that for all physically realistic interactions leading to the phase transitions: $R \to +\infty$ near the critical point. Thus we accept some sort of new principle of statistical thermodynamics.

Next we apply this principle to a class of models described by the generalised homogeneous potential functions. It is known that these models are in accordance with the well known statistical scaling hypothesis. It is also well known that, among nine critical indices, only two are independent and no theory exists which gives any estimation of their values.

If we adopt the principle $R \to +\infty$ for the above class of models, we obtain new inequalities of the general character for the indices α, γ, β: $\beta + \gamma > 1$ (or equivalently $\gamma > \alpha$) and independently $\beta < 1$. These inequalities are observed for all magnetic systems.

2. Geometrical structure in the case of the ideal classical gas

We start from the R-T distribution

$$f(q, p, V; \alpha, \beta) = Z^{-1}(\alpha, \beta)\exp(-\beta H - \alpha V) \tag{2.1}$$

where $Z(\alpha, \beta)$ is the partition function:

$$Z(\alpha, \beta) = \frac{1}{aN!\,h^{3N}}\int_0^\infty \mathrm{d}V\left(\int \exp(-\beta H)\,\mathrm{d}q\,\mathrm{d}p\right)\exp(-\alpha V). \tag{2.2}$$

$\beta = 1/kT$ and $\alpha = P/kT$ (T is the temperature and P is the pressure), h is the Planck constant, a is an arbitrary quantity which possesses a dimension of volume V and N is the number of particles. Integration in (2.2) is taken over phase space and volume.

We have two stochastic variables: Hamiltonian H and volume V. β and α are statistical variables (temperatures) conjugated to the mean value of H and V:

$$\begin{aligned}\langle H\rangle &= -\frac{\partial \ln Z(\alpha, \beta)}{\partial \beta}\\ \langle V\rangle &= -\frac{\partial \ln Z(\alpha, \beta)}{\partial \alpha}.\end{aligned} \tag{2.3}$$

As in our previous papers, the metric structure of the parameter space B, parametrised by the statistical temperatures α and β, is given by

$$\begin{aligned}\mathrm{d}l^2 &= \langle(\mathrm{d}\ln f(q, p, V; \beta, \alpha))^2\rangle = \left\langle\frac{\partial \ln f}{\partial \beta^i}\frac{\partial \ln f}{\partial \beta^j}\right\rangle \mathrm{d}\beta^i\,\mathrm{d}\beta^j\\ &= -\left\langle\frac{\partial^2 \ln f}{\partial \beta^i\,\partial \beta^j}\right\rangle \mathrm{d}\beta^i\,\mathrm{d}\beta^j = \frac{\partial^2 \ln Z}{\partial \beta^i\,\partial \beta^j}\,\mathrm{d}\beta^i\,\mathrm{d}\beta^j\end{aligned} \tag{2.4}$$

$\beta^1 = \beta$, $\beta^2 = \alpha$ and the differential d is taken with respect to β and α only. We are interested only in changes of state caused by the changes of environment. Due to (2.1) and (2.2) the elements of the metric tensor are the second moments of the stochastic variables H and V:

$$g_{11}=\frac{\partial^2 \ln Z}{\partial\beta^2}=\langle H^2\rangle-\langle H\rangle^2$$

$$g_{22}=\frac{\partial^2 \ln Z}{\partial\alpha^2}=\langle V^2\rangle-\langle V\rangle^2 \tag{2.5}$$

$$g_{12}=g_{21}=\frac{\partial^2 \ln Z}{\partial\beta\,\partial\alpha}=\langle HV\rangle-\langle H\rangle\langle V\rangle.$$

In our case $H=\Sigma_{i=1}^{\mu} p_{1/2m}^2$ and the formula (2.2) gives

$$Z(\alpha_1\beta)=\frac{1}{a}\left(\frac{2\pi m}{h^2\beta}\right)^{3/2N}\alpha^{-(N+1)}. \tag{2.6}$$

In the thermodynamical limit we get

$$\gamma=\lim_{N\to\infty}\frac{\ln Z(\alpha,\beta)}{N}=\frac{3}{2}\ln\frac{2\pi m}{h^2\beta}-\ln\alpha. \tag{2.7}$$

In the coordinates T and P, $\gamma=-\mu/T$, where μ is the chemical potential (Gibbs function per one particle) and $\alpha=P/kT$.

The components of the metric tensor per one particle are

$$g_{\alpha\alpha}=\frac{\partial^2\gamma}{\partial\alpha^2}=\alpha^{-2}\qquad g_{\beta\beta}=\frac{\partial^2\gamma}{\partial\beta^2}=\tfrac{3}{2}\beta^2\qquad g_{2\beta}=g_{p\alpha}=0. \tag{2.8}$$

In accordance with the results of papers [6, 7] the scalar curvature R is given by the formula

$$R=\frac{1}{2g^2}\begin{vmatrix} g_{\alpha\alpha} & g_{\beta\beta} & g_{\alpha\beta} \\ \dfrac{\partial g_{\alpha\alpha}}{\partial\alpha} & \dfrac{\partial g_{\beta\beta}}{\partial\alpha} & \dfrac{\partial g_{\alpha\beta}}{\partial\alpha} \\ \dfrac{\partial g_{\alpha\alpha}}{\partial\beta} & \dfrac{\partial g_{\beta\beta}}{\partial\beta} & \dfrac{\partial g_{\alpha\beta}}{\partial\beta} \end{vmatrix} \tag{2.9}$$

where $|\cdot|=\det$ and $g=\det(g_{ij})$. Because the covariance of H and V is 0, i.e. $g_{\alpha\beta}$, we immediately obtain $R=0$. Similar considerations based on the grand canonical distribution lead also to $R=0$ (see [5, 7]). For the ideal gas (lack of interaction) we have $R=0$ [5].

Our geometrical app:oach to statistical thermodynamics makes sense if it can introduce a metrical Riemannian structure in the space of parameters which cannot be done if $r=1$. So the well known canonical distribution cannot be adopted in our consideration. We enlarged the number of stochastic variables up to two, choosing the density of particles N/V as a stochastic variable. It is necessary to take into account V or N as a stochastic variable. In the first case we obtain the P-T distribution. In the second case we get the grand canonical distribution. Because the fluctuations of density particles are not essential in the case of the ideal gas, these descriptions are equivalent to those given by the canonical distribution.

3. Geometrical structure in the case of a real gas

Our considerations are based also on the P-T distribution:

$$f(q, p, V; \alpha, \beta) = Z^{-1}(\alpha, \beta) \exp(-\beta H - \alpha V) \tag{3.1}$$

where

$$Z(\alpha, \beta) = \frac{1}{bN!\, h^{3N}} \int_{Nb}^{\infty} \exp(-\alpha V)\left(\int \exp(-\beta H)\, \mathrm{d}q\, \mathrm{d}p\right) \mathrm{d}V. \tag{3.2}$$

By b we denote the smallest volume available for one particle treated as a hard core, and b serves as the volume unit. The volume as the stochastic variable ranges from Nb to infinity. It is easy to show that the P-T distribution produces only states which are stable:

$$\begin{aligned} &\bar{V} = \langle V \rangle = -\frac{\partial \ln Z}{\partial \alpha} \qquad \frac{\partial^2 \ln Z}{\partial \alpha^2} = \langle V^2 \rangle - \langle V \rangle^2 > 0 \\ &\langle V^2 \rangle - \langle V \rangle^2 = -\frac{\partial \bar{V}}{\partial \alpha} = -\frac{1}{\beta}\frac{\partial \bar{V}}{\partial p} \Rightarrow -\frac{\partial \bar{V}}{\partial p} > 0. \end{aligned} \tag{3.3}$$

After integration (3.2) over phase space we obtain

$$Z(\alpha, \beta) = \frac{1}{b} \int_{Nl}^{\infty} \exp(-\alpha V) Z(\beta, V)\, \mathrm{d}V \tag{3.4}$$

where

$$Z(\beta, V) = \frac{1}{N!\, h^{3N}} \int \exp(-\beta H)\, \mathrm{d}q\, \mathrm{d}p \tag{3.5}$$

is the partition function of the canonical distribution.

Throughout this paper $Z(\beta, V)$ will be taken as that for a real gas in the mean field approximation [9, 10], i.e.

$$Z(\beta, V) \simeq \frac{1}{N!}\left(\frac{2\pi m}{\beta h^2}\right)^{3/2N} (V - Nb) \exp(\beta a N^2/V) \tag{3.6}$$

where $(V-Nb)^N$ is due to the hard core part of the particle potential, whereas $\exp(\alpha\beta N^2 V^{-1})$ is due to the attractive part of this potential, i.e. $-aN^2V^{-1}$ (a is positive). If the canonical distribution is adopted then formula (3.6) leads to the well known van der Waals equation of state:

$$P = \frac{1}{\beta}\frac{\partial \ln Z(\beta, V)}{\partial V} = \frac{1}{\beta}\frac{N}{V - Nb} - \frac{aN^2}{V^2} \tag{3.7}$$

which also supplies us with unphysical (unstable) states with $\partial P/\partial V > 0$. This seems to be caused by the fact that the canonical distribution does not take account of fluctuations of the particle density. V and N are fixed. Fluctuations of V are essential in the region of phase transitions. As we have shown, the P-T distribution does not lead to unstable states.

We are not able to calculate $Z(\alpha, \beta)$ directly and therefore we will try to evaluate $N^{-1} \ln Z(\alpha, \beta)$ in the limit $N \to +\infty$. For this reason we rewrite the integrand in (3.4) in the form

$$\exp(-\alpha V) Z(\beta, V) = \exp[-\alpha V + \ln Z(\beta, V)] = \exp[\bar{H}(\alpha, \beta, V)] \tag{3.8}$$

where

$$\begin{aligned} &\bar{H}(\alpha, \beta, V) = -\alpha V + \ln Z(\beta, V) = N\bar{h}(\alpha, \beta, v) \\ &\bar{h}(\alpha, \beta, v) = -\alpha v + 1 + \ln\left(\frac{2\pi m}{\beta h^2}\right)^{3/2} (v - b) + \beta a / v \end{aligned} \qquad v = V/N. \tag{3.9}$$

We have used here (3.6) and the Stirling formula $\ln N! \simeq N \ln N - N$. Physically $Z^{-1}(\alpha, \beta) \exp \bar{H}(\alpha, \beta, V)$ is the probability distribution for V. This distribution depends parametrically on α and β. The investigation of $\bar{H}(\alpha, \beta, V)$ is equivalent to the investigation of this probability distribution. $\bar{h}(\alpha, \beta, v)$ tends to $-\infty$ if $v \to b$ or if $v \to +\infty$. Therefore one may expect that $\bar{h}(\alpha, \beta, v)$ has at least one maximum for $v \in [b, +\infty)$. The condition $\partial \bar{h}/\partial v = 0$ for the maximum takes the form

$$\alpha = -\beta \frac{a}{v^2} + \frac{1}{v - b} \qquad P = -\frac{1}{v^2} + \frac{kT}{v - b}. \tag{3.10}$$

Remark. Despite an evident identity of this expression with the van der Waals equation (3.7) which was obtained from the canonical distribution, (3.10) is here not treated as an equation of state. The equation of state resulting from the P–T distribution has the form

$$\bar{V} = \langle V \rangle = -\frac{\partial \ln Z(\alpha, \beta)}{\partial \alpha}. \tag{3.11}$$

Equation (3.10) gives us those values of v, which maximise $\bar{h}(\alpha, \beta, v)$ for given values of α and β (or P and T). For $T > T_c$ (T_c is the critical temperature) we always gave one solution of (3.10) which gives only one maximum. The integral (3.4) may be written in the form

$$Z(\alpha, \beta) = \frac{N}{b} \int_b^\infty \exp[N\bar{h}(\alpha, \beta, v)] \, dv. \tag{3.12}$$

Applying the well known Laplace method, in the thermodynamical limit we obtain

$$\lim_{N \to \infty} \frac{\ln Z(\alpha, \beta)}{N} = \bar{h}(\alpha, \beta, \tilde{\sigma}) = -\alpha \tilde{v} + \ln Z(\beta, \tilde{v}) \tag{3.13}$$

where $\tilde{v}$ is the value of v corresponding to the maximum of $\bar{h}(\alpha, \beta, v)$. In the case of two maxima $\tilde{v}_1$ and $\tilde{v}_3$ (for $T < T_c$) we take the larger one. In the case of equal maxima we take, for v, $\tilde{v}_1$ or $\tilde{v}_3$ (the third solution $\tilde{v}_2$ corresponds to a minimum).

Thermodynamically $\bar{h}(\alpha, \beta, \tilde{v})$ is connected with the Gibbs potential per particle:

$$\tilde{g}(\alpha, \beta) = -\frac{1}{\beta} \bar{h}(\alpha, \beta, \tilde{v}) = P\tilde{v}(\alpha, \beta) - \frac{1}{\beta} \ln Z(\beta, \tilde{v}). \tag{3.14}$$

One can easily show that $\tilde{v}$ is equal to the mean value $\bar{v}$ of v, namely

$$\bar{v} = \langle v \rangle = -\frac{\partial \bar{h}(\alpha, \beta)}{\partial \alpha} = \frac{\partial \tilde{g}(\alpha, \beta)}{\partial P} = \tilde{v} + P \frac{\partial \tilde{v}}{\partial P} - \frac{1}{\beta} \frac{\partial \ln Z(\beta, \tilde{v})}{\partial P}.$$

But

$$\frac{\partial \ln Z(\beta, \tilde{v})}{\partial P} = \frac{\partial \ln Z(\beta, \tilde{v})}{\partial \tilde{v}} \frac{\partial \tilde{v}}{\partial P} = \beta P \frac{\partial \tilde{v}}{\partial P}$$

and finally we get $\bar{v} = \tilde{v}$. If we return to the formula (3.10) which gives $\tilde{v}$, we see that the equation of state is

$$P = \frac{kT}{\bar{v} - b} - \frac{a}{\bar{v}^2} \qquad \text{for } \bar{v} \notin [\tilde{v}_1, \tilde{v}_3]$$

(see also [11]).

So we obtain the van der Waals equation in the region $\bar{v} < \tilde{v}_1$ and $\bar{v} > \tilde{v}_3$. In the interval $[\tilde{v}_1, \tilde{v}_3]$ corresponding to $P = P_s$, $\bar{v}$ does not exist. This interval corresponds to the horizontal part of the van der Waals isotherm. In the real situation, i.e. N very large but not infinite, the isotherm of a non-ideal gas is near to the horizontal part. For $P = P_s$ we have the gas–liquid phase transition. Because for $P = P_s$ we have two equal maxima, P_s is the value of pressure for which the Gibbs potentials corresponding to $\tilde{v}_1$ and $\tilde{v}_3$ are equal. Summarising, we obtained the correct condition for the phase transition without invoking the Maxwell rule.

Now we pass to the investigation of a geometrical structure of the parameter space. Similar to the case of the ideal gas we can start from the potential $\gamma = \bar{h}(\alpha, \beta)$. But $\gamma(\alpha, \beta)$ is a very complicated function of α and β, so we must pass to the potential $\ln Z(\beta, \bar{v}) = \bar{h} + \alpha\bar{v}$ depending on two parameters β and $\bar{v} \equiv v$. In this representation the metric is diagonal (see [12]):

$$\mathrm{d}l^2 = \frac{\partial^2 \ln Z(\beta, v)}{\partial \beta^2} \mathrm{d}\beta^2 - \frac{\partial^2 \ln Z(\beta, v)}{\partial v^k} \mathrm{d}v^2. \tag{3.15}$$

If we pass from β to T we obtain

$$\mathrm{d}l^2 = -\frac{1}{T} \frac{\partial^2 \bar{f}}{\partial T^2} \mathrm{d}T^2 + \frac{1}{T} \frac{\partial^2 \bar{f}}{\partial v^2} \mathrm{d}v^2 \tag{3.16}$$

where $\bar{f} = -kT \ln Z(\beta, v)$ is the free energy per particle.

In our case

$$\bar{f} = -kT - kT \ln\left(\frac{2\pi \ln kT}{h^2}\right)^{3/2} (v - b) + kTa/v \tag{3.17}$$

and the components of the metric tensor and its determinant are

$$g_{TT} = -\frac{1}{T} \frac{\partial^2 \bar{f}}{\partial T^2} = \frac{3}{2} T^{-2} \qquad g_{vv} = \frac{1}{T} \frac{\partial^2 \bar{f}}{\partial v^2} = \frac{1}{(v-b)^2} - \frac{2a}{v^3} \frac{1}{T}$$
$$g = \det(g_{ij}) = \frac{3}{2} T^{-2} \left(\frac{1}{(v-b)^2} - \frac{2a}{v^3} \frac{1}{T} \right) \qquad (k-1). \tag{3.18}$$

In order to calculate the scalar curvature R we use the formula

$$R = -\frac{1}{\sqrt{g}} \frac{\partial}{\partial T} \left(\frac{1}{\sqrt{g}} \frac{\partial g_{vv}}{\partial T} \right) - \frac{1}{\sqrt{g}} \frac{\partial}{\partial v} \left(\frac{1}{\sqrt{g}} \frac{\partial g_{TT}}{\partial v} \right) \tag{3.19}$$

which corresponds to the diagonal form of the metric. In our case g_{TT} does not depend on v, which implies that the second term in (3.19) vanishes. After calculations we finally get

$$R = -\frac{1}{\sqrt{g}}\frac{\partial}{\partial T}\left(\frac{1}{\sqrt{g}}\frac{\partial g_{vv}}{\partial T}\right) = \frac{2a}{gT^3v^3} + \frac{3a^2}{g^2T^6v^6}. \tag{3.20}$$

From this formula formula we see that R is always positive. The critical point is given by the following parameters:

$$v_b = 3b \qquad T_c = \frac{8}{27}\frac{a}{b} \qquad P_c = \frac{1}{27}\frac{a}{b^2}. \tag{3.21}$$

At this point $g_{vv} = 0$ and $g = 0$. If the critical point is approached then $R \to +\infty$. If $v \to b$ or $v \to \infty$, R tends to 0.

As was mentioned in the introduction, R is interpreted as the measure of stability of the system. This example confirms our interpretation of the scalar curvature R. It expresses the global fluctuations in the system caused by the interaction of particles.

Up to now, the behaviour of the system near the critical point was characterised by the isothermal compressibility $\chi_T = -(1/V)\partial V/\partial P$, the correlation function $\nu(r)$ and the correlation length ξ. All these quantities are strictly connected and express the influence of interaction of particles on the density fluctuations. It seems that this characteristic is not complete, because fluctuations of energy of the system are not accounted for. The scalar curvature gives a full characteristic of the fluctuations in the system (strictly connected with interaction of particles).

4. Magnetic systems

In our previous paper [6] we investigated the two simplest models of magnetic systems: the one-dimensional Ising model with short-range interaction, and the mean-field model corresponding to a very long-range interaction. It turned out that in both cases the scalar curvature of the parameter space tends to $+\infty$ while approaching the critical points.

Now we investigate the class of magnetic models conforming to the scaling laws. The singular part of the Gibbs function per spin may be expressed near the critical point as [13]

$$\bar{g}(\varepsilon, B) = \lambda^{-1}\bar{g}(\varepsilon\lambda^{a_\varepsilon}, B\lambda^{a_B}) \qquad \lambda > 0. \tag{4.1}$$

Functions of such a type are obtained using renormalisation group methods (see [14]). This function is a generalised homogeneous function of parameters ε and B. $\varepsilon = (T - T_c)/T_c$ is the dimensionless measure of deviation from the critical temperature and B is the external magnetic field. The parameter λ is only a mathematical construction. It must cancel out in the right-hand side. For $\varepsilon > 0$ we can set $\lambda = \varepsilon^{-1/a_\varepsilon}$ and for $\varepsilon < 0$ we get $\lambda = |-\varepsilon|^{-1/a_\varepsilon}$. Regarding these facts we can write (4.1) in the form

$$\begin{aligned} \bar{g}_+(\varepsilon, B) &= -\varepsilon^{1/a_\varepsilon}\psi_+(B\varepsilon^{-a_\beta/a_\varepsilon}) \qquad && \varepsilon > 0 \\ \bar{g}_-(\varepsilon, B) &= -|-\varepsilon|^{1/a_\varepsilon}\psi_-(B|-\varepsilon|^{-a_\beta/a_\varepsilon}) \qquad && \varepsilon < 0 \end{aligned} \tag{4.2}$$

where ψ_+ and ψ_- are, in general, different functions of ε and B. Now we can calculate various thermodynamical derivatives. It is well known that critical indices may be expressed by the two scaling parameters a_ε and a_B, namely

$$\beta = \frac{1-a_B}{a_\varepsilon} \qquad \delta = \frac{a_B}{1-a_B} \tag{4.3}$$

$$\alpha = \alpha' = \frac{2a_\varepsilon - 1}{a_\varepsilon} \qquad \gamma = \gamma' = \frac{2a_B - 1}{a_\varepsilon}. \tag{4.4}$$

It is also well known that thermodynamical inequalities for critical indices became equalities, namely

$$\alpha + 2\beta + \gamma = 2 \tag{4.5}$$

$$\alpha + \beta(1+\delta) = 2. \tag{4.6}$$

From the above equalities we see that

$$\beta\delta = \gamma + \beta. \tag{4.7}$$

Among all the indices, two are independent. The scaling law does not give a possibility of evaluation of those two independent indices. For particular models they may be calculated using renormalisation group methods [14]. If we adopt the principle $R \to +\infty$, we automatically restrict the class of models leading to (4.1) for the Gibbs potential. In order to calculate R we start from the metric expressed in the Gibbs potential representation [12]:

$$\mathrm{d}l^2 = -\frac{1}{T}\frac{\partial^2 \bar{g}}{\partial T^2}\,\mathrm{d}T^2 - 2\frac{1}{T}\frac{\partial^2 \bar{g}}{\partial T\,\partial B}\,\mathrm{d}T\,\mathrm{d}B - \frac{1}{T}\frac{\partial^2 \bar{g}}{\partial B^2}\,\mathrm{d}B^2. \tag{4.8}$$

All differentiations we perform are with respect to parameters T and B and we are left with only the most singular terms, so the factor $1/T$ in (4.8) may be omitted. It is useful to pass from the coordinates T and B to ε and B. In order to calculate the Riemann scalar curvature we start from the formula

$$R = \frac{1}{2(\det g_{ij})^2}\begin{vmatrix} -\dfrac{\partial^2 \bar{g}}{\partial \varepsilon^2} & -\dfrac{\partial^2 \bar{g}}{\partial B^2} & -\dfrac{\partial^2 \bar{g}}{\partial B\,\partial \varepsilon} \\ -\dfrac{\partial^2 \bar{g}}{\partial \varepsilon^3} & -\dfrac{\partial^3 \bar{g}}{\partial B^2 \partial \varepsilon} & -\dfrac{\partial^3 \bar{g}}{\partial B\,\partial \varepsilon^2} \\ -\dfrac{\partial^3 \bar{g}}{\partial \varepsilon^2\,\partial B} & -\dfrac{\partial^3 \bar{g}}{\partial B^3} & -\dfrac{\partial^3 \bar{g}}{\partial \varepsilon\,\partial B^2} \end{vmatrix}. \tag{4.9}$$

First we consider the case $T > T_c$, $B = 0$. In this case no spontaneous magnetisation exists, i.e.

$$m = -\frac{\partial \bar{g}}{\partial B}\bigg|_{B=0} = \varepsilon^{(1-a_B)a_\varepsilon}\psi_+^1(0) = 0 \Rightarrow \psi_+^1(0) = 0$$
$$\psi_+^1 = \frac{\partial \psi_+}{\partial(B\varepsilon^{-a_B/a_\varepsilon})}. \tag{4.10}$$

In order to simplify the notation we denote $1/a_\varepsilon = A$ and $a_{B/a_\varepsilon} = -C$. Regarding the fact that $\psi_+^1(0)=0$, we successively obtain

$$\begin{aligned}
&-\frac{\partial^2\bar{g}}{\partial\varepsilon^2}=A(A-1)\varepsilon^{A-2}\psi_+(0)>0\\
&-\frac{\partial^2\bar{g}}{\partial B^2}=\varepsilon^{A+2C}\psi_+''(0)>0\\
&-\frac{\partial^3\bar{g}}{\partial B\,\partial\varepsilon}=0\\
&-\frac{\partial^3\bar{g}}{\partial\varepsilon^3}=A(A-1)(A-2)\varepsilon^{A-3}\psi_+(0)\\
&-\frac{\partial^3 g}{\partial\varepsilon^2\,\partial B}=0\\
&-\frac{\partial^3\bar{g}}{\partial B^2\,\partial\varepsilon}=(A+2C)\varepsilon^{A+2C-1}\psi_+''(0)\\
&-\frac{\partial^3\bar{g}}{\partial B^3}=\varepsilon^{A+3C}\psi_+'''(0)
\end{aligned}\tag{4.11}$$

and

$$\det(g_{ij})=A(A-1)\varepsilon^{2A-2C-2}\psi_+(0)\psi_+''(0)>0.\tag{4.12}$$

As a final result we get for R

$$R=\frac{\varepsilon^{-A}(A+2C)[(A+2C)-(A-2)]}{2A(A-1)\psi_+(0)}.\tag{4.13}$$

The term $A(A-1)\psi_+(0)$ is always positive and proportional to the diagonal term of the metric tensor $-\partial^2\bar{g}/\partial\varepsilon^2$. The curvature R given by the above formula may be expressed by the critical indices as

$$R=\frac{\varepsilon^{\alpha-2}\gamma(\gamma-\alpha)}{2(2-\alpha)(1-\alpha)\psi_+(0)}.\tag{4.14}$$

The index α is no larger than 2, which follows from the equality (4.3) (γ and β are positive). The denominator in the above formula is positive due to the mentioned positivity of $A(A-1)\psi_+(0)$ $(A=2-\alpha)$. The positivity of this term does not imply $\alpha<1$ or $\alpha>1$, because $\psi_+(0)$ may be positive or negative. Since for our models we postulate $R\to+\infty$, we automatically obtain $\gamma>\alpha$. This inequality implies $\beta+\gamma>1$ (due the equality (4.5)) and vice versa. The inequality $\beta+\gamma>1$ automatically gives $\alpha<1$ and $\beta\delta>0$. The obtained results are in accordance with model analysis and experiment.

Next we investigate the case $T<T_c$. Now the situation is more complicated, since we have spontaneous magnetisation and $\psi_-^1(0)$ is no longer zero. In this case it is plausible to pass to the representation of free energy $\bar{f}(\varepsilon, m)$. In this representation the components of the metric tensor are [6]

$$g_{11}=-\frac{1}{T}\frac{\partial^2\bar{f}}{\partial T^2}\qquad g_{12}=0\qquad g_{22}=\frac{1}{T}\frac{\partial^2\bar{g}}{\partial m^2}.\tag{4.15}$$

The free energy is a generalised homogeneous function of the parameters ε and m (m is the magnetisation per spin):

$$\bar{f}(\varepsilon, m) = \lambda^{-1}\bar{f}(\varepsilon\lambda_1^{a_\varepsilon} m\lambda^{1-a_B/a_\varepsilon}). \tag{4.16}$$

For details see [15]. If we set $\varepsilon\lambda^{a_\varepsilon} = -1$, we obtain

$$\bar{f}(\varepsilon_1 m) = |-\varepsilon|^{1/a_\varepsilon}\varphi_-(m|-\varepsilon|^{-1/a_\varepsilon + a_B/a_\varepsilon}) = |-\varepsilon|^A\varphi_-(m|-\varepsilon|^{-A-C}). \tag{4.17}$$

In the following calculation we omit the term $1/T$ and pass to the coordinate ε. In this case the metric is diagonal and we calculate R from the formula

$$R = -\frac{1}{\sqrt{g}}\left[\frac{\partial}{\partial\varepsilon}\left(\frac{1}{\sqrt{g}}\frac{\partial}{\partial\varepsilon}\frac{\partial^2\bar{f}}{\partial m^2}\right) + \frac{\partial}{\partial m}\left(\frac{1}{\sqrt{g}}\frac{\partial}{\partial m}\left(-\frac{\partial^2\bar{f}}{\partial\varepsilon^2}\right)\right)\right] \tag{4.18}$$

which is equivalent to the expression

$$R = \frac{1}{2(\det g_{ij})^2}\begin{vmatrix} -\dfrac{\partial^2\bar{f}}{\partial\varepsilon^2} & \dfrac{\partial^2\bar{f}}{\partial m^2} & 0 \\ \dfrac{\partial^3\bar{f}}{\partial\varepsilon^3} & \dfrac{\partial^3\bar{f}}{\partial m^2\,\partial\varepsilon} & \dfrac{\partial^3\bar{f}}{\partial m\,\partial\varepsilon^2} \\ \dfrac{\partial^3\bar{f}}{\partial\varepsilon^2\,\partial m} & \dfrac{\partial^3\bar{f}}{\partial m^3} & \dfrac{\partial^3\bar{f}}{\partial\varepsilon\,\partial m^2} \end{vmatrix}. \tag{4.19}$$

It is easy to see that the argument of function φ_-, i.e. $m|-\varepsilon|^{-A-C}$ is the reduced magnetisation $m|-\varepsilon|^{-\beta} = \tilde{m}$ and the equation of state has the form [13]

$$B = \frac{\partial\bar{f}}{\partial m} = |-\varepsilon|^{-C}\varphi_-^1(\tilde{m}). \tag{4.20}$$

In turn $C = -\gamma-\beta$. If we divide both sides of (4.20) by $|-\varepsilon|^{-\gamma-\beta}$, we obtain the equation of state in the reduced variables

$$\tilde{B} = \varphi^1(\tilde{m}). \tag{4.21}$$

This equation may be presented as the Widom expansion [13]

$$\varphi_-^1(\tilde{m}) = b_0\tilde{m}^\delta - b_1\tilde{m}^{\delta-1/\beta} + b_2\tilde{m}^{\delta-2/\beta} \qquad b_0, b_1, b_2 > 0. \tag{4.22}$$

In our considerations we restrict ourselves to the first two terms of (4.22). By the tensor transformation we can pass to the coordinates ε and $m^1 = am$ (a is positive, and is such that, for $B = 0$, we get reduced spontaneous magnetisation $\tilde{m}^1 = 1$). Then the equation of the state has the form

$$\tilde{B} = a\varphi_-^1(\tilde{m}^1) = a^1(\tilde{m}_-^{1\delta}\tilde{m}^{1\delta-1/\beta}) \qquad a^1 > 0. \tag{4.23}$$

In the following calculations we omit the factor a^1, corresponding to the conformal transformation of the metric. The second and third derivatives of $\bar{f}(m_1^1\varepsilon)$ by $B = 0$ are

$$\frac{\partial^2\bar{f}}{\partial m'^2} = |-\varepsilon|^{-2C-A}\varphi_-''(1) \qquad \varphi_-''(1) > 0$$

$$\frac{\partial^3\bar{f}}{\partial m'^3} = |-\varepsilon|^{-3C-2A}\varphi_-'''(1) = |-\varepsilon|^{\gamma-\beta}\varphi_-'''(1)$$

$$\frac{\partial^2\bar{f}}{\partial m'\,\partial\varepsilon} = (A+C)|-\varepsilon|^{-C-1}\varphi_-''(1)$$

$$\frac{\partial^3 \bar{f}}{\partial m' \partial \varepsilon^2} = (A+C)(3C+A+1)\varphi''_-(1)|-\varepsilon|^{-C-2} + (A+C)^2|-\varepsilon|^{-C-2}\varphi'''_-(1) \tag{4.24}$$

$$\frac{\partial^3 \bar{f}}{\partial m'^2 \partial \varepsilon} = (2C+A)|-\varepsilon|^{-2C-A-1}\varphi''_-(1) + (A+C)|-\varepsilon|^{-2C-A-1}\varphi'''_-(1)$$

$$\frac{\partial^2 \bar{f}}{\partial \varepsilon^2} = A(A-1)|-\varepsilon|^{A-2}\varphi_-(1) + (A+C)^2|-\varepsilon|^{A-2}\varphi''_-(1)$$

$$\frac{\partial^3 f}{\partial \varepsilon^3} = -A(A-1)(A-2)|-\varepsilon|^{A-3}\varphi_-(1) + (A+C)(3C+3)|-\varepsilon|^{A-3}\varphi''_-(1)$$
$$+ (A+C)^3|-\varepsilon|^{A-3}\varphi'''_-(1).$$

The determinant of the metric tensor is

$$\det(g_{ij}) = |-\varepsilon|^{-2C-2}[-A(A-1)\varphi_-(1) - (A+C)^2\varphi''_-(1)]\varphi''_-(1). \tag{4.25}$$

Substituting (4.24) and (4.25) into the formula for R we get

$$R = \frac{|-\varepsilon|^{-A}(\gamma+\beta-1)[\varphi_-(1)\varphi'''(1)A(A-1)\beta + \beta^2(\beta-1)\varphi''^2_-(1) - 2A(A-1)\gamma\varphi_-(1)\varphi''_-(1)]}{[-A(A-1)\varphi_-(1) - (A+C)^2\varphi''(1)]^2\varphi''_-(1)}. \tag{4.26}$$

The factor $\gamma+\beta-1$ is positive due to $R>0$ by $T>T_c$. If we postulate $R>0$, we obtain the inequality

$$\varphi_-(1)\varphi'''_-(1)A(A-1)\beta + \beta^2(\beta-1)\varphi''^2_-(1) - 2A(A-1)\gamma\varphi_-(1)\varphi''_-(1) > 0. \tag{4.27}$$

Next we calculate $\varphi''_-(1)$, $\varphi'''_-(1)$, $\varphi_-(1)$ using the expansion

$$\varphi'_-(\tilde{m}^1) = \tilde{m}'^{\delta} - \tilde{m}'^{\delta-1/\beta}$$

$$\varphi''_-(1) = \frac{1}{\beta} \qquad \varphi'''_-(1) = \frac{1}{\beta}\left(2\delta - \frac{1}{\beta} - 1\right)$$

$$\varphi_-(1) = \frac{1}{\delta+1} - \frac{1}{\delta+1-1/\beta} + m_0 \tag{4.28}$$

where m_0 is an additive constant resulting from the integration of $\varphi'_-(\tilde{m}')$. In order to estimate this constant, we investigate the determinant of g_{ij}, which is positive:

$$-A(A-1)\varphi_-(1)\varphi''_-(1) - (A+C)^2\varphi''^2_-(1) > 0. \tag{4.29}$$

Substituting $\varphi_-(1)$ and $\varphi''_-(1)$ and using $A = 2-\alpha$, $2-\alpha = \gamma + 2\beta$, $A+C = \beta$, $\gamma+\beta = \beta\delta$ we get $m_0 < 0$. Next we substitute (4.28) into (4.27) and finally obtain

$$m_0(\beta-1) > 0 \Rightarrow \beta - 1 < 0 \Rightarrow \beta < 1. \tag{4.30}$$

This inequality is fulfilled for all magnetic models and is in agreement with experiment.

We can also show that $\gamma > \beta$. It is the consequence of the fact that $\partial^2 B/\partial m^2 \sim \partial^3 f/\partial m'^3 = |-\varepsilon|^{\gamma-\beta}\varphi''_-(1)$ must tend to 0 if $\varepsilon \to 0$, so $\gamma - \beta$ as the exponent must be positive.

Now we investigate a class of models, which are not necessarily described by a generalised homogeneous Gibbs function [15, 16]

$$\begin{aligned} -\bar{g}_+(\varepsilon_1 B) &= \varepsilon^{1/a_\varepsilon}\psi_+(B\varepsilon^{-a_B/a_\varepsilon}) - a\varepsilon^{1/a_\varepsilon}\ln|\varepsilon| \qquad (T>T_c) \\ -\bar{g}_-(\varepsilon_1 B) &= |-\varepsilon|^{1/a_\varepsilon}\psi_-(B|-\varepsilon|^{-a_B/a_\varepsilon}) - a|-\varepsilon|^{1/a_\varepsilon}\ln|\varepsilon| \qquad (T<T_c). \end{aligned} \tag{4.31}$$

These functions lead to the same critical indices as the first terms (4.31). The factor with $\ln|\varepsilon|$ has no influence on either the critical indices or equation of state. Analogously as in the preceding case, we have left in the calculations the terms which are most singular. First we investigate the case of $T > T_c$ and $B = 0$. The scalar curvature R will be calculated from the formula (4.9). In our case the elements of this determinant are

$$
\begin{aligned}
&-\frac{\partial^2 \bar{g}}{\partial \varepsilon^2} = -a(A-1)A\varepsilon^{A-2}\ln|\varepsilon| > 0 \\
&-\frac{\partial^2 \bar{g}}{\partial \varepsilon \partial B} = 0 \\
&-\frac{\partial^2 \bar{g}}{\partial B^2} = \varepsilon^{A+2C}\psi''_+(1) > 0 \\
&-\frac{\partial^3 \bar{g}}{\partial \varepsilon^2 \partial B} = 0 \\
&-\frac{\partial^3 \bar{g}}{\partial \varepsilon^3} = -a(A-1)(A-2)A\varepsilon^{A-3}\ln|\varepsilon| \\
&-\frac{\partial^3 \bar{g}}{\partial B^3} = \varepsilon^{A+3C}\psi'''_+(0) \\
&-\frac{\partial^3 \bar{g}}{\partial B^2 \partial \varepsilon} = (A+2C)\varepsilon^{A+2C-1}\psi_+(0).
\end{aligned}
\tag{4.32}
$$

The determinant of the metric tensor is

$$\det(g_{ij}) = -aA(A-1)\varepsilon^{2A+2C-2}\psi''_+(0)\ln|\varepsilon| > 0. \tag{4.33}$$

Substituting (4.32) and (4.33) into (4.9) we get

$$R = \frac{-\varepsilon^{-A}(A+2C)[(A+2C)-(A-2)]}{2aA(A-1)\ln|\varepsilon|}. \tag{4.34}$$

If we express (4.34) by the critical indices, we obtain

$$R = \frac{-\varepsilon^{\alpha-2}\gamma(\gamma-\alpha)}{2a(2-\alpha)(1-\alpha)\ln|\varepsilon|}. \tag{4.35}$$

An application of the principle $R \to +\infty$ leads to the inequality $\gamma > \alpha$.

Now we investigate the case of $T < T_c$ and $B = 0$. Analogously as in the case of generalised homogeneous models we pass to the free energy representation:

$$\bar{f}(\varepsilon, m') = |-\varepsilon|^A \varphi_-(m'|-\varepsilon|^{-A-C}) + a|-\varepsilon|^A \ln|\varepsilon|. \tag{4.36}$$

The scalar curvature will be calculated from (4.19). In all the calculation we left only the most singular terms. The second and third derivatives of $\bar{f}(\varepsilon, m')$ are

$$
\begin{aligned}
&-\frac{\partial^2 \bar{f}}{\partial \varepsilon^2} = -aA(A-1)|-\varepsilon|^{A-2}\ln|\varepsilon| > 0 \\
&\frac{\partial^2 \bar{f}}{\partial \varepsilon\, \partial m'} = (A+C)|-\varepsilon|^{-C-1}\varphi''_-(1)
\end{aligned}
$$

$$\frac{\partial^2 \bar{f}}{\partial m'^2} = |-\varepsilon|^{-2C-A} \varphi''_-(1) > 0$$

$$\frac{\partial^3 \bar{f}}{\partial m' \partial \varepsilon^2} = (A+C)(3C+A+1)\gamma - \varepsilon|^{-C-2} \varphi''_-(1) + (A+C)^2 |-\varepsilon|^{-C-2} \varphi'''_-(1) \tag{4.37}$$

$$\frac{\partial^3 f}{\partial m'^2 \partial \varepsilon} = (2C+A)|-\varepsilon|^{-2C-A-1} \varphi''_-(1) + (A+C)|-\varepsilon|^{-2C-A-1} \varphi'''_-(1)$$

$$\frac{\partial^3 \bar{f}}{\partial m'^3} = |-\varepsilon|^{-3C-2A} \varphi'''_-(1)$$

$$\frac{\partial^3 \bar{f}}{\partial \varepsilon^3} = -aA(A-1)(A-2)|-\varepsilon|^{A-3} \ln|\varepsilon|.$$

The determinant of the metric tensor is

$$\det(g_{ij}) = -aA(A-1)|-\varepsilon|^{-2C-2} \varphi''_-(1) \ln|\varepsilon| > 0. \tag{4.38}$$

If we substitute (4.37) and (4.38) into (4.19) we get

$$R = \frac{-|-\varepsilon|^{\alpha-2}(\gamma+\beta-1)[\gamma\varphi''_-(1) - \frac{1}{2}\beta\varphi'''_-(1)]}{a\varphi''_-(1)(2-\alpha)(1-\alpha)\ln|\varepsilon|} \tag{4.39}$$

$\gamma+\beta-1>0$ due to $\gamma>\alpha$. If we suppose $R \to +\infty$, we obtain the inequality

$$\gamma\varphi''_-(1) - \tfrac{1}{2}\beta\varphi'''_-(1) > 0. \tag{4.40}$$

After calculations ($\varphi''_-(1)$ and $\varphi'''_-(1)$ are given by the formula (4.28)) we get $\beta < 1$.

The principle $R \to +\infty$ in both cases leads to the two independent inequalities for the critical indices $\alpha < \gamma$ and $\beta < 1$.

5. Concluding remarks

The traditional approach to statistical thermodynamics is based on the idea of entropy. If we can find a formula for entropy, we are able to calculate various thermodynamical potentials. The second derivatives of those potentials are connected with the second moments of fluctuations. Up to now statistical investigations have been restricted to the analysis of second moments. This approach gives many inequalities for critical indices. In our geometrical approach, second derivatives of the respective potentials are the components of the metric tensor in various coordinates. The positivity of the metric expresses the well known stability conditions.

The scalar curvature R is the function of second and third moments. In this paper and in [6, 7] we showed that, for a wide class of statistical models, $R \to +\infty$ when the critical point is approached. The geometrisation of statistical thermodynamics is possible if there exist no less than two linearly independent stochastic variables. In the case of magnetic models such observables are the energy of interaction of spins and the sum of spins. The conjugated statistical temperatures are β and magnetic field B. The scalar curvature R expresses a measure of global-interaction-induced fluctuations of these stochastic variables. It seems that all physically plausible models have the property $R \to +\infty$ at the critical point.

On the other hand, many regularities are observed for critical indices. The scaling hypothesis introduced explains the independence only of two critical indices, and gives the equalities for triple indices. The scaling hypothesis does not give any estimation of the values of the critical indices. It is evident that the following inequalities are generally observed: $\gamma > 1, \beta < 1, \alpha < 1, \gamma + \beta > 1, \delta > 2$. It seems that there was a lack of some statistical principle. The geometrical approach to statistical thermodynamics presented gives some sort of such a principle. This principle is based on good statistical and geometrical arguments.

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