Grüneisen parameter of quantum magnets with spin gap

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Abstract

Using Hartree-Fock-Bogoliubov (HFB) approach we obtained analytical expressions for thermodynamic quantities of the system of triplons in spin gapped quantum magnets such as magnetization, heat capacity and the magnetic Grüneisen parameter $\Gamma_H$. Near the critical temperature, $\Gamma_H$ is discontinuous and changes its sign upon the Bose-Einstein condensation (BEC) of triplons. On the other hand, in the widely used Hartree-Fock-Popov (HFP) approach there is no discontinuity neither in the heat capacity nor in the Grüneisen parameter. We predict that in the low-temperature limit and near the critical magnetic field $H_c$, $\Gamma_H$ diverges as $\Gamma_H \sim 1/T^2$, while it scales as $\Gamma_H \sim 1/(H - H_c)$ as the magnetic field approaches the quantum critical point at $H_c$. 

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I. INTRODUCTION

The properties of condensed matter at low temperatures have always been of high interest. Phenomena such as novel types of superconductivity/superfluidity, quantum phase transitions or different types of topological order still fascinate a growing community of researchers. For condensed matter systems, P. Debye and W. F. Giauque independently suggested in 1926 to use the magnetocaloric effect (MCE) of paramagnetic materials to reach temperatures significantly below 1 K. This effect, which describes the temperature changes of a magnetic material in response to an adiabatic variation of the magnetic field, forms the basis of magnetic refrigeration. The observation of a giant MCE even around room temperature, indicating the potential of the MCE for an environment-friendly room-temperature refrigeration, has stimulated additional work (see recent review by Wolf et al. [1]).

The magnetocaloric effect (MCE) and the related magnetic Grüneisen parameter,\[ \Gamma_H = \frac{1}{T} \left( \frac{\partial T}{\partial H} \right)_S, \] quantify the cooling or heating of a material when an applied magnetic field is changed under adiabatic conditions with constant entropy \( S \). In such a process the exchanged heat is zero,\[ \delta Q = T dS = T \left( \frac{\partial S}{\partial T} \right)_H dT + T \left( \frac{\partial S}{\partial H} \right)_T dH = 0, \] and hence\[ \Gamma_H = -\frac{1}{C_H} \left( \frac{\partial S}{\partial H} \right)_T, \] where \( C_H = T(\partial S/\partial T)_H \) is the heat capacity at constant magnetic field \( H \). Experimentally \( \Gamma_H \) can be directly accessed by measuring the change in temperature at constant entropy upon magnetic field variation using Eq. (1). Mathematically \( \Gamma_H \) corresponds to the gradient of the temperature in the \( T(H) \) landscape along an isoentropic line. Another equivalent expression for the Grüneisen parameter using the magnetization \( M \),\[ \Gamma_H = -\frac{1}{C_H} \left( \frac{\partial M}{\partial T} \right)_H, \] can be derived from the grand thermodynamic potential \( \Omega \) and suitable Maxwell relations using \( d\Omega = -SdT - pdV - Nd\mu - MdH \), with \( \mu \) the chemical potential, \( N \) the number of
particles, and $p$ and $V$ pressure and volume, respectively, which we assume in the following to be constant as we restrict ourselves only to the magnetic subsystem.

The Grüneisen parameter is usually discussed in terms of the quantum critical point\(^1\), where quantum fluctuations play the major role. Although here we concentrate on a mean-field analysis, where these fluctuations are not taken into account, for the sake of comparison, we briefly discuss the quantum critical point properties. First, if the transition occurs at a given $H_c$, then $\Gamma_H(T \to 0, r) = G_r / (H - H_c)$, where in our notation $G_r \geq 0$ is a universal prefactor [2, 3]. For example, for a dilute Bose gas in the symmetry-broken state $G_r = 1/2$ [3]. The temperature dependence of $\Gamma_H$ in the critical regime also shows a divergence as $\Gamma_H(T, H \to H_c) \sim 1/T^x$ with a certain critical index. It is predicted that $\Gamma_H$ has a different sign on each side of the quantum phase transition [3]. These divergences and the sign change of $\Gamma_H$ are the hallmarks to identify quantum critical points. These properties have been experimentally confirmed by Gegenwart et al., who developed a low-frequency alternating-field technique to measure $\Gamma_H$ down to low temperatures [4], in order to classify a number of magnetic systems ranging from heavy-fermion compounds to frustrated magnets [5, 6].

There is class of quantum magnets referred to as zero field gap quantum magnets [7, 8]. In a subclass of these materials containing dimers of two $S = 1/2$ entities, the spin gap between exited triplet ($S = 1$) and singlet ground ($S = 0$) states closes beyond a critical magnetic field $H_c$ due to the Zeeman effect. As a result, bosonic quasiparticles ("triplons") arise, which may undergo a BEC below a critical temperature $T_c$. Although experimental data on thermodynamic properties are available for many of such systems (for a review, see [4, 8]), quantitative measurements of the MCE and the associated Grüneisen parameter are rare [7, 3, 10]. Experimentally it is very difficult to explore the behavior of $\Gamma_H$ in the zero-temperature limit. This topic has not yet been systematically addressed for these materials, to the best of our knowledge, neither theoretically nor experimentally, with, perhaps, only a single exception [9]. From simple arguments, the property $\Gamma_H \sim 1/T^x$ can be easily considered for non-interacting Bose systems using $C_H(T \to 0) \sim T^{3/2}$ and $M \sim 1 - (T/T_c)^{3/2}$. From Eq. [4], all materials belonging to the non-interacting BEC universality class should therefore obey $\Gamma_H \sim 1/T$ i.e. $x = 1$ [9]. Nevertheless, as the triplon bosonic quasiparticles in the magnetic insulators to be considered here are known to constitute an interacting

\(^1\) Below we consider only the magnetic Grüneisen parameter
Bose gas \([7, 8, 11]\), a consideration of the effects of interaction on the Grüneisen parameter is of utmost interest. The aim of the present work is to investigate the properties of \(\Gamma_H\) for such magnets within a mean field approximation. We will show that \(\Gamma_H \sim 1/(H - H_c)\) and \(\Gamma_H \sim 1/T^2\), and demonstrate that \(\Gamma_H\) changes its sign at the transition.

II. THE FREE ENERGY AND ENTROPY OF THE TRIPLON GAS

For \(H > H_{c1} \equiv H_c\) the thermodynamics of a dimerized quantum magnet is determined by the system of triplon quasiparticles with integer spin if we neglect the phonon contribution for the moment. In a constant external magnetic field, the number of triplons is conserved in the thermodynamic limit, and they can experience a Bose-Einstein condensation (BEC) \([7, 8, 11]\). Although the critical temperature \(T_c\) or the density of triplons of the BEC may be obtained within Hamiltonian formalism \([12, 13]\), the thermodynamic potential and, in particular, the entropy can be also derived by using a Gaussian functional approximation \([16]\), which is in fact, equivalent to the Hartree-Fock-Bogoliubov (HFB) approach.

In this formalism one starts with the action

\[
A[\psi^\dagger, \psi] = \int_0^\beta d\tau \int d^3r \left\{ \psi^\dagger \left[ \frac{\partial}{\partial \tau} - \hat{K} - \mu \right] \psi + \frac{U}{2} (\psi^\dagger \psi)^2 \right\},
\]

where \(\beta = 1/T\), \(\mu\) is the chemical potential, here given as \(\mu = \mu_B g (H - H_c)\) with the Lande g-factor \([7, 8, 11, 17]\), \(\hat{K}\) is the operator of kinetic energy, \(U\) represents a constant for repulsive triplon-triplon interaction, and \(\mu_B\) is the Bohr magneton. The complex fields, \(\psi^\dagger\) and \(\psi\) satisfy the standard bosonic periodicity conditions in that \(\psi(\tau, r)\) and \(\psi^\dagger(\tau, r)\) are periodic in \(\tau\) with period \(\beta\). The operator \(\hat{K}\) gives rise to the bare dispersion of triplons \(\varepsilon_k\) as defined, for example, in the bond operator representation \([18]\). The integration in coordinate space may be taken in the first Brillouin zone with the volume \(V\), which we set here \(V = 1\) \([19]\). Then the thermodynamical potential \(\Omega\) can be obtained from

\[
\Omega = -T \ln \mathcal{Z}
\]

where the grand-canonical partition function \(\mathcal{Z}\) is given by the path integral \([20]\)

\[
\mathcal{Z} = \int \mathcal{D}\psi^\dagger \mathcal{D}\psi e^{-A[\psi^\dagger, \psi]}.
\]

Due to the complications related to the \(\psi^4\) term in \([5]\), the path integral cannot be evaluated exactly. In the present work we shall use a variational perturbation theory \([21]\) as outlined in...
for finite systems. Referring the reader to the Appendix A for the calculation details, we obtain for $\Omega$

$$
\Omega = \Omega_{\text{cl}} + \Omega_2 + \Omega_4, \\
\Omega_{\text{cl}} = -\mu \rho_0 + \frac{U \rho_0^2}{2} + \frac{1}{2} \sum_k (E_k - \varepsilon_k) + T \sum_k \ln(1 - e^{-\beta E_k}), \quad (8)
$$

$$
\Omega_2 = \frac{1}{2} \left[ A_1 (U \rho_0 - X_2 - \mu_1) + A_2 (3U \rho_0 - X_1 - \mu_1) \right], \\
\Omega_4 = \frac{U}{8} \left( 3A_1^2 + 2A_1 A_2 + 3A_2^2 \right),
$$

and for $(i,j) = (1,2)$ or $(2,1)$, respectively,

$$
A_i = G_{j\bar{j}} (\tau, r, \tau', r') |_{r \rightarrow r', \tau \rightarrow \tau'} = T \sum_n \sum_k \frac{\varepsilon_k + X_i}{\omega_n^2 + E_k^2} = \sum_k \frac{\varepsilon_k + X_i}{E_k} W_k, \quad (9)
$$

where

$$
W_k = \frac{1}{2} \coth \left( \frac{\beta E_k}{2} \right) = \frac{1}{2} + n_B(\varepsilon_k), \\
n_B(x) = \frac{1}{e^x - 1}, \quad (10)
$$

with

$$
\varepsilon_k = \sqrt{\varepsilon_k + X_1} \sqrt{\varepsilon_k + X_2} \quad (11)
$$

being the dispersion relation of the quasiparticles. Here $X_1$ and $X_2$ are variational parameters defined from the principle of minimal sensitivity [16] as

$$
\frac{\partial \Omega(X_1, X_2, \rho_0)}{\partial X_1} = 0, \\
\frac{\partial \Omega(X_1, X_2, \rho_0)}{\partial X_2} = 0. \quad (12)
$$

The normal $\rho_1$ and the anomalous $\sigma$ densities become

$$
\rho_1 = \int \langle \tilde{\psi}^\dagger \tilde{\psi} \rangle d^3r = \frac{A_2 + A_1}{2}, \\
\sigma = \int \langle \tilde{\psi} \tilde{\psi} \rangle d^3r = \frac{A_2 - A_1}{2}, \quad (13)
$$

respectively. From (12), (8) and (13) one obtains for $X_1$ and $X_2$

$$
X_1 = -\mu + U \left( 2\rho_1 + 3\rho_0 + \sigma \right), \quad (14) \\
X_2 = -\mu + U \left( 2\rho_1 + \rho_0 - \sigma \right). \quad (15)
$$
The stability condition $d\Omega/d\rho_0 = 0$ yields

$$\mu - U\rho_0 - 2U\rho_1 - U\sigma = 0, \quad (16)$$

where $\rho_0$ is the condensed fraction summing up to the total density $\rho = \rho_0 + \rho_1$. In general, explicit expressions for all thermodynamic quantities can be inferred from $\Omega$ given in [8]. In particular, differentiating $\Omega$ with respect to temperature yields the entropy

$$S = -\left( \frac{\partial \Omega}{\partial T} \right)_H = -\sum_k \ln [1 - \exp(-\beta \mathcal{E}_k)] + \beta \sum_k \frac{\mathcal{E}_k}{(e^{\beta \mathcal{E}_k} - 1)}, \quad (17)$$

while the heat capacity in constant magnetic field becomes

$$C_H = T \left( \frac{\partial S}{\partial T} \right)_H = \beta^2 \sum_k \frac{\mathcal{E}_k (\mathcal{E}_k - T \mathcal{E}_{k,T}^\prime) e^{\beta \mathcal{E}_k}}{(e^{\beta \mathcal{E}_k} - 1)^2}. \quad (18)$$

The resulting magnetic Grüneisen parameter is

$$\Gamma_H = -\frac{g\mu_B}{C_H} \left( \frac{\partial S}{\partial \mu} \right)_T = \frac{\mu_B g \beta^2}{C_H} \sum_k \frac{\mathcal{E}_k \mathcal{E}_{k,\mu}^\prime e^{\beta \mathcal{E}_k}}{(e^{\beta \mathcal{E}_k} - 1)^2}, \quad (19)$$

where $\mathcal{E}_{k,T}^\prime = (d\mathcal{E}_k/dT)_H$ and $\mathcal{E}_{k,\mu}^\prime = (d\mathcal{E}_k/d\mu)_T$, which are given explicitly in the Appendix B.

As we noted above, the present approximation is equivalent to the HFB approximation. Another similar approach, the Hartree - Fock - Popov (HFP) approximation which is widely used in the literature [7, 11, 24], can be formally obtained from the HFB relations by neglecting the anomalous density, i.e. by setting $\sigma = 0$ in the above equations.

For further considerations, we have to discuss the normal ($T \geq T_c$) and the condensed phase ($T < T_c$) of the system separately.

**A. Normal phase, $T \geq T_c$**

When the temperature exceeds a critical temperature $T \geq T_c$, the condensate fraction as well as the anomalous density vanish, i.e., $\rho_0 = \sigma = 0$, and $\rho_1 = \rho$. In this normal phase both approximations, HFB and HFP, coincide.

The basic equations (14) and (15) have the same trivial solutions as

$$X_1 = X_2 = 2U\rho - \mu. \quad (20)$$
Inserting this into Eq. (11) gives
\[ E_k(T \geq T_c) \equiv \omega_k = \varepsilon_k - (\mu - 2U\rho) \equiv \varepsilon_k - \mu_{\text{eff}}, \quad (21) \]
defining the effective chemical potential \( \mu_{\text{eff}} \). Differentiating both sides of Eq. (21) with respect to \( T \) and using Eq. (18) gives the following expression for the heat capacity:
\[ C_H(T \geq T_c) = \beta^2 \sum_k \frac{\omega_k e^{\beta \omega_k} (\omega_k - 2U\rho')}{(e^{\beta \omega_k} - 1)^2}. \quad (22) \]

The triplon density, which defines the longitudinal magnetization (i.e., the component parallel to \( H \)) via
\[ M = -\frac{\partial \Omega}{\partial H} = -\frac{\partial \Omega}{\partial \mu} \frac{\partial \mu}{\partial H} = \mu_B g \rho, \quad (23) \]
is given by the solution of the nonlinear equation
\[ \rho(T) = \rho_1 = \frac{A_1 + A_2}{2} = \sum_k \frac{1}{e^{\beta \omega_k} - 1} = \sum_k \frac{1}{e^{(\varepsilon_k - \mu + 2U\rho')/\beta} - 1}, \quad (24) \]
where we used Equations (9), (13) and (20). Note that in this phase, the staggered magnetization \( M_\perp \), which is a hallmark for the BEC state in dimerized spin systems, vanishes.

For the Grüneisen parameter we have from Eqs. (11) and (23)
\[ \Gamma_H(T > T_c) = -\frac{g\mu_B}{C_H \rho'_T}, \quad (25) \]
where \( \rho'_T = d\rho/dT \) may be obtained from Eq. (24) (see Appendix B).

The critical density \( \rho_c \), i.e. the density of quasiparticles at the critical temperature \( T_c \), is reached as soon the effective chemical potential \( \mu_{\text{eff}} \) vanishes, and hence
\[ \rho_c = \rho(T_c) = \frac{\mu}{2U}. \quad (26) \]
With this condition we may obtain the critical temperature as the solution of the equation
\[ \frac{\mu}{2U} = \sum_k \frac{1}{e^{\varepsilon_k/T_c} - 1}, \quad (27) \]
which will later be used to optimize the input parameters of the model by comparing experimental data with the calculated \( T_c(H) \) dependence.
B. Condensed phase, $T < T_c$

In the condensed phase where the $U(1)$ symmetry is spontaneously broken, one has to implement the Hugenholtz - Pines theorem relating the normal and the anomalous self energies $\Sigma_n$ and $\Sigma_{\text{an}}$ to each other, i.e.

$$\Sigma_n - \Sigma_{\text{an}} = \mu. \quad (28)$$

In our notation this leads to the equation

$$X_2 = \Sigma_n - \Sigma_{\text{an}} - \mu = 0, \quad (29)$$

or

$$\mu - U(2\rho_1 + \rho_0 - \sigma) = 0, \quad (30)$$

where we have used Eq. (15). Due to Hugenholtz- Pines theorem, the excitation energy becomes gapless,

$$E_k(T < T_c) \equiv E_k = \sqrt{\varepsilon_k + X_1\varepsilon_k} = c_k + O(k^2), \quad (31)$$

where $c = \sqrt{X_1/2m}$ is the velocity of the first sound for the quasiparticles with effective mass $m$. Eliminating $\rho_0 = \rho - \rho_1$ from Eqs. (14) and (30) one obtains the basic equation

$$\Delta = X_1^2 = \mu + 2U(\sigma - \rho_1), \quad (32)$$

where

$$\sigma = -\Delta \sum_k \frac{W_k}{E_k}, \quad (33)$$

$$\rho_1 = \sum_k \left[ \frac{W_k(\varepsilon_k + \Delta)}{E_k} - \frac{1}{2} \right], \quad (34)$$

and

$$E_k = \sqrt{\varepsilon_k + \varepsilon_k + 2\Delta}. \quad (35)$$

Equation (30) with $\rho_0 = \sigma = 0$ gives the same expression for the critical density $\rho_c = \rho(T_c) = \mu/2U$ as in Eq. (26), which proves the self consistency of this approach. Taking $dE_k/dT \equiv E'_{k,T}$ from Eq. (35) with $E'_{k,T} = \varepsilon_k\Delta_T/E_k$ into Eq. (18) gives

$$C_H(T < T_c) = \beta^2 \sum_k e^{\beta E_k} \frac{(E_k^2 - T\varepsilon_k\Delta_T)}{(e^{\beta E_k} - 1)^2}, \quad (36)$$

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2 see ref. [26] for the origin of the term $1/2$ in (34)
where $\Delta'_T$ is given in the Appendix B.

For practical calculations Eq. (32) can be rewritten as

$$Z = 1 + \bar{\sigma}(Z) - \bar{\rho}_1(Z),$$

where $Z = \Delta/\mu$, $\bar{\sigma} = \sigma/\rho_c$, and $\bar{\rho}_1 = \rho_1/\rho_c$. After solving the equation (37), the longitudinal and the staggered magnetizations $M$ and $M_\perp$ in the condensed phase, respectively, become

$$M(T \leq T_c) = g\mu_B \rho = g\mu_B \rho_c(Z + 1),$$
$$M_\perp^2(T \leq T_c) = \frac{1}{2}g^2\mu_B^2\rho_0 = \frac{1}{2}g^2\mu_B^2\rho_c(2Z - \bar{\sigma}),$$

where we used

$$\rho = \frac{\Delta + \mu}{2U}, \quad \rho_0 = \frac{\Delta}{U} - \sigma.$$ (39)

The Grüneisen parameter is with Eqs. (38) and (39)

$$\Gamma_H(T \leq T_c) = -\frac{g\mu_B \rho'_T}{C_H} = -\frac{g\mu_B \Delta'_T}{2UC_H},$$ (40)

where $C_H$ is given in Eq. (36).

The main difference between the HFB and HFP approximations manifests itself in the condensed phase. In particular, the basic equation (32) simplifies to

$$\Delta_{HFP} = \mu - 2U\rho_1 = U\rho_0,$$

where $\rho_1$ is formally the same as in Eq. (31).

III. LOW TEMPERATURE EXPANSION

In the present section we will derive analytical expressions in the $T \to 0$ limit. We shall perform the low-temperature expansion as a function of the dimensionless parameter $Tm = \tilde{T}$. In fact, for the majority of spin gap quantum magnets, the effective mass $m$ is small, e.g. $m \approx 0.02 \text{K}^{-1}$ for TlCuCl$_3$ [27], so that any power series in the small parameter $\tilde{T}$ should quickly converge.

In general, three dimensional momentum integrals e.g in Eq. (34) can not be taken analytically. So, to overcome this difficulty we use Debye - like approximation [28]. To
this end the integration over momentum in Brillouine zone is replaced by the Debye sphere, whose radius \( k_D \) is chosen such that to retain the normalization condition

\[
\sum_{k \in B} \to \frac{V}{(2\pi)^3} \int_B dk = \frac{V}{(2\pi)^3} \int_{-\pi/a}^{\pi/a} dk_x dk_y dk_z = \frac{1}{8} \int_0^1 dq_x dq_y dq_z \approx \frac{\pi}{2} \int_0^{Q_0} q^2 dq = 1 \tag{42}
\]

which gives the dimensionless Debye radius \( Q_0 = (6/\pi)^{1/3} \approx 1.24 \), i.e \( k_D = Q_0\pi/a \). In practical calculations we use dimensionless momentum variable \( q = ka/\pi \). Next, we replace the simple symmetric three-dimensional bare dispersion

\[
\varepsilon_k = J_0(3 - \cos k_x a - \cos k_y a - \cos k_z a), \tag{43}
\]

which is frequently used as a model dispersion relation in gapped quantum magnets \[8\], by \( \varepsilon_k \approx J_0 k^2/2 \equiv k^2/2m \). Then the momentum integration may be approximated as

\[
\sum_k f(\varepsilon_k) = \frac{V}{(2\pi)^3} \int_{-\pi/a}^{\pi/a} f(\varepsilon_k) dk_x dk_y dk_z = \int_0^1 f(\varepsilon_q) dq_x dq_y dq_z \approx \frac{\pi}{2} \int_0^{Q_0} q^2 dq f(\varepsilon_q) \tag{44}
\]

where \( \varepsilon_q \approx q^2\pi^2/2m \). As to the phonon dispersion, similarly to the case of optical lattices, one may use long-wave approximation \[28\]:

\[
E_q = \sqrt{\varepsilon_q \varepsilon_q + 2\Delta} \approx c\pi q \tag{45}
\]

with the sound velocity at zero temperature \( c = \sqrt{\Delta(T = 0)/m} \). With these approximations for the low-temperature limit, most of the integrals can be evaluated explicitly in terms of logarithmic and polylogarithmic functions \( \text{Li}_s(z) \) of the argument \( z = \exp(-Q_0c\pi\beta) \), i.e., as a function \( F(T, z) \) \[29\]. Since \( z \) decreases quickly with increasing \( \beta \) we may expand \( F(T, z) \) in powers of \( z \) to extract a leading term. On the other hand one may also introduce the Debye temperature \( T_D = ck_D \) and make an expansion in powers of \( T/T_D \) as in solid state physics.

We refer the reader to the Appendix B for the further details of the calculation. The final result for the entropy becomes

\[
S = \frac{2\pi^2 (\tilde{T})^3}{45\gamma^3} + O(\tilde{T}^5) \tag{46}
\]

where \( \gamma = cm \) and \( \tilde{T} = Tm \). The derivative of \( (46) \) with respect to \( T \) gives the heat capacity

\[
C_H = T \frac{dS}{dT} \approx \frac{2\pi^2 (\tilde{T})^3}{15\gamma^3} = \frac{2\pi^2 T^3}{15c^3}, \tag{47}
\]

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which is common for interacting BEC systems since its measurement in superfluid helium [30]. Note that for an ideal Bose gas, i.e., for a system of noninteracting particles, the dispersion is not linear but quadratic, and $C_H \sim T^{3/2}$ [31].

To find an expression for the Grüneisen parameter, we use Eq. (38) with the relations:

$$\Gamma_H = \frac{1}{C_H} \left( \frac{dM}{dT} \right)_H = -\frac{g\mu_B}{C_H} \left( \frac{d\rho}{dT} \right)_H = -\frac{g\mu_B}{2U C_H} \Delta'_T. \quad (48)$$

The expansion for $\Delta'_T$ becomes

$$\Delta'_T = -\alpha_1 \bar{T} - \alpha_3 \bar{T}^3 + O(\bar{T}^5) \quad (49)$$

where

$$\alpha_1 = \frac{8}{3} \frac{U}{U Q_0^2 + 4c^2}, \quad \alpha_3 = \frac{8U}{45\gamma^2} \frac{3\pi^2 U Q_0^2 + 12\pi^2 c + 10 U \gamma^2}{U Q_0^2 + 4c^2}. \quad (50)$$

Inserting $C_H$ from (47) we find

$$\Gamma_H = \frac{15g\mu_B \alpha_1 \gamma^2}{4\pi^2 U} \frac{1}{\bar{T}^2} + \frac{15g\mu_B (2\gamma \alpha_3 - \alpha_1^2)}{8U \pi^2 \gamma} + O(\bar{T}^2). \quad (52)$$

This is one of the central results of our paper. We will further simplify and discuss it later in the Discussion section (see Eqs. (73) to (75)).

Using Eqs. (38), (B.13) and (B.14), the low-temperature expansions for the magnetizations become

$$M = g\mu_B \rho(T) = M(0) - \frac{g\mu_B \alpha_1}{4U \gamma m} \bar{T}^2 + O(\bar{T}^4) \quad (53)$$

and

$$M^2_\perp = M^2_\perp(0) - \frac{g^2 \mu_B^2 \gamma^- (3\alpha_1 + U m) \bar{T}^2}{24U \gamma^2} + O(\bar{T}^4). \quad (54)$$

Both quantities vary as $-T^2$ in the low-temperature limit while for a non-interacting Bose Einstein condensate, one has the $-T^{3/2}$ dependence.

Finally, we mention that the above relations for thermodynamic quantities given in Eqs. (40)-(54) are also valid in the HFP approximation, but with slightly modified

$$\alpha_1|_{\text{HFP}} = \frac{8}{3} \frac{U}{U Q_0^2 + 8c}, \quad (55)$$

$$\alpha_3|_{\text{HFP}} = \frac{16U}{45\gamma^2} \frac{3\pi^2 U Q_0^2 + 24\pi^2 c + 5U \gamma^2}{U Q_0^2 + 8c^2}. \quad (56)$$
IV. PROPERTIES NEAR $T_c$

The behavior of thermodynamic quantities in the temperature region $T \rightarrow T_c \pm 0$ is crucial for the nature of a phase transition. According to the Ehrenfest classification, a discontinuity in a second derivative of $\Omega$ at $T_c$ with a continuous first derivative indicates that the transition is of second order \[32\]. In the present section we will study $C_H^{(\pm)} \equiv C_H(T_c \pm 0)$, $\Gamma_H \equiv \Gamma_H(T_c \pm 0)$ and $S^{(\pm)} \equiv S^{(\pm)}(T_c \pm 0)$.

A. $T \rightarrow T_c + 0$ region

Here $E_k = \omega_k = \varepsilon_k$ and $\mu = 2U \rho$. From Eqs. \[22\] and \[B.1]-\[B.3\] we have

$$C_H^{(+)} = -S_3 + 2US_1 \rho' T$$

(57)

where with $\beta_c = 1/T_c$

$$S_3 = -\beta_c^2 \sum_k \frac{\varepsilon_k^2 e^{\beta_c \varepsilon_k}}{(e^{\beta_c \varepsilon_k} - 1)^2},$$
$$S_1 = -\beta_c \sum_k \frac{\varepsilon_k e^{\beta_c \varepsilon_k}}{(e^{\beta_c \varepsilon_k} - 1)^2},$$
$$\rho' = \frac{\beta_c S_1}{2S_2 - 1},$$
$$S_2 = -U \beta_c \sum_k \frac{e^{\beta_c \varepsilon_k}}{e^{\beta_c \varepsilon_k} - 1}.$$

(58)

It can be easily shown that

$$\lim_{T \rightarrow T_c + 0} \rho' T = 0$$

(59)

since in this limit, $S_2$ in the denominator of Eq. \[58\] at small momentum has an infrared divergence, since the integrand behaves as $k^{-2}$ in this limit, while the numerator is finite. Thus, Eq. \[57\] becomes

$$C_H^{(+)} = -S_3 = \beta_c^2 \sum_k \frac{\varepsilon_k^2 e^{\beta_c \varepsilon_k}}{(e^{\beta_c \varepsilon_k} - 1)^2}.$$

(60)

From Eq. \[59\] we may immediately conclude that the Grüneisen parameter at $T = T_c$ vanishes,

$$\Gamma_H^{(+)} = -\frac{1}{C_H^{(+)} T \rightarrow T_c + 0} \left( \frac{dM}{dT} \right)_H = -\frac{g \mu B}{C_H^{(+)} T \rightarrow T_c + 0} \left( \frac{d\rho}{dT} \right)_H = 0,$$

(61)

in agreement with the prediction of Garst \textit{et al.} \[3\]. The entropy of Eq. \[17\] is with $E_k = \varepsilon_k$

$$S^{(+)} = -\sum_k \ln [1 - \exp(-\beta_c \varepsilon_k)] + \beta_c \sum_k \frac{\varepsilon_k}{e^{\beta_c \varepsilon_k} - 1}.$$

(62)
In the HFP approximation, the equations (57) - (62) remain unchanged, since it coincides for \( T \geq T_c \) with the HFB approximation.

**B. \( T \to T_c - 0 \) region**

Here \( \rho_0 = 0, \sigma = 0 \) and \( \Delta = 0 \) and hence \( \mathcal{E}_k = E_k = \varepsilon_k \) again, i.e., the dispersion is the same on both sides of the critical temperature. For this reason the entropy is continuous at \( T = T_c, S^(-) = S^+(+) \). The heat capacity and the Grüneisen parameter are

\[
C_H^(-) = \beta_c^2 \sum_k \frac{\varepsilon_k (\varepsilon_k - T_c \Delta'_T) e^{\beta_c \varepsilon_k}}{(e^{\beta_c \varepsilon_k} - 1)^2},
\]

\[
\Gamma_H^(-) = -\frac{g \mu_B \Delta'_T}{2UC_H^(-)},
\]

where we used the relation \( \rho'_T = \Delta'_T/2U \). The \( \Delta'_T \) defined in (B.7) for the HFB approximation may be rewritten as

\[
\Delta'_T|_{\text{HFP}} = \frac{\beta_c US_4}{2(2S_5 + 1)},
\]

\[
S_5 = -U \beta_c \sum_k T_c \frac{\varepsilon_k e^{\beta_c \varepsilon_k} - T_c e^{\beta_c \varepsilon_k}}{(e^{\beta_c \varepsilon_k} - 1)^2},
\]

\[
S_4 = -4 \beta_c \sum_k \frac{\varepsilon_k e^{\beta_c \varepsilon_k}}{(e^{\beta_c \varepsilon_k} - 1)^2}.
\]

In the HFP approach,

\[
\Delta'_T|_{\text{HFP}} = \frac{2 \beta_c US_1}{2S_2 + 1},
\]

where \( S_1 \) and \( S_2 \) are the same as in Eqs. (58).

1. **HFB approximation**

From Eqs. (50), (51) and (63) we can express the discontinuities in \( C_H \) and \( \Gamma_H \) as

\[
\Delta C_H = C_H^(-) - C_H^+ = -\beta_c \sum_k \frac{\varepsilon_k \Delta'_T e^{\beta_c \varepsilon_k}}{(e^{\beta_c \varepsilon_k} - 1)^2} > 0,
\]

\[
\Delta \Gamma_H = \Gamma_H^(-) - \Gamma_H^+ = -\frac{g \mu_B \Delta'_T}{2UC_H^(-)} > 0,
\]

where \( \Delta'_T \) is given in (64) and \( C_H \) in (63).
From Eqs. (67) and (68) it is clear that not only \(C_H\) but also the Grüneisen parameter has a finite jump near the critical temperature, and therefore the transition is of second order according to the Ehrenfest classification.

It is easy to show that our results satisfy self-consistently the Ehrenfest relation

\[
\Delta C_H = -T_c \left( \frac{dH_c}{dT} \right)_{T=T_c} \Delta \left( \frac{dM}{dT} \right)_{T=T_c}.
\]

Using equations (27), (38), (59) and (67) leads to a modified Ehrenfest relation for the discontinuity in the Grüneisen parameter in triplon systems,

\[
\Delta \Gamma_H = \frac{\Delta C_H}{T_c C_H^{(-)} (dH_c/dT)}.
\]

which can be easily derived from Eqs. (27), (63), (67) and (68).

2. HFP approximation

Here \(\Delta'_T\) is given by Eq. (66), where \(S_1\) is finite but \(S_2\) diverges as it has been shown in the previous section. Thus \(\Delta'_T|_{\text{HFP}} = 0\), and hence

\[
\rho'_T|_{\text{HFP}} = \left( \frac{\Delta + \mu}{2U} \right)' = 0.
\]

Therefore, we may conclude from Eqs. (60), (63) and (71)

\[
C_H^{(-)}|_{\text{HFP}} = C_H^{(+)}|_{\text{HFP}} \quad \Gamma_H^{(-)}|_{\text{HFP}} = \Gamma_H^{(+)}|_{\text{HFP}}.
\]

In other words, there is no discontinuity in the HFP approximation, neither in the heat capacity nor in the Grüneisen parameter, which is in sharp contrast to the HFB approximation used here, and to experimental heat-capacity measurements.

V. DISCUSSION

A. Sign change of \(\Gamma_H\) at \(T_c\)

In the previous section, we have shown that \(\Gamma_H = 0\) at the critical temperature \(T_c\). It is also easy to show that \(\Gamma_H(T)\) must change its sign there. Using Eqs. (61) and (13.3) we have with \(d\rho/dT > 0\) a \(\Gamma_H(T) < 0\) for \(T > T_c\). Approaching the critical temperature from below where \(d\rho/dT < 0\) (see Eq. (64)), \(\Gamma_H(T) > 0\) for \(T < T_c\).
B. Divergence of $\Gamma_H$ near the transition

Rewriting Eq. (52) around the QCP in the limit $r = (H - H_c)/H_c \to 0$ in a compact form (see Appendix C), we obtain

$$\Gamma_H \approx \frac{G_t(H - H_c)}{T^2} + \frac{G_r}{H - H_c},$$

(73)

with

$$G_t = \frac{10g^2\mu_B^2}{UmQ_0^2\pi^2} = \frac{5g^2\mu_B^2}{\pi^2}G_r,$$

(74)

and

$$G_r = \frac{2}{UmQ_0^2},$$

(75)

where the next higher-order terms are $O((\bar{T})^2)$ and $O(r)$, respectively. Here we used the relation

$$U = \frac{4\pi a_s}{m},$$

(76)

where $a_s$ is the s-wave scattering length. The first term in Eq. (73) dominates $\Gamma_H(T, H)$ in a fixed magnetic field $H > H_c$ for temperatures $T \ll \eta(H - H_c)$, with $\eta = \sqrt{5g\mu_B}/\pi$, while the second term dominates in the opposite limit when $H$ approaches the QCP $H_c$ from above at a fixed low temperature $T$.

The fact that $\Gamma_H$ diverges as $\Gamma_H = 1/T^2$ at low enough temperatures is one of our main results. Remarkably, the classification of a number of magnetic systems ranging from heavy-fermion compounds to frustrated magnets done by Gegenwart et al. [5] reveals that the majority of considered systems shows indeed a similar behavior, with some exceptions like [9], however.

The phase boundary between the condensed and the uncondensed states in spin gapped quantum magnets, respectively, can be expressed by a power law of the form $T_c \propto (H - H_c)^\phi$. As experimental data on insulating spin systems often show $\phi \approx 0.5$ (see Table I in the next section), and our results are in line with experimental observations.

The behavior $\Gamma_H \approx G_r(H - H_c)^{-1}$, being well established [3, 5] in the QCP systems, is obviously also realized in the systems discussed in the present work (see Eq. (73)). We note, however, that this relation cannot be directly applied to the continuous systems such as atomic gases where $Q_0 \to \infty$. In this case, renormalization procedures may lead to different dependences.
C. Universality of $G_r$

We now discuss whether the value of the dimensionless parameter $G_r$ is universal in spin-gapped triplon systems or not. We make use of our result (75), and state that $G_r$ only depends on the product of the material parameters $U$ and $m$. We will now show that within our assumptions, $U$ and $m$ are not really independent of each other. The full width of the model dispersion relation (43) is $D = 3J_0 = 3/m$. The lower and the upper bounds of the gapped lowest magnon band with bandwidth $D$ determine, in a crude approximation, the width of the magnetic phase (i.e., the values of $H_{c1}$ and $H_{c2}$, respectively) by the Zeeman shift of the corresponding lowest and highest lying triplet states, respectively [8]. Although our approach is only valid in the dilute limit near $H_{c1}$, we can formally extrapolate it to the fully polarized state with $M = g\mu_B$ at $H_{c2}$, and then $\mu(H_{c2}) - \mu(H_{c1}) = \mu(H_{c2}) \approx D = 3J_0$. The state at $H_{c2}$ corresponds with Eq. (38) to $\rho = \rho_0 = 1$ at $T = 0$. With Eq. (30) we find $\mu(H_{c2}) \approx U \approx 3J_0$, and therefore $Um \approx 3$.

In real systems, however, the dispersion relation will deviate from Eq. (43), and the bandwidth $D$ then differs from the value $3/m$ containing the low-energy effective mass $m$. Moreover, the magnon bands are not rigidly shifted by the Zeeman effect in magnetic fields between $H_{c1}$ and $H_{c2}$ [18], so that $U \approx D \approx 3J_0$ can hold only by up to a factor of unity. In this sense, relations (74) and (75) are not strictly universal, but depend on the details of the magnon spectrum. In Table I to be presented below, we have indeed a ratio $U/J_0 = Um$ between 3.2 - 6.3, deviating from the value of 3.

D. Numerical results for real systems

In the previous sections, we have given general expressions for $\Gamma_H$, $S$, $C_H$, $M$ and $M^2_\perp$, and elaborated the limiting cases $T \to 0$ and $T \to T_c$. We can use these results to numerically evaluate these quantities over the full range of temperatures. In the following we will restrict ourselves to $\Gamma_H$ and $S$. To do this, we have to assume a set of realistic material parameters $g$, $H_c$, $U$ and $J_0$ which we take from experimental data for Ba$_3$Cr$_2$O$_8$, Sr$_3$Cr$_2$O$_8$ and TlCuCl$_3$ [11, 27, 34–36] (see Table I).

To begin with, we show in Fig. 1 the phase diagrams $T_c(H)$ as calculated from Eq. (27) for Ba$_3$Cr$_2$O$_8$ and Sr$_3$Cr$_2$O$_8$, together with experimental data taken from Refs. [34, 36]. For
our calculation, we fixed $g$, $H_c$, and $U$, and fitted $J_0$ according to Eq. (27).

FIG. 1: The dependence of $T_c$ on the external magnetic field $H$ for (a) Ba$_3$Cr$_2$O$_8$ and (b) Sr$_3$Cr$_2$O$_8$ (solid lines from Eq. (27)). The dashed lines correspond to the $\phi = 2/3$ law. The experimental data are taken from (a) [35] and (b) [34, 36].

In Table I we compare the exponent $\phi$ as obtained from a power-law fit according to $T_c \propto (H-H_c)^{\phi}$ to our numerically obtained data, with corresponding fits to the experimental data in the same temperature range ($\phi_{exp}$) and to a range of values for TlCuCl$_3$ from the literature [11, 37]. These exponents are in fair agreement with our expectation $\phi = \nu z = 1/2$.

| Material     | $g$  | $H_c(T)$ | $J_0 = 1/m(K)$ | $U(K)$ | $\Delta_{st}(K)$ | $G_r$ | $\phi$ | $\phi_{exp}$ | $a_s/\bar{a}$ |
|--------------|------|----------|----------------|--------|------------------|------|-------|--------------|---------------|
| Ba$_3$Cr$_2$O$_8$ | 1.95 | 12.10    | 5.045          | 20     | 15.85            | 0.84 | 0.5   | 0.49         | 0.315         |
| Sr$_3$Cr$_2$O$_8$ | 1.95 | 30.40    | 15.86          | 51.2   | 39.8             | 0.9  | 0.65  | 0.65         | 0.257         |
| TlCuCl$_3$     | 2.06 | 5.1      | 50             | 315    | 7.1              | 0.72 | 0.62  | 0.45-0.71    | 0.5           |

TABLE I: Material parameters used for our numerical calculations. From the input parameters $g$, $H_c$ and $U$ we derived $J_0$ from fitting the experimental phase boundary $T_c(H)$ to Eq. (27). $\Delta_{st}$ corresponds to the energy scale of $H_c$ in Kelvin, while $G_r$ and $a_s/\bar{a}$ come from Eqs. (75) and (76). The exponents $\phi$ and $\phi_{exp}$ are results from fitting our numerically generated and experimental $T_c(H)$ data, respectively, to a power law.

Corresponding calculations for $\Gamma_H(T)$ using Eqs. (25) and (40) are shown in Fig. 2 and
FIG. 2: The dependence of the Grüneisen parameter on temperature for (a) Ba$_3$Cr$_2$O$_8$ and (b) Sr$_3$Cr$_2$O$_8$ in different magnetic fields. At the respective $T_c$, $\Gamma_H(T)$ shows a discontinuity and changes its sign.

FIG. 3: The entropy $S$ vs. temperature $T$ for Ba$_3$Cr$_2$O$_8$ and Sr$_3$Cr$_2$O$_8$ for different values of the magnetic field $H$. As expected, $S(T)$ changes its slope at $T_c$.

for $S(T)$ in Fig. 3 while in Fig. 4 we display a series of isoentropic lines with $S = \text{const}$ for Ba$_3$Cr$_2$O$_8$ and Sr$_3$Cr$_2$O$_8$.

The phase transition is clearly visible in all of these figures. The Grüneisen parameter $\Gamma_H(T)$ shows a discontinuity according to Eq. (70) and changes its sign at $T_c(H)$, while the entropy $S(T)$ exhibits a change in its slope, thereby reflecting a discontinuity in the heat
FIG. 4: Isoentropic lines for the magnetic system of (a) Ba$_3$Cr$_2$O$_8$ and (b) Sr$_3$Cr$_2$O$_8$ in the $(H, T)$ plane. Each color corresponds to a constant entropy value. The white lines show the phase boundaries separating the condensed (right side) from the uncondensed phases (left side), respectively.

capacity $C_H$ according to Eq. \(67\).

The isoentropic lines shown in Fig. 4 have a minimum at $H_c(T)$, which can be easily understood by recalling that $\Gamma_H = T^{-1}(dT/dH)$ vanishes at the phase transition. In a perfectly adiabatic experiment, the temperature would ideally follow these lines upon a change of the external magnetic field, reaching its lowest temperature at $H_c$. The diagram shown in Fig. 4 for Sr$_3$Cr$_2$O$_8$ compares favorably with that measured by Aczel et al. \[34\].

We note that in most conventional magnetocaloric experiments, a sample is subject to a controlled heat link, so that the corresponding $T(H)$ curves become time-dependent \[7, 34, 38, 39\] and change their shape in comparison with those displayed in Fig. 4.

VI. MEASURABILITY

While the discontinuities in $C_H$ and $\Gamma_H$ (Eqs. \(67\) and \(68\)) and the sign change in $\Gamma_H$ at $T_c$ can, in principle, be directly measured in a dedicated experiment, an examination of the temperature dependence of these quantities in the low-temperature limit may face the problem that the heat capacity $C_H$ of the magnetic subsystem exhibits the same temperature dependence as that of the crystal lattice, i.e., $C_H \sim T^3$, and the magnetic contribution has
then to be extracted from the total signal. This is possible, e.g., by performing a series of measurements in different magnetic fields (and in $H = 0$ in the case of $C_H$) provided that the lattice heat capacity $C_{\text{lat}}$ does not entirely dominate $C_H$. For $N_{\text{at}}$ atoms in the crystal lattice, we have in the low-temperature limit the Debye result

$$C_{\text{lat}} \approx N_{\text{at}} \frac{12\pi^4 T^3}{5\Theta_D^3},$$

(77)

with the Debye temperature of the lattice $\Theta_D$. The number of dimers $N_{\text{dim}} < N_{\text{at}}$ enters as a prefactor in Eq. (47) to express the heat capacity of the whole system, and the ratio of the two contributions then becomes

$$\frac{C_H}{C_{\text{lat}}} = \frac{1}{18\pi^2} \frac{N_{\text{dim}} \Theta_D^3}{N_{\text{at}} c^3},$$

(78)

where $c$ from $E_k = ck$ is expressed in Kelvin. This ratio seems to be unfavorably small. However, by performing an experiment close enough to the QCP one can force $c \ll \Theta_D$, and the two contributions may become separable. The qualitative field dependence $\Gamma_H \sim (H - H_c)^{-1}$ from Eq. (38) and the magnetizations (73), (53) and (54) remain unaffected by these arguments and should be readily accessible in a corresponding experiment, while the absolute value of the measured $\Gamma_H$ has to be corrected for the contribution of $C_{\text{lat}}$ to Eq. (3).

VII. CONCLUSION

We have performed a variational Gaussian-approximation analysis of gapped dimerized quantum magnets showing a Bose-Einstein condensation of magnetic quasiparticles (triplons). We calculated the free energy $\Omega$ and the associated entropy $S$, the heat capacity $C_H$, the magnetization $M$ and the Grüneisen parameter $\Gamma_H$, and derived explicit expressions for these quantities in the limits $T \to T_c$ and $T \to 0$, respectively. Near the critical temperature, both the heat capacity and the Grüneisen parameter show a discontinuity, while $\Gamma_H$ also changes its sign. Such a behavior is expected for systems with a magnetically controlled quantum critical point \[3\]. In the low-temperature limit near this QCP, we find

$^3$ With a $J_0 = 15$ K and $g \approx 2$ as for $\text{Sr}_3\text{Cr}_2\text{O}_8$, we estimate $c \approx 4.5$ K for $H - H_c = 1$ T, so that with $N_{\text{dim}}/N_{\text{at}} = 1/13$ and $\Theta_D \approx 120$ K [40], $C_H/C_{\text{lat}} \approx 8$.
that $C_H \sim T^3$, which is universal for Bose condensed interacting systems. The Grüneisen parameter diverges there as $\Gamma_H \sim T^{-2}$ as a function of temperature. To the best of our knowledge this is a new result, and we have confirmed that a corresponding experiment to verify this conjecture should be feasible. Approaching the transition field as $H \to H_c$ we find $\Gamma_H \sim (H - H_c)^{-1}$, which is common to a variety of magnetic systems [5]. We have also shown that the Grüneisen parameter and heat capacity are continuous near critical temperature in the HFP approximation which is in contrast to experimental heat capacity measurements.

Acknowledgments

We are indebted to Evgeny Sherman and Philipp Gegenwart for useful discussions. This work is partially supported by the Swiss National Foundation SCOPES project IZ74Z0_160527.
Appendix A

Here we derive the free energy given in (8) by using a variational perturbative theory, which is similar to HFB approach in Hamiltonian formalism [16]. This perturbative scheme includes the following steps:

1) We parameterize the quantum field $\psi$ in terms of a time-independent condensate $\rho_0$ and a quantum fluctuation field $\bar{\psi}$ as

$$\psi = \sqrt{\rho_0} + \bar{\psi}$$  \hspace{1cm} (A.1)

which defines the number of uncondensed particles as

$$\rho_1 = \int d^3 r (\bar{\psi}^\dagger \bar{\psi}),$$  \hspace{1cm} (A.2)

where the expectation value of an operator $\langle \hat{O}(\bar{\psi}^\dagger, \bar{\psi}) \rangle$ is defined as

$$\langle \hat{O} \rangle = \frac{1}{Z} \int D\bar{\psi}^\dagger D\bar{\psi} \hat{O}(\bar{\psi}^\dagger, \bar{\psi}) e^{-\mathcal{A}[\bar{\psi}^\dagger, \bar{\psi}]},$$  \hspace{1cm} (A.3)

Then the total number of particles is given by

$$\rho = \rho_1 + \rho_0.$$  \hspace{1cm} (A.4)

2) We replace $U$ in (5) as $U \to \delta U$ and add to (5) following term:

$$S_\Sigma = (1 - \delta) \int d\tau d^3 r \left[ \Sigma_n \bar{\psi}^\dagger \bar{\psi} + \frac{1}{2} \Sigma_{an} (\bar{\psi}^\dagger \bar{\psi}^\dagger + \bar{\psi}\psi) \right],$$  \hspace{1cm} (A.5)

where the variational parameters $\Sigma_n$ and $\Sigma_{an}$ may be interpreted as the normal and the anomalous self energies, respectively.

3) Now the perturbation scheme may be considered as an expansion in powers of $\delta$ by using the propagators

$$G_{ab}(\tau, r; \tau', r') = \frac{1}{\beta} \sum_{n,k} e^{i\omega_n(\tau - \tau') + ik(r - r')} G_{ab}(\omega_n, k)$$  \hspace{1cm} (A.6)

(a, b = 1, 2), where $\omega_n = 2\pi n T$ is the $n$-th Matsubara frequency, $\sum_{n,k} = \sum_{n=-\infty}^{\infty} \int d^3 k/(2\pi)^3$, and

$$G_{ab}(\omega, k) = \frac{1}{\omega_n^2 + E_k^2} \begin{pmatrix} \xi_k + X_2 & \omega_k \\ -\omega_k & \xi_k + X_1 \end{pmatrix}.$$  \hspace{1cm} (A.7)
In \( \text{(A.7)} \) \( E_k \) corresponds to the dispersion of quasiparticles
\[
E_k = \sqrt{\varepsilon_k + X_1 \sqrt{\varepsilon_k + X_2}},
\]
where \( X_1 \) and \( X_2 \), given by
\[
X_1 = \Sigma_n + \Sigma_{an} - \mu,
\]
\[
X_2 = \Sigma_n - \Sigma_{an} - \mu
\]
may be considered as variational parameters instead of \( \Sigma_n, \Sigma_{an} \).

The parameter \( \delta \) should be set \( \delta = 1 \) at the end of the calculations. This perturbation scheme is known as the \( \delta \)-expansion method \([41]\).

4) After subtraction of discontinuous and one-particle reducible diagrams, we obtain the free energy \( \Omega \) as a function of \( \rho_0, X_1 \) and \( X_2 \).

The variational parameters \( X_1 \) and \( X_2 \) may be fixed by the requirements
\[
\frac{\partial \Omega(X_1, X_2, \rho_0)}{\partial X_1} = 0,
\]
\[
\frac{\partial \Omega(X_1, X_2, \rho_0)}{\partial X_2} = 0.
\]

The condensed density \( \rho_0 \) it is determined by stationary condition
\[
\frac{d\Omega}{d\rho_0} = \frac{\partial \Omega}{\partial X_1} \frac{\partial X_1}{\partial \rho_0} + \frac{\partial \Omega}{\partial X_2} \frac{\partial X_2}{\partial \rho_0} + \frac{\partial \Omega}{\partial \rho_0} = 0,
\]
that is, by partially differentiating \( \Omega \) with respect to \( \rho_0 \) and setting it to zero.

Note that \( \text{(A.11)} \) is equivalent to the condition \( \langle \tilde{\psi} \rangle = 0 \), which is obtained by the requirement \( H^{(1)}(\tilde{\psi}, \tilde{\psi}^\dagger) = 0 \) in the Hamiltonian formalism \([42]\), where \( H^{(1)} \) the part of the Hamiltonian which is linear at \( \tilde{\psi} \).

The accuracy of the \( \delta \)-expansion to calculate \( \Omega \) is somewhat limited by the fact that the inclusion of loop integrals which are complicating the calculation process \([21, 43]\), is not carried out here.

**Appendix B**

Here we present explicit expressions for \( E'_{k,T} = dE_k/dT \) and \( E'_{k,\mu} = dE_k/d\mu \), which are needed for the evaluation of the entropy and heat capacity in Equations \( \text{(17)-(19)} \). In the normal phase when \( E_k = \omega_k = \varepsilon_k - \mu + 2U \rho \), the density of particles is given by
\[
\rho = \sum_k f_B(\omega_k)
\]

\( \text{(B.1)} \)
where \( f_B(x) = 1/(e^{\beta x} - 1) \). Clearly,
\[
\frac{d\omega_k}{dT} = 2U \frac{d\rho}{dT},
\]
which does not depend on momentum \( k \). Differentiating both sides of the equation (B.1) with respect to \( T \) and solving by \( dp/dT \), we find
\[
\frac{d\rho}{dT} = \frac{\beta S_1}{2S_2 - 1},
\]
\[
S_1 = -\beta \sum_k \omega_k f_B^2(\omega_k)e^{\omega_k \beta},
\]
\[
S_2 = -U \beta \sum_k f_B^2(\omega_k)e^{\omega_k \beta}.
\]
Taking the derivative with respect to \( \mu \) gives
\[
\frac{d\omega_k}{d\mu} = 2U \frac{d\rho}{d\mu} - 1,
\]
\[
\frac{d\rho}{d\mu} = \frac{S_2}{U(2S_2 - 1)}.
\]
In the condensed phase, \( T < T_c \), \( E_k = \sqrt{\varepsilon_k(\varepsilon_k + 2\Delta)} \), and hence we have
\[
\frac{dE_k}{dT} = \frac{\varepsilon_k}{E_k} \Delta_T',
\]
\[
\frac{dE_k}{d\mu} = \frac{\varepsilon_k}{E_k} \Delta_{\mu}'.
\]
To find, e.g., \( \Delta_T' \) we can differentiate both sides of the equation (32) with respect to \( T \) and solve it with respect to \( \Delta_T' \).

The results are
\[
\Delta_T' = \frac{d\Delta}{dT} = US_4 \frac{U}{2T(2S_5 + 1)},
\]
\[
\Delta_{\mu}' = \frac{d\Delta}{d\mu} = \frac{1}{2S_5 + 1},
\]
\[
S_4 = \sum_k W_k'(\varepsilon_k + 2\Delta),
\]
\[
S_5 = U \sum_k \frac{4W_k + E_k W_k'}{4E_k},
\]
\[
W_k' = \beta(1 - 4W_k^2),
\]
\[
W_k = \frac{1}{2} + f_B(E_k).
In the HFP approximation, $\Delta'_T$ is formally given by (B.7), but with the following $S_4$ and $S_5$:

$$S_{4|\text{HFP}} = \sum_k W'_k(\varepsilon_k + \Delta),$$

$$S_{5|\text{HFP}} = \frac{U}{4} \sum_k \varepsilon_k \frac{4\Delta W_k + E_k W'_k(\Delta + \varepsilon)}{E_k^4}. \quad (B.7)$$

Below we illustrate the low-temperature expansion explicitly. For this purpose we follow the strategy outlined in Sect. III. and start with $\rho_1$. The Eq. (34) may be rewritten as

$$\rho_1 = \sum_k \frac{\varepsilon_q + \Delta}{E_q(\exp(E_q\beta) - 1)} + \rho_1(0), \quad (B.8)$$

and its $T$ dependent part as

$$I_1 = \sum_k \frac{\varepsilon_q + \Delta}{E_q(\exp(E_q\beta) - 1)} = \frac{1}{4mc} \int_0^{Q_0} dq q(q^2\pi^2 + 2m^2c^2) \frac{\exp(\pi cq\beta) - 1}{\exp(\pi c q\beta) - 1}. \quad (B.9)$$

This integral can be evaluated explicitly,

$$I_1 = \frac{TQ_0 \left( \pi^2 Q_0^2 + 2m^2c^2 \right) \ln (1 - z^{-1})}{4mc^2\pi} + \frac{T^2 \left( 3\pi^2 Q_0^2 + 2m^2c^2 \right) \text{Li}_2(z^{-1})}{3T^3 \left( -Q_0 \text{Li}_3(z^{-1}) c\pi + T\text{Li}_4(z^{-1}) \right)} + \frac{T^2 \left( \pi^2 T^2 + 5m^2c^4 \right)}{60mc^5} - \frac{Q_0^2 \left( \pi^2 Q_0^2 + 4m^2c^2 \right)}{16mc}, \quad (B.10)$$

where $z = \exp(-Q_0 c\pi / T)$ and $\text{Li}_n(z) = \sum_{n=1}^{\infty} z^n / n^n$ is a polylogarithmic function. Since $z \leq 1$ at small $T$, we can perform an expansion in $z$ and obtain

$$I_1 = \frac{mT^2}{12c} + \frac{\pi^2 T^4}{60mc^5} - \left[ \frac{3T^4}{2mc^5\pi^2} + \frac{3T^3 Q_0}{2mc^4\pi} + \frac{3T^2 Q_0^2}{4mc^3} + \frac{mT^2}{2c\pi^2} + \frac{\pi TQ_0^3}{4mc^2} + \frac{mTQ_0}{2\pi} \right] z + O(z^2). \quad (B.11)$$

The leading terms of this expansion are

$$\rho_1 = \rho_1(0) + \frac{T^2}{12\gamma} + \frac{\pi^2 T^4}{60\gamma^5} + O(T^6), \quad (B.12)$$

where $\gamma = cm$. Using the expansion of the total magnetization Eq. (53), one may find the low-temperature expansion for the total triplon density as

$$\rho = \rho(T) - \frac{\alpha_1}{4U\gamma m} T^2 - \frac{\alpha_3}{8Um\gamma^3} T^4 + O(T^6). \quad (B.13)$$
The previous two equations yield for the condensed fraction
\[ \rho_0 = \rho - \rho_1 = \rho_0(0) - \frac{(3\alpha_1 + Um)}{12Um\gamma} \tilde{T}^2 - \frac{15\gamma \alpha_3 + 2U\pi^2}{120U\gamma^5} \tilde{T}^4 + O(\tilde{T}^6). \] (B.14)

Finally, excluding \( \Delta \) from equations (39) gives the low temperature expansion for the anomalous density
\[ \sigma = \sigma(0) + \frac{Um - 3\alpha_1}{12Um\gamma} \tilde{T}^2 + \frac{2\pi^2 U - 15c\gamma \alpha_3}{120U\gamma^5} \tilde{T}^4 + O(\tilde{T}^6). \] (B.15)

Low-temperature expansions for other quantities can be obtained in a similar way.

**Appendix C**

Here we will show that if \( r = (H - H_c)/H_c = \mu/\Delta_{st} \) is small (where \( \Delta_{st} = g\mu_B H_c \) is the spin gap), the Grüneisen parameter diverges as \( \Gamma_H \sim 1/r \) at low temperatures.

To do this we study the second term of Eq. (52) which can be written as
\[ \gamma_0 = \frac{2g\mu_B (3UQ_0^2 \pi^2 + 12c\pi^2 + 10U\gamma^2 - 20U\gamma)}{3\gamma^2 \pi^2 (UQ_0^2 + 4c)^2}, \] (C.1)

where \( c^2 = \Delta(0)/m \). The \( \Delta(0) \) is given by Eq. (32), where \( \sigma \) and \( \rho_1 \) are taken from (33) and (34) with \( W_k = 1/2 \), and it can be simplified as
\[ \Delta = \mu + U \sum_k \left( 1 - \frac{E_k}{\varepsilon_k} \right) \] (C.2)

with \( E_k = \sqrt{\varepsilon_k} \sqrt{\varepsilon_k + 2\Delta} \). In the Debye-like approximation, the momentum integration in (C.2) can be taken explicitly, even without linear approximation for \( E_k \), resulting in
\[ \Delta = \mu + \frac{U}{6\pi^2} \left[ 8(\Delta m)^{3/2} + \pi^3 Q_0^3 - (\pi^2 Q_0^2 + 4m\Delta)^{3/2} \right]. \] (C.3)

It is clear that for small \( r \), \( \Delta \) becomes also arbitrarily small, and \( \pi^2 Q_0^2 + 4m\Delta \approx \pi^2 Q_0^2 \approx 15.2 \). Thus the equation (C.3) can be simplified to
\[ \Delta = \mu + \frac{4U(\Delta m)^{3/2}}{3\pi^2}, \] (C.4)

or in terms of \( r \), to
\[ \Delta = r\Delta_{st} + \frac{4U(\Delta m)^{3/2}}{3\pi^2}. \] (C.5)

For small \( r \), the solution of this equation can be found by iteration,
\[ \Delta \approx r\Delta_{st} + r^{3/2}d_{32}, \] (C.6)
where \( d_{32} = 4U(m\Delta_{st})^{3/2}/3\pi^2 \) is constant. Thus we come to the conclusion that the velocity \( c \) of the first sound is given by \( c = \sqrt{r}\sqrt{\Delta_{st}/m} + O(r^{3/2}) \). Inserting this into (C.1) and taking only the leading term, we obtain

\[
\gamma_0 = \frac{2}{UmQ_0^2(H - H_c)} + O(r).
\]  

(C.7)

Thus, at low temperatures near \( H_c \), the Grüneisen parameter scales as

\[
\Gamma_H \approx \frac{2}{UmQ_0^2(H - H_c)}.
\]  

(C.8)

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