# Pauli paramagnetic gas in the framework of Riemannian geometry

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We investigate the thermodynamic curvature resulting from a Riemannian geometry approach to thermodynamics for the Pauli paramagnetic gas which is a system of identical fermions each with spin $\frac{1}{2}$, and also for classical ideal paramagnetic gas. We find that both the curvature of classical ideal paramagnetic gas and the curvature of the Pauli gas in the classical limit reduce to that of a two-component ideal gas. On the other hand, it is seen straightforwardly that the curvature of classical gas satisfies the geometrical equation exactly. Also a simple relationship between the curvature of Pauli gas and the correlation volume is obtained. We see that it is only in the classical and semiclassical regime that the absolute value of the thermodynamic curvature can be interpreted as a measure of the stability of the system. [S1063-651X(99)09009-1]

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## I. INTRODUCTION

Thermodynamic fluctuation theory, whose basic goal is to express the time independent probability distribution for the state of a fluctuating system in terms of thermodynamic quantities, is usually attributed to Einstein, who applied it to the problem of blackbody radiation [1]. The full formalism for classical thermodynamic fluctuation theory was worked out by Green and Callen [2] in 1951 and elaborated upon by Callen [3].

However, despite wide applicability, the classical fluctuation theory fails near critical points and at volumes of the order of the correlation volume and less.

In 1979 Ruppeiner [4] introduced a Riemannian metric structure representing thermodynamic fluctuation theory, which is related to the second derivatives of the entropy. His theory offered a good interpretation for the distance between thermodynamic states. He showed that the classical theory breaks down because it does not take into account local correlations [5]. This deficiency of the classical theory is precluded in the covariant fluctuation theory of Ruppeiner by using a hierarchy of concentric subsystems, each of which samples only the thermodynamic state of the subsystem immediately larger than itself [6,7]. One of the most significant topics of this theory is the introduction of the Riemannian thermodynamic curvature as a qualitative tool for the study of fluctuation phenomena. This paper is based on this geometrical approach.

Here we investigate the thermodynamic curvature for two cases: the Pauli paramagnetic gas that is a gas of identical spin 1/2 fermions in the presence of an external magnetic field, and the classical ideal paramagnetic gas. Although in each case the thermodynamic state space is three dimensional we obtain very simple expressions for thermodynamic curvatures. It is demonstrated that the curvatures of both classical gas and Pauli gas in the classical limit reduce to that of a two-component ideal gas [8]. We also demonstrate that the curvature of classical gas satisfies the geometrical equation. It is a good example that corroborates the general theory of Ruppeiner which generalizes the geometrical equation to cases with more thermodynamic variables [9].

The outline of this paper is as follows. First the Riemannian geometry of thermodynamic fluctuation theory is summarized. Second, the Riemannian scalar curvature of the Pauli paramagnetic gas is evaluated. Finally the curvature of the classical ideal paramagnetic gas is calculated and is compared to the the curvature of Pauli paramagnetic gas in the classical limit.

## II. THE GEOMETRICAL APPROACH TO THERMODYNAMICS

In this section we review the Riemannian geometrical approach to thermodynamics, we discuss its connection to the covariant thermodynamic fluctuation theory, and we consider the interpretations offered for thermodynamic curvature.

The second derivatives of a thermodynamic potential density define the Riemannian metric tensor for the thermodynamic state space [7]. If we choose extensive densities as coordinates, we can use the density of either energy or entropy as the potential and these two descriptions are thermodynamically equivalent. However, the metric tensor is different in these two representations. Here we work in entropy representation where the meaning of distance, measured in units of average fluctuations, is very transparent. When some extensives are replaced by intensives, the potential becomes a Massieu function [3]. Let us consider as our thermodynamic system a fluid $A_{V_0}$ with a very large volume $V_0$, and within it an open subsystem $A_V$ of fixed volume $V$. The system $A_{V_0}$ consists of $r$ fluid components and is in equilibrium. We denote by the $n$-tuple $a_0=(a_0^0,a_0^1,a_0^2, \dots ,a_0^r)$ the internal energy per volume and the number of particles per volume of the $r$ components of $A_{V_0}$ [7]. These parameters are the standard densities in the entropy representation. They define the thermodynamic state of $A_{V_0}$. The subsystem $A_V$ has a corresponding thermodynamic state $a$. In classical ther-

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modynamic fluctuation theory, in the Gaussian approximation the probability of finding the thermodynamic state of $A_V$ between $a$ and $a+da$ is [7]

$$P_V(a|a_0)da^0\cdots da^r=\left(\frac{V}{2\pi}\right)^{(r+1)/2}\times\exp\left(-\frac{V}{2}g_{\mu\nu}(a_0)\Delta a^\mu\Delta a^\nu\right)\times\sqrt{g(a_0)}da^0da^1\cdots da^r, \quad (2.1)$$

where

$$\Delta a^\mu=a^\mu-a_0^\mu, \quad g_{\mu\nu}=-\frac{1}{k_B}\frac{\partial^2 s}{\partial a^\mu\partial a^\nu}\bigg|_{a=a_0}, \quad (2.2)$$

and $s$ is the entropy per volume in the thermodynamic limit, $k_B$ is Boltzmann's constant, and $g(a_0)=\det[g_{\mu\nu}(a_0)]$.

The quadratic form in Eq. (2.1),

$$(\Delta l)^2=g_{\mu\nu}(a_0)\Delta a^\mu\Delta a^\nu, \quad (2.3)$$

constitutes a positive definite Riemannian metric on the thermodynamic state space. The positive definiteness is a consequence of entropy being a maximum at equilibrium $a=a_0$. Equations (2.1) and (2.3) provide the physical interpretation for the distance between two thermodynamic states. The less the probability of fluctuation between states, the further apart they will be. The quantity

$$\sqrt{g(a_0)}da^0da^1\cdots da^r$$

in Eq. (2.1) is the invariant Riemannian thermodynamic state space volume element. The particular form of Eq. (2.2) holds only for standard densities. To express the metric tensor in a general set of thermodynamic coordinates $x=x(a)$, one can use the following transformation rule:

$$g'_{\alpha\beta}(x)=\frac{\partial a^\mu}{\partial x^\alpha}\frac{\partial a^\nu}{\partial x^\beta}g_{\mu\nu}(a). \quad (2.4)$$

Having the metric we can calculate the Riemannian curvature tensor. For our metric, the scalar curvature $R$ has units of real space volume, regardless of the dimension of the state space [8,9]. It is a measure of the effective interaction between the components of the system, it is proportional to the correlation volume, and it diverges near the critical point of a pure interacting fluid.

Covariant thermodynamic fluctuation theory indicates that curvature is a measure of the smallest volume where classical thermodynamic fluctuation theory can work. This theory was proposed as the correct way to extend classical thermodynamic fluctuation theory beyond the Gaussian approximation [7]. An alternative interpretation of thermodynamic curvature was offered by Janyszek and Mrugala [10]. They suggested that thermodynamic curvature is a measure of the stability of the system under consideration. The system becomes less stable if the curvature increases and vice versa. Also these authors calculated the curvature of ideal Fermi and Bose gases [11]. They show that these systems have curvatures of opposite sign.

In this paper we interpret the absolute value of curvature as a measure of stability because in the sign convention we use the curvature of an ideal Bose gas diverges to negative infinity at Bose-Einstein condensation [11].

## III. THE GEOMETRY OF PAULI PARAMAGNETIC GAS

We now turn our attention to the study of the equilibrium state of a gas of noninteracting fermions in the presence of an external magnetic field $H$.

The extensive parameter which describes the magnetic properties of such a system is $M$, which is the component of the total magnetic moment parallel to the external field. The entropic intensive parameters are defined as [3]

$$F^1=\frac{\partial S}{\partial U}=\frac{1}{T}, \quad F^2=\frac{\partial S}{\partial N}=-\frac{\mu}{T}, \quad F^3=\frac{\partial S}{\partial M}=-\frac{H}{T}. \quad (3.1)$$

We use the thermodynamic potential $\phi$, which is defined as

$$\phi=s\left[\frac{1}{T},-\frac{\mu}{T},-\frac{H}{T}\right]=s-\frac{1}{T}u+\frac{\mu}{T}\rho+\frac{H}{T}m=\frac{P}{T}, \quad (3.2)$$

where $u$, $\rho$, $m$, and $P$ are energy per volume, density, magnetization, and pressure, respectively. The energy of a particle, in the presence of an external magnetic field $H$, is given by

$$\mathcal{E}=\frac{p^2}{2m_0}-\vec{J}\cdot\vec{H}, \quad (3.3)$$

where $\vec{J}$ is the intrinsic magnetic moment of the particle and $m_0$ is its mass. For a Pauli paramagnetic gas the spin of each particle is $\frac{1}{2}$; the vector $\vec{J}$ must then be either parallel to $\vec{H}$ or antiparallel. From the grand canonical distribution (using Fermi-Dirac statistics) one can obtain the following equations [12]:

$$\ln Q=\frac{PV}{k_BT}=\frac{V}{\lambda^3}(f_{5/2}^{+}+f_{5/2}^{-}), \quad (3.4)$$

$$\rho=\frac{N}{V}=\frac{1}{\lambda^3}(f_{3/2}^{+}+f_{3/2}^{-}), \quad (3.5)$$

where

$$f_n^{\pm}=f_n(\eta^{\pm}), \quad (3.6)$$

$$\eta^{\pm}=\eta\exp\left(\mp\frac{JH}{k_BT}\right)=\exp\left(\frac{\mu}{k_BT}\mp\frac{JH}{k_BT}\right) \quad (3.7)$$

and $\lambda=h/(2\pi m_0k_BT)^{1/2}$ is the mean thermal wavelength of the particle, $h$ is the Planck constant and

$$f_n(\eta)=\frac{1}{\Gamma(n)}\int_0^\infty\frac{X^{n-1}dX}{e^X/\eta+1} \quad (3.8)$$

we have used the standard symbol for fugacity $\eta=\exp(\mu/k_BT)$. From Eqs. (3.2) and (3.4) we can find the thermodynamic potential:

$$\phi(x,y,z)=Ix^{-3/2}[f_{5/2}(e^{-y-Jz})+f_{5/2}(e^{-y+Jz})], \quad (3.9)$$

where $I=(2\pi m)^{3/2}/h^3$ and $x=F^1, y=F^2, z=F^3$. We have set $k_B=1$.

Now it is straightforward to obtain the metric elements in $F$ coordinates [7]:

$$g_{\mu\nu}=\frac{\partial^2\phi}{\partial F^\mu \partial F^\nu}. \quad (3.10)$$

According to Eqs. (3.9) and (3.10) and noting that $\partial f_n(\eta)/\partial\eta=(1/\eta)f_{n-1}(\eta)$, the components of the metric tensor are as follows:

$$g_{11}=\frac{15}{4}Ix^{-7/2}(a+b), \quad g_{12}=\frac{3}{2}Ix^{-5/2}(c+d),$$

$$g_{13}=-\frac{3}{2}IJx^{-5/2}(c-d), \quad g_{22}=Ix^{-3/2}(e+f), \quad (3.11)$$

$$g_{23}=-IJx^{-3/2}(e-f), \quad g_{33}=IJ^2x^{-3/2}(e+f),$$

where $a=f^+_{5/2}$, $b=f^-_{5/2}$, $c=f^+_{3/2}$, $d=f^-_{3/2}$, $e=f^+_{1/2}$, $f=f^-_{1/2}$; they are functions of $y$ and $z$. Their derivatives with respect to $y$ and $z$ are as follows:

$$\frac{\partial a}{\partial y}=-c, \quad \frac{\partial a}{\partial z}=Jc, \quad \frac{\partial b}{\partial y}=-d, \quad \frac{\partial b}{\partial z}=-Jd,$$

$$\frac{\partial c}{\partial y}=-e, \quad \frac{\partial c}{\partial z}=Je, \quad \frac{\partial d}{\partial y}=-f, \quad \frac{\partial d}{\partial z}=-Jf, \quad (3.12)$$

$$\frac{\partial e}{\partial y}=-h, \quad \frac{\partial e}{\partial z}=Jh, \quad \frac{\partial f}{\partial y}=-k, \quad \frac{\partial f}{\partial z}=-Jk,$$

where $h=f^+_{-1/2}$, $k=f^-_{-1/2}$. We shall use these quantities to obtain the scalar curvature. The Riemann and the Ricci tensors and the scalar curvature, respectively, are

$$R^\kappa_{\lambda\mu\nu}=\partial_\nu\Gamma^\kappa_{\mu\lambda}-\partial_\mu\Gamma^\kappa_{\nu\lambda}+\Gamma^\eta_{\mu\lambda}\Gamma^\kappa_{\nu\eta}-\Gamma^\eta_{\nu\lambda}\Gamma^\kappa_{\mu\eta},$$

$$Ric_{\mu\nu}=R^\lambda_{\mu\lambda\nu}, \quad (3.13)$$

$$R=g^{\mu\nu}Ric_{\mu\nu},$$

where $\Gamma$'s are the Christoffel symbols [13]. In our sign convention the sign of $R$ for Fermi gas is positive and that of Bose gas is negative (just like the sign convention of Ref. [7]). The scalar curvature may be worked out from Eqs. (3.11), (3.12), and (3.13):

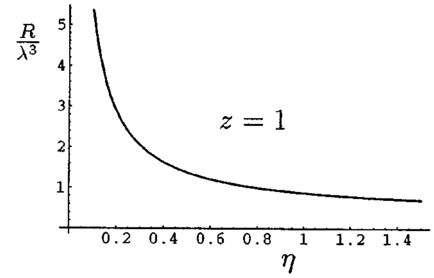


FIG. 1. Thermodynamic curvature as a function of fugacity for an isotherm ($z=1$).

$$R=\frac{\lambda^3}{2(5efa+5efb-3c^2f-3d^2e)^2}[55f^2ae^2+55f^2be^2 -28f^2ec^2-25f^2ach-25f^2bch-28fd^2e^2 +12fd^2ch-25e^2dka-25e^2bdk+12c^2dke +15cdhka+15cdbhk]. \quad (3.14)$$

As can be seen from Eq. (3.14), $R$ is a symmetric function of $z$; this means that scalar curvature is independent of the orientation of external magnetic field, $R(-H)=R(H)$.

In the classical limit and in the absence of an external magnetic field, we have $\eta^\pm\rightarrow\eta\rightarrow 0$ and $f^\pm_n(\eta)\rightarrow\eta$; so $R$ is obtained as follows:

$$R=\frac{1}{4}\frac{\lambda^3}{\eta}. \quad (3.15)$$

On the other hand in this limit, Eq. (3.5) gives

$$\rho=\frac{2}{\lambda^3}\eta. \quad (3.16)$$

From Eqs. (3.15) and (3.16) the classical limit of $R$ is given by

$$R=\frac{1}{2\rho}. \quad (3.17)$$

This surprising simple result shows that in the classical limit, the scalar curvature is of the order of the volume occupied by a single particle. It is in complete agreement with the scalar curvature obtained by Ruppeiner for a multicomponent ideal gas [8]. It means that in the classical limit the scalar curvature of the Pauli paramagnetic gas behaves like that of a two-component ideal gas.

Figure 1 shows the dependence of $R$ on $\eta$ for a fixed value of $H$ and for a fixed temperature in units of $\lambda^3$. In the classical region where $\eta<1$, $R$ diverges near $\eta=0$. This is related to the fact that in this limit $\rho$ goes to zero [as can be seen from Eq. (3.17)] i.e., there are not enough particles for a continuous thermodynamic description. In the quantum mechanical region, where $\eta\gg 1$, $R$ tends to a constant value.

Figure 2 shows the dependence of $R$ on $H$ for a fixed value of $\eta$ and for a fixed temperature in units of $\lambda^3$. $R$ is a monotonically decreasing function of $H$. Physically, as the external magnetic field increases, the relative fluctuations of

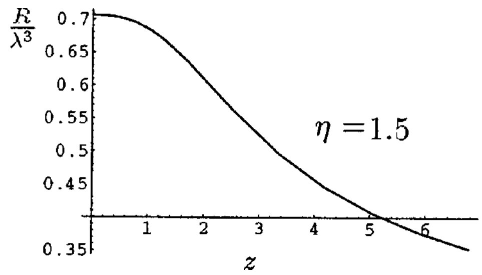


FIG. 2. Thermodynamic curvature as a function of magnetic field for an isotherm ($z=-H/T$ and $\eta=1.5$).

magnetization decrease. So, the system becomes more stable. Here we can interpret $R$ as a measure of the stability of the system. The less the magnitude of $R$, the more stable the system becomes.

Figure 3 shows the dependence of $R$ on $H$ for $\eta=40$. It can be seen that in this quantum regime, $R$ has a maximum. We cannot explain this in terms of the relative fluctuations of magnetization, because $\langle(\Delta m)^2\rangle/\langle m\rangle^2$ versus $z$ has no such maximum. In Fig. 4 we have shown the dependence of the inverse of $\langle(\Delta m)^2\rangle$ on $z$ for $\eta=40$. It is observed that the behavior of this curve is very similar to that of $R$. So it seems that the stability interpretation of thermodynamic curvature fails in a strong quantum regime.

For the last point we allude to a relationship between $R$ and the correlation volume. We note that the correlation function of Fermi gas in classical regime ($\rho\lambda^3 \ll 1$ or $\eta \ll 1$) is given by the formula [14]

$$\nu(r)=-\frac{1}{2}e^{-2\pi r^2/\lambda^2}. \tag{3.18}$$

So one can see that the correlation volume in this regime is

$$V_{\text{cor}}=\frac{\lambda^3}{(2\pi)^{3/2}}. \tag{3.19}$$

By comparing the above with Eq. (3.15) we can see that in the classical regime $R\eta$ is proportional to the correlation volume. The possible relationship between the curvature and the correlation volume in the quantum regime has not been explored yet.

### IV. CLASSICAL IDEAL PARAMAGNETIC GAS

In this section we calculate the scalar curvature of a classical paramagnetic gas and compare it to the scalar curvature of Pauli paramagnetic gas in the limit of low fugacity and low magnetic fields.

Consider a gas of identical mutually noninteracting and

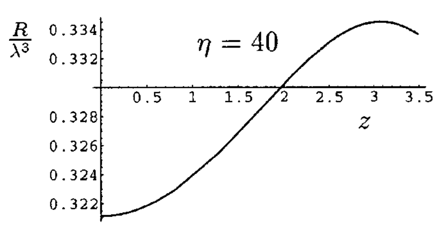


FIG. 3. Thermodynamic curvature as a function of magnetic field for an isotherm ($z=-H/T$ and $\eta=40$).

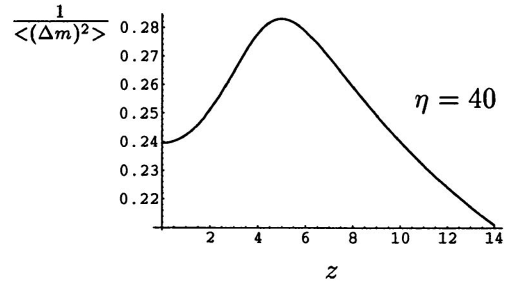


FIG. 4. The inverse of magnetization fluctuation as a function of magnetic field ($z=-H/T$ and $\eta=40$).

freely orientable dipoles, each having a magnetic moment $J$. In the presence of an external magnetic field $H$, the dipoles experience a torque tending to align them in the direction of the field. The energy of a particle is given by

$$\mathcal{E}=\frac{p^2}{2m_0}-JH\cos\theta. \tag{4.1}$$

Here we have neglected the effect of the induced magnetic field. Mijatovic *et al.* used the *energy form* of the metric to evaluate the geometry of the paramagnetic ideal gas [15]. They considered the particle number to be fixed. Here we use the *entropy form* of the metric. We also take the volume to be fixed. The logarithm of the grand canonical partition function (using Maxwell-Boltzmann statistics) is

$$\ln Q_c=\frac{PV}{k_BT}=4\pi\eta\frac{V}{\lambda^3}\frac{\sinh(Jz)}{Jz} \tag{4.2}$$

and the thermodynamic potential can again be obtained from Eqs. (4.2) and (3.2):

$$\phi_c=4\pi Ix^{-3/2}e^{-y}\frac{\sinh(Jz)}{Jz}, \tag{4.3}$$

where $x$, $y$, and $z$ are defined in Sec. III and $k_B=1$. The metric elements are obtained from Eq. (3.10):

$$\begin{aligned}
g_{11}&=15\pi Ix^{-7/2}e^{-y}\frac{\sinh(Jz)}{Jz},\\
g_{12}&=6\pi Ix^{-5/2}e^{-y}\frac{\sinh(Jz)}{Jz},\\
g_{13}&=-6\pi Ix^{-5/2}e^{-y}\left(\frac{\cosh(Jz)}{z}-\frac{\sinh(Jz)}{Jz^2}\right),\\
g_{22}&=4\pi Ix^{-3/2}e^{-y}\frac{\sinh(Jz)}{Jz},\\
g_{23}&=-4\pi Ix^{-3/2}e^{-y}\left(\frac{\cosh(Jz)}{z}-\frac{\sinh(Jz)}{Jz^2}\right),\\
g_{33}&=4\pi Ix^{-3/2}e^{-y}\left(\frac{J\sinh(Jz)}{z}-2\frac{\cosh(Jz)}{z^2}+2\frac{\sinh(Jz)}{Jz^3}\right).
\end{aligned} \tag{4.4}$$

Using Eqs. (3.13) and (4.4), one can calculate the scalar curvature:

$$R_c = \frac{1}{8\pi}\frac{\lambda^3}{\eta}\frac{Jz}{\sinh Jz}. \tag{4.5}$$

Equations (4.3) and (4.5) clearly show that $R_c$ and $\phi_c$ satisfy the following equation:

$$R_c = \kappa\frac{k_B}{\phi_c}, \tag{4.6}$$

where $\kappa = \frac{1}{2}$ and $k_B = 1$. This interesting result is nothing but the geometrical equation with $\kappa = \frac{1}{2}$ [7]. It is a good example which shows that the geometrical equation can be satisfied in more than two dimensions [9].

On the other hand, the equation of state of the classical ideal gas ($PV = Nk_BT$) and Eqs. (4.6) and (3.2) give

$$R_c = \frac{1}{2\rho}. \tag{4.7}$$

Equation (4.7) shows that the curvature of the classical ideal paramagnetic gas is of the same order as the volume occupied by a single particle.

We can see the dependence of $R_c$ on the magnetic field through Eq. (4.5). $R_c$ is a monotonically decreasing function of $z$ and has a maximum at $z = 0$. Here we can interpret the curvature as a measure of stability, since the relative fluctuations of magnetization $\langle(\Delta m)^2\rangle/\langle m\rangle^2$ dominate near $z = 0$, and decrease monotonically with increasing $z$.

Now let us look at Eq. (3.14) for the curvature of Pauli gas in the limit of low fugacity and low magnetic fields, where $f_n^{\pm} \to \eta^{\pm}$; one can obtain

$$R = \frac{1}{4}\frac{\lambda^3}{\eta}\frac{1}{\cosh Jz}. \tag{4.8}$$

Equation (4.8) is similar to Eq. (4.5), because the behavior of $\cosh z$ is similar to that of $\sinh z/z$; but they are somewhat different. The source of this difference is related to the fact that in the case of a classical ideal paramagnetic gas, each dipole is freely orientable whereas each particle in the Pauli paramagnetic gas can choose only two directions (even in the limit of low fugacity).

In fact, had we constrained the dipoles to choose only two directions (parallel or anti-parallel to $H$) i.e., had we set $\cos\theta = \pm 1$ in Eq. (4.1) and used the classical grand partition function we would have obtained

$$\ln Q_c' = 2\eta\frac{V}{\lambda^3}\cosh Jz. \tag{4.9}$$

This is just Eq. (3.4) in the limit of low fugacity and low magnetic fields (where $f_n^{\pm} \to \eta^{\pm} = \eta e^{\pm zJ}$). The thermodynamic potential is

$$\phi_c' = 2Ix^{-3/2}e^{-y}\cosh Jz. \tag{4.10}$$

Again this is the classical limit of Eq. (3.9). Using Eqs. (3.10) and (3.13) one can obtain the scalar curvature, which is just Eq. (4.8).

## V. CONCLUSION

We have evaluated the thermodynamic curvature for Pauli paramagnetic gas which is a system of identical spin $\frac{1}{2}$ fermions, and for the classical ideal paramagnetic gas. The curvature of the classical ideal paramagnetic gas, just like that of a two-component ideal gas, is seen to be of the same order as the volume occupied by a single particle. Also we have rigorously demonstrated that this curvature satisfies the geometrical equation.

In the classical limit (i.e., $\eta \ll 1$) and in the absence of the external magnetic fields the curvature of the Pauli gas reduces to that of a two-component ideal gas. In this regime we can find a simple relationship between the curvature and the correlation volume.

In the limit of low fugacity and for a finite value of external magnetic field the curvature of the Pauli gas coincides with that of the classical ideal paramagnetic gas which is a monotonically decreasing function of the magnetic field; here we can interpret the curvature as a measure of stability. The system becomes more stable if the absolute value of the curvature decreases.

The curvature as a function of the magnetic field has a maximum in the quantum regime (where $\eta \gg 1$). Therefore, the curvature can no longer be interpreted as a measure of stability, however, the inverse of the magnetization fluctuation $\langle(\Delta m)^2\rangle^{-1}$ is observed to have a behavior similar to that of the thermodynamic curvature.

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