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Spin-fluctuation theory beyond Gaussian approximation

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Abstract

A characteristic feature of the Gaussian approximation in the functional-integral approach to the spin-fluctuation theory is the jump phase transition to the paramagnetic state. We eliminate the jump and obtain a continuous second-order phase transition by taking into account high-order terms in the expansion of the free energy in powers of the fluctuating exchange field. The third-order term of the free energy renormalizes the mean field, and the fourth-order term, responsible for the interaction of the fluctuations, renormalizes the spin susceptibility. The extended theory is applied to the calculation of magnetic properties of Fe-Ni Invar.

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1. Introduction

Fluctuations of the electron spin density play a predominant role in the thermodynamics of ferromagnetic metals (see, e.g., [1] and references therein). Most of the progress in the spin-fluctuation theory (SFT) has been achieved within the functional-integral approach [2, 3]. Using the single-site and static approximation, Hubbard [4], Hasegawa [5] and Grebennikov *et al* [6] obtained a quantitative description of magnetic properties at finite temperatures, which was much better than in the Stoner mean-field theory (figure 1, left). To go beyond the single-site approximation, Hertz and Klenin [7] suggested a self-consistent Gaussian approximation. However, it used the static long-wave limit and was restricted to paramagnets. To ferromagnetic metals, the variational approach [7] was extended by Grebennikov [8] who took into account

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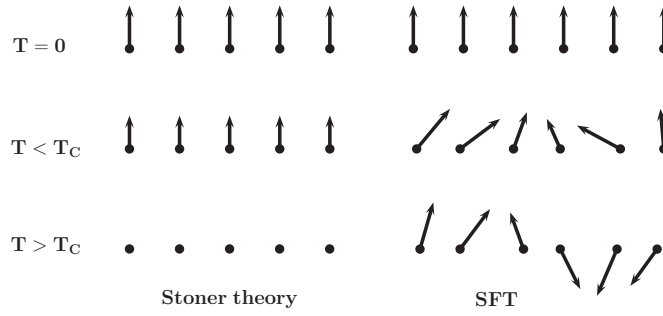


Figure 1. A schematic picture of exchange field configurations in the Stoner mean-field theory and SFT.

dynamics and space correlations of the fluctuations, the latter again only in the paramagnetic state. A complete dynamic non-local approximation to the SFT for ferromagnetic metals was developed by Reser and Grebennikov [9].

The Gaussian SFT [9] shows good agreement with experiment over a wide range of temperatures. However, at high temperatures, the Gaussian approximation yields a discontinuous change in magnetic characteristics (see [10] and references therein). The main reason for the first-order phase transition is that Gaussian approximation implies independent ‘harmonic’ fluctuations of the spin density and thus fails to account for their interaction.

The first-order phase transition has been observed in various versions of the self-consistent renormalization (SCR) theory of spin fluctuations, developed for weak ferromagnetic metals (for a review, see [1]). Particularly, in [11] it was argued that the first-order discontinuity in the SCR theory can be eliminated by taking into account the rotational invariance of the system. This leads to two integro-differential equations for the longitudinal χ_{\parallel} and transverse χ_{\perp} susceptibilities. A simple relation that couples χ_{\parallel} and χ_{\perp} was suggested in [12] from the assumption that the total local spin fluctuation, i.e. the sum of the zero-point and thermal spin fluctuations, is conserved as it is in the Heisenberg local moment theory and may be somehow justified for weak ferromagnets.

In the present paper, we improve the coupling of the fluctuations in the Gaussian SFT [9] by taking into account high-order terms of the free energy of electrons $F(V)$ in the fluctuating exchange field V (see [13] for a brief summary). First, in the fourth-order Taylor expansion of the free energy $F(V)$, we take a partial average with respect to ΔV in the third- and fourth-order terms replacing them by linear and quadratic terms, respectively. Adding these corrections to the Taylor terms of the first and second order, we come to the *extended* function $F(V)$. The best quadratic approximation is constructed as in [7–9], with the help of the free energy minimum principle [14], but using the first- and second-order derivatives of the *extended* function $F(V)$. In the final computational formulae, the third-order term renormalizes the mean field, and the fourth-order term renormalizes the susceptibility (this includes the Gaussian SFT [9] as a special case with the renormalizations set to unity).

The fundamental difference between our treatment of the high-order terms and the previous ones is that in our approach the ferromagnetic state is changed self-consistently (for treatments of the fourth-order term in the paramagnetic state see [1, 15–17] and references therein). Another advantage of our approximation to the SFT is that the integral equation for the mean Green’s function (coherent potential equation) is finally reduced to a system of four nonlinear equations with four unknowns, which is only slightly more complex than the Stoner

mean-field theory. It is significant to note that solving the coherent potential equation directly requires a number of additional simplifications, such as neglect of rotational invariance and the mode–mode ‘frequency’ interactions, and, most important, the single-site approximation [18, 19].

The extended Gaussian approximation of the SFT is applied to the numerical calculations of magnetic properties of the $\text{Fe}_{0.65}\text{Ni}_{0.35}$ Invar alloy at finite temperatures. This alloy has been intensively studied recently (see, e.g., [20] and references therein), but mostly at zero temperature, i.e. without the quantum statistics. Our choice of Fe–Ni Invar to illustrate the possibilities of the extended SFT is motivated by problems of temperature dependence which were found in the quantum-statistical treatment of this Invar [10, 21–23]. (Obviously, before that the new method has been tested on a simplified clean system, such as elemental Fe.)

It is known that Fe–Ni Invar is a complex disordered system. However, the comparison of the calculation results for the disordered alloy $\text{Fe}_{0.65}\text{Ni}_{0.35}$ [10, 21] and ordered compound Fe_3Ni [22, 23] showed that the effect of disorder in the filling of sites with Fe and Ni atoms on the magnetic properties of Fe–Ni Invar is insignificant. This conclusion agrees with earlier results for the ordered and disordered $\text{Fe}_{0.72}\text{Pt}_{0.28}$ Invars (see, e.g., [24], table 10-1). The weak influence of the atomic disorder on the magnetic properties of Fe–Ni Invar at finite temperatures is explained by the *integral* dependence on the electronic energy structure in all the equations of the SFT. The details of the initial density of states (DOS) do not exert the decisive effect on the results of the calculation.

2. Quadratic approximation taking into account high-order terms

2.1. Free energy of electrons in a fluctuating field

The Stratonovich–Hubbard transformation [2, 3] replaces the pair interaction of electrons by the interaction of the electrons with the exchange field⁴

$$V \equiv (V_1, V_2, \dots), \quad V_j = \sum_{\alpha} V_j^{\alpha}(\tau) \sigma^{\alpha}, \quad (1)$$

fluctuating in space (see figure 1, right) and in ‘time’ $\tau \in [0, 1/T]$ (j being the site number, σ^{α} the Pauli matrix, $\alpha = x, y, z$, and T the temperature, in energy units). Hence, the partition function can be written as a functional integral

$$Z = e^{-\mathcal{F}/T} = \left(\int e^{-F_0(V)/T} \mathcal{D}V(\tau) \right)^{-1} \int e^{-F_0(V)/T} e^{-F_1(V)/T} \mathcal{D}V(\tau), \quad (2)$$

where

$$F_0(V) = N_d T \int_0^{1/T} \sum_j \text{Sp} \left(\frac{V_j^2(\tau)}{2U} \right) d\tau \equiv \text{Tr} \left(\frac{V^2}{2U} \right) \quad (3)$$

is the energy of the exchange field, and

$$F_1(V) = T \text{Tr} \ln G(V) \quad (4)$$

is the free energy of non-interacting electrons in the field V expressed in terms of the Green’s function

$$G(V) = (z + \mu - H_0 - V)^{-1}. \quad (5)$$

Here, $N_d = 5$ is the number of *degenerate* d bands, U is the single-site electron–electron interaction constant, z is the energy variable, μ is the chemical potential and H_0 is the sum of

⁴ We neglect the charge field, same as in [9].

kinetic and potential energy of the non-interacting band electrons. The symbol Sp denotes the trace over spin indices, and Tr stands for the full matrix trace, independent of the particular representation. To simplify the notation, we omit the band index and write the prefactor N_d in the trace Tr . In expression (4), we omit the terms independent of the field V (for details, see appendix A).

2.2. Partial averaging of high-order terms of the free energy

Since H_0 and V cannot be diagonalized simultaneously in either coordinate-‘time’ or momentum-‘frequency’ spaces, exact formulae (4) and (5) are of little use to calculate the partition function (2) without an appropriate approximation. Therefore, integral (2) is replaced by a Gaussian integral or, equivalently, the exact expression

$$F(V) = F_0(V) + F_1(V) = T \text{Tr} \left(\frac{V^2}{2UT} + \ln G(V) \right) \quad (6)$$

is replaced by a *quadratic* form:

$$F(V) \rightarrow F^{(2)}(V) = \text{Tr}(\Delta V A \Delta V), \quad \Delta V = V - \tilde{V}. \quad (7)$$

Hence, we arrive at the Gaussian fluctuating field V with the probability density

$$p(V) \propto \exp \left(-\frac{1}{T} \text{Tr}(\Delta V A \Delta V) \right), \quad (8)$$

the mean field \tilde{V} and matrix A being the unknown parameters of the SFT to be determined. Compared to conventional Gaussian SFTs, we take into account the ‘anharmonicity’ of the fluctuations by renormalizing the parameters \tilde{V} and A .

First, we expand function (6) in Taylor series to the fourth order in $\Delta V = V - \tilde{V}$:

$$F(V) \approx F(\tilde{V}) + T \text{Tr} \left(\frac{\tilde{V} \Delta V}{UT} + G(\tilde{V}) \Delta V \right) + \frac{1}{2} T \text{Tr} \left(\frac{\Delta V^2}{UT} + (G(\tilde{V}) \Delta V)^2 \right) \\ + \frac{1}{3} T \text{Tr} (G(\tilde{V}) \Delta V)^3 + \frac{1}{4} T \text{Tr} (G(\tilde{V}) \Delta V)^4, \quad (9)$$

where \tilde{V} is some *arbitrary* value of the exchange field. For the third-order term, we define the Gaussian partial averaging by the formula

$$\text{Tr}(G \Delta V G \Delta V G \Delta V) \approx \text{Tr}(G \Delta V \underbrace{G \Delta V G \Delta V}_{\text{avg}}) + \text{Tr}(G \Delta V \underbrace{G \Delta V G \Delta V}_{\text{avg}}) \\ + \text{Tr}(G \Delta V \underbrace{G \Delta V G \Delta V}_{\text{avg}}) = 3 \text{Tr}(G \Delta V \underbrace{G \Delta V G \Delta V}_{\text{avg}}) \quad (10)$$

and for the fourth-order term by the formula

$$\text{Tr}(G \Delta V G \Delta V G \Delta V G \Delta V) \\ \approx 4 \text{Tr}(G \Delta V \underbrace{G \Delta V G \Delta V}_{\text{avg}} G \Delta V G \Delta V) + 2 \text{Tr}(G \Delta V \underbrace{G \Delta V G \Delta V}_{\text{avg}} G \Delta V G \Delta V) \\ - 2 \text{Tr}(G \Delta V \underbrace{G \Delta V G \Delta V}_{\text{avg}} \underbrace{G \Delta V G \Delta V}_{\text{avg}}) - \text{Tr}(G \Delta V \underbrace{G \Delta V G \Delta V}_{\text{avg}} \underbrace{G \Delta V G \Delta V}_{\text{avg}}), \quad (11)$$

where the underbrace denotes the averaging with the Gaussian probability density (8):

$$(\dots \underbrace{\Delta V \dots \Delta V}_{\text{avg}} \dots) = \int (\dots \Delta V \dots \Delta V \dots) p(V) DV.$$

In formulae (10) and (11), the combinatorial multipliers correspond to the number of all possible pairings of the terms ΔV with the cyclic invariance of the trace taken into account. In formula (11), the last two terms are chosen so that both sides have equal mean values. These terms will be omitted for brevity since they do not contain the variable ΔV and lead only

to a change of an unimportant free term in expansion (9). Furthermore, we approximate the second term on the right-hand side of (11) by the first one. Thus, relation (11) takes the form

$$\text{Tr}(G\Delta V G\Delta V G\Delta V G\Delta V) \approx 6 \text{Tr}(G\Delta V \underline{G\Delta V} G\Delta V G\Delta V). \quad (12)$$

Using formulae (10) and (12), we transform the third- and fourth-order terms in expansion (9) into corrections to the first- and second-order terms, respectively:

$$F(V) \approx F(\tilde{V}) + T \text{Tr} \left(\frac{\tilde{V}\Delta V}{UT} + G(\tilde{V})\Delta V + G(\tilde{V})\Delta V \underline{G(\tilde{V})\Delta V} G(\tilde{V})\Delta V \right) + \frac{1}{2} T \text{Tr} \left(\frac{\Delta V^2}{UT} + G(\tilde{V})\Delta V G(\tilde{V})\Delta V + 3G(\tilde{V})\Delta V \underline{G(\tilde{V})\Delta V} G(\tilde{V})\Delta V G(\tilde{V})\Delta V \right). \quad (13)$$

2.3. Quadratic approximation based on the free energy minimum principle

Following [7–9], the best quadratic approximation $F^{(2)}(V)$ is constructed using the free energy minimum principle [14].

Define the average with the Gaussian density (8) by the formula

$$\langle \dots \rangle = \left(\int \exp(-F^{(2)}(V)/T) DV \right)^{-1} \int (\dots) \exp(-F^{(2)}(V)/T) DV,$$

where $F^{(2)}(V)$ is a quadratic function of the form (7). Then the identity

$$\int \exp(-F(V)/T) DV = \int \exp(-(F(V) - F^{(2)}(V))/T) \exp(-F^{(2)}(V)/T) DV$$

can be rewritten as

$$\left(\int \exp(-F^{(2)}(V)/T) DV \right)^{-1} \int \exp(-F(V)/T) DV = \langle \exp(-(F(V) - F^{(2)}(V))/T) \rangle.$$

Applying the inequality $\langle \exp f \rangle \geq \exp \langle f \rangle$, f being an arbitrary set of real quantities, and taking the logarithm, we come to the upper bound for the free energy:

$$\mathcal{F} \leq \mathcal{F}^{(2)} + \langle F(V) - F^{(2)}(V) \rangle, \quad (14)$$

where

$$\mathcal{F} = -T \ln \int \exp(-F(V)/T) DV, \quad \mathcal{F}^{(2)} = -T \ln \int \exp(-F^{(2)}(V)/T) DV.$$

To get the ‘best’ approximation in the class of all quadratic functions (7), one minimizes the right-hand side of (14) to obtain the equation (for details, see [25])

$$\left\langle \frac{\partial F(V)}{\partial V} \right\rangle = 0, \quad (15)$$

so that \tilde{V} is equal to the mean field $\bar{V} \equiv \langle \tilde{V} \rangle$. The matrix of the quadratic form is given by

$$A = \frac{1}{2} \left\langle \frac{\partial^2 F(V)}{\partial V^2} \right\rangle. \quad (16)$$

In the present paper, we apply formulae (15) and (16) to the modified function (13) instead of the original free energy (6), as it was done in [9]. In expression (13), we average over \tilde{V} with the Gaussian density (8), everywhere but in ΔV , and replace the $\Delta V = V - \tilde{V}$ terms by $\Delta V = V - \bar{V}$. The averaged linear term in (13) annihilates

$$T \text{Tr} \left(\frac{\bar{V}\Delta V}{UT} + \langle G(\tilde{V}) \rangle \Delta V + \langle G(\tilde{V}) \Delta V \underline{G(\tilde{V})\Delta V} G(\tilde{V}) \Delta V \rangle \right) = 0 \quad (17)$$

identically over ΔV . Hence, the quadratic form $F^{(2)}(V)$ contains only the second-order term:

$$F(V) \approx F^{(2)}(V) = \frac{1}{2}T \operatorname{Tr} \left(\frac{\Delta V^2}{UT} + \langle G(\tilde{V}) \Delta V G(\tilde{V}) \Delta V \rangle + 3 \langle G(\tilde{V}) \Delta V \underbrace{G(\tilde{V}) \Delta V G(\tilde{V}) \Delta V}_{\text{triple}} G(\tilde{V}) \Delta V \rangle \right). \quad (18)$$

To simplify expressions (17) and (18) one step further, we introduce yet another partial averaging:

$$G \Delta V \underbrace{G \Delta V}_{\text{double}} G \Delta V \approx (\operatorname{Tr}(\mathbf{1}))^{-1} \operatorname{Tr}(G \Delta V \underbrace{G \Delta V}_{\text{double}}) G \Delta V.$$

Finally, we replace the average over \tilde{V} of the product of the Green's functions $G(\tilde{V})$ by the product of the mean Green's functions $\langle G(\tilde{V}) \rangle \equiv \bar{G}$. Hence, relation (17) reduces to

$$U^{-1} \operatorname{Tr}(\bar{V} \Delta V) + (1 + \eta)T \operatorname{Tr}(\bar{G} \Delta V) = 0, \quad (19)$$

and the quadratic form (18) transforms to

$$F^{(2)}(V) = \frac{1}{2U} \operatorname{Tr}(\Delta V^2) + \frac{1}{2}(1 + 3\eta)T \operatorname{Tr}(\bar{G} \Delta V \bar{G} \Delta V), \quad (20)$$

where the correction coefficient is

$$\eta = (\operatorname{Tr}(\mathbf{1}))^{-1} \operatorname{Tr}(\bar{G} \Delta V \underbrace{\bar{G} \Delta V}_{\text{double}}). \quad (21)$$

2.4. Equations for the mean field and chemical potential

In the ferromagnetic state, we choose the z -axis along the direction of the mean field:

$$\bar{V} = \bar{V}^z \sigma^z.$$

Then the mean Green's function is spin-diagonal due to

$$\bar{G}^x = 0, \quad \bar{G}^y = 0. \quad (22)$$

Hence, using the well-known relation for the Pauli matrices, $\operatorname{Sp}(\sigma^\alpha \sigma^\beta) = 2\delta_{\alpha\beta}$, we rewrite equation (19) as

$$U^{-1} \operatorname{Tr}(\bar{V}^z \Delta V^z) + (1 + \eta)T \operatorname{Tr}(\bar{G}^z \Delta V^z) = 0. \quad (23)$$

In order to transform (23) to the mean-field equation, we use the momentum-‘frequency’ representation. Since the exchange field (1) is diagonal in the coordinate-‘time’ representation, its Fourier transform is homogeneous:

$$V_{\mathbf{k}\mathbf{k}'n n'}^\alpha = V_{\mathbf{k}-\mathbf{k}', n-n'}^\alpha, \quad (24)$$

where \mathbf{k} is the wave vector, taking values in the Brillouin zone, and $\omega_n = (2n + 1)\pi T$ are the thermodynamic ‘frequencies’. Furthermore, the mean field \bar{V} is a constant in the coordinate-‘time’ representation, and hence its Fourier transform has the single non-zero coefficient:

$$\bar{V}_{\mathbf{q}m}^\alpha = \bar{V}_{00}^z \delta_{\mathbf{q}0} \delta_{m0} \delta_{\alpha z}.$$

Thus, the first term on the left-hand side of (23) reduces to

$$U^{-1} \operatorname{Tr}(\bar{V}^z \Delta V^z) = u^{-1} \bar{V}_{00}^z \Delta V_{00}^z, \quad (25)$$

where $u = U/N_d$. Similarly, the mean Green's function is transitionally invariant in space and ‘time’: $\bar{G}_{j j'}(\tau, \tau') = \bar{G}_{j-j'}(\tau - \tau')$; hence its Fourier transform is diagonal:

$$\bar{G}_{\mathbf{k}\mathbf{k}'n n'}^\gamma = \bar{G}_{\mathbf{k}n}^\gamma \delta_{\mathbf{k}\mathbf{k}'} \delta_{n n'}, \quad \gamma = 0, z. \quad (26)$$

Therefore, the trace in the second term of (23) can be written as

$$\text{Tr}(\bar{G}^z \Delta V^z) = \sum_{\mathbf{kn}} \bar{G}_{\mathbf{kn}}^z \Delta V_{00}^z = \text{Tr}(\bar{G}^z) \Delta V_{00}^z. \quad (27)$$

Substituting (25) and (27) to (23), we come to

$$u^{-1} \bar{V}_{00}^z + (1 + \eta) T \text{Tr} \bar{G}^z = 0. \quad (28)$$

The mean Green's function \bar{G} is related to the mean spin moment (per atom) s_z by the formula (see (B.4) in appendix B)

$$s_z = N_a^{-1} T \text{Tr} \bar{G}^z.$$

Thus, the mean-field equation (28) takes the form

$$\bar{V}_z = -u(1 + \eta)s_z, \quad (29)$$

$\bar{V}_z \equiv N_a^{-1} \bar{V}_{00}^z$ being the value of the mean exchange field. The conservation of the total number of electrons condition ($\partial \mathcal{F} / \partial \mu = 0$) yields the equation on the chemical potential (see appendix B):

$$N_e = T \text{Tr} \bar{G}. \quad (30)$$

2.5. Equations for the spin fluctuations

The quadratic form (20) is reduced to a sum of squares using the momentum-‘frequency’ representation. By Parseval's identity, the first term in (20) can be rewritten as

$$\frac{1}{U} \sum_{\alpha} \text{Tr}(\Delta V^{\alpha})^2 = \frac{N_d}{U} \sum_{\mathbf{qm}\alpha} |\Delta V_{\mathbf{qm}}^{\alpha}|^2 = u^{-1} \sum_{\mathbf{qm}\alpha} |\Delta V_{\mathbf{qm}}^{\alpha}|^2. \quad (31)$$

For the trace in the second term of (20), using (24) and (26) we have

$$\text{Tr}(\bar{G} \Delta V \bar{G} \Delta V) = N_d \sum_{\mathbf{k}\mathbf{k}_1 n_1} \sum_{\alpha\beta\gamma_1\gamma_2} \bar{G}_{\mathbf{kn}}^{\gamma_1} \Delta V_{\mathbf{k}-\mathbf{k}_1, n-n_1}^{\alpha} \bar{G}_{\mathbf{k}_1 n_1}^{\gamma_2} \Delta V_{\mathbf{k}_1-\mathbf{k}, n_1-n}^{\beta} \text{Sp}(\sigma^{\gamma_1} \sigma^{\alpha} \sigma^{\gamma_2} \sigma^{\beta}),$$

where $\gamma_1, \gamma_2 = 0, z$. Calculations show that the summands with $\alpha \neq \beta$ are equal to zero (see appendix C). Hence,

$$\frac{1}{2} (1 + 3\eta) T \text{Tr}(\bar{G} \Delta V \bar{G} \Delta V) = \sum_{\mathbf{qm}\alpha} \Delta V_{\mathbf{qm}}^{\alpha} \chi_{\mathbf{qm}}^{\alpha} \Delta V_{-\mathbf{q}-m}^{\alpha} = \sum_{\mathbf{qm}\alpha} \chi_{\mathbf{qm}}^{\alpha} |\Delta V_{\mathbf{qm}}^{\alpha}|^2, \quad (32)$$

where $\mathbf{q} = \mathbf{k} - \mathbf{k}_1$, $m = n - n_1$ and

$$\begin{aligned} \chi_{\mathbf{qm}}^{\alpha} &\equiv -\frac{1}{2} \frac{\partial^2 F_1^{(2)}}{\partial(\Delta V_{\mathbf{qm}}^{\alpha}) \partial(\Delta V_{-\mathbf{q}-m}^{\alpha})} \\ &= -\frac{N_d}{2} (1 + 3\eta) T \sum_{\mathbf{kn}} \sum_{\gamma_1\gamma_2} \bar{G}_{\mathbf{kn}}^{\gamma_1} \bar{G}_{\mathbf{k}-\mathbf{q}, n-m}^{\gamma_2} \text{Sp}(\sigma^{\gamma_1} \sigma^{\alpha} \sigma^{\gamma_2} \sigma^{\alpha}) \end{aligned} \quad (33)$$

is the unenhanced dynamic susceptibility. Substituting (31) and (32) to (20), we obtain

$$F^{(2)}(V) = \sum_{\mathbf{qm}\alpha} (u^{-1} - \chi_{\mathbf{qm}}^{\alpha}) |\Delta V_{\mathbf{qm}}^{\alpha}|^2 \equiv \sum_{\mathbf{qm}\alpha} A_{\mathbf{qm}}^{\alpha} |\Delta V_{\mathbf{qm}}^{\alpha}|^2. \quad (34)$$

Thus $\Delta V_{\mathbf{qm}}^{\alpha}$ are statistically independent Gaussian fluctuations, with the mean squares of fluctuations

$$\langle |\Delta V_{\mathbf{qm}}^{\alpha}|^2 \rangle = \frac{T}{2A_{\mathbf{qm}}^{\alpha}} = \frac{T}{2(u^{-1} - \chi_{\mathbf{qm}}^{\alpha})}. \quad (35)$$

3. Local approximation of the SFT

3.1. Reduction to local fluctuations

Expressing the mean Green's function \bar{G} in terms of the chemical potential μ , mean field \bar{V}_z and fluctuations $\langle |\Delta V_{\mathbf{q}m}^\alpha|^2 \rangle$, we come to the closed system of equations (29), (30) and (35). However, this system of equations is still excessively difficult for practical computations of average quantities, such as magnetization. Moreover, as a result of the quadratic approximation (34), the fluctuations at different momenta and 'frequencies' $\Delta V_{\mathbf{q}m}^\alpha$ become independent, which is an acceptable approximation only at low temperatures. Therefore, we proceed with the local approximation of the quadratic form (34):

$$\begin{aligned} F^{(2)}(V) &= \sum_{\mathbf{q}m\alpha} A_{\mathbf{q}m}^\alpha |\Delta V_{\mathbf{q}m}^\alpha|^2 \approx \sum_{\alpha} A^\alpha \sum_{\mathbf{q}m} |\Delta V_{\mathbf{q}m}^\alpha|^2 \\ &= \sum_{\alpha} N_a A^\alpha \left(\frac{1}{N_a} \sum_{\mathbf{q}m} |\Delta V_{\mathbf{q}m}^\alpha|^2 \right) \equiv \sum_{\alpha} A_\alpha \Delta V_\alpha^2. \end{aligned}$$

Here, the coefficient $A_\alpha \equiv N_a A^\alpha$ is related to the mean square of the local fluctuation $\langle \Delta V_\alpha^2 \rangle$ by the formula

$$A_\alpha = \frac{T}{2} \langle \Delta V_\alpha^2 \rangle^{-1} = \frac{T}{2} \left(\frac{1}{N_a} \sum_{\mathbf{q}m} \langle |\Delta V_{\mathbf{q}m}^\alpha|^2 \rangle \right)^{-1},$$

where

$$\langle \dots \rangle = \left(\int \exp \left(- \sum_{\alpha} A_\alpha \Delta V_\alpha^2 / T \right) d\mathbf{V} \right)^{-1} \int \dots \exp \left(- \sum_{\alpha} A_\alpha \Delta V_\alpha^2 / T \right) d\mathbf{V}.$$

Taking into account (35), for the mean square of the local fluctuation ('fluctuation', for short), we have

$$\langle \Delta V_\alpha^2 \rangle = \frac{1}{N_a} \sum_{\mathbf{q}m} \langle |\Delta V_{\mathbf{q}m}^\alpha|^2 \rangle = \frac{1}{N_a} \sum_{\mathbf{q}m} \frac{T}{2(u^{-1} - \chi_{\mathbf{q}m}^\alpha)}. \quad (36)$$

3.2. Summation over momenta and 'frequencies'

The calculation of the sum (36) follows [9] and yields essentially the same formulae but with the renormalization prefactor $1 + 3\eta$ for the susceptibility. By analytic continuation from the points $i\omega_m = i2\pi mT$, summation over 'frequencies' is replaced by the integration over the energy variable (for details, see [25]):

$$\sum_m \langle |\Delta V_{\mathbf{q}m}^\alpha|^2 \rangle = \frac{u}{2} \frac{2}{\pi} \int_0^\infty \left(B(\varepsilon) + \frac{1}{2} \right) \text{Im} \frac{1}{1 - u\chi_{\mathbf{q}}^\alpha(\varepsilon + i0)} d\varepsilon, \quad (37)$$

where $B(\varepsilon) = (\exp(\varepsilon/T) - 1)^{-1}$ is the Bose function. We discard the temperature-independent term with $1/2$, assuming that the zero-point fluctuations are already taken into account in the initial DOS $\nu(\varepsilon)$ calculated by the density-functional method and in the effective interaction constant u . Using the Taylor expansion $\chi_{\mathbf{q}}(\varepsilon) \approx \chi_{\mathbf{q}}(0) + i\varphi_{\mathbf{q}}\varepsilon$ and approximation

$$\frac{1}{e^{\varepsilon/T} - 1} \approx \begin{cases} T/\varepsilon, & \varepsilon < \varepsilon_0 = (\pi^2/6)T, \\ 0, & \varepsilon > \varepsilon_0 \end{cases} \quad (38)$$

for the Bose function, we come to

$$\sum_m \langle |\Delta V_{\mathbf{q}m}^\alpha|^2 \rangle = \frac{uT}{2\lambda_{\mathbf{q}}^\alpha} \frac{2}{\pi} \arctan \frac{u\varphi_{\mathbf{q}}^\alpha \pi^2 T}{6\lambda_{\mathbf{q}}^\alpha}, \quad (39)$$

where

$$\lambda_{\mathbf{q}}^{\alpha} = 1 - u\chi_{\mathbf{q}}^{\alpha}(0), \quad \varphi_{\mathbf{q}}^{\alpha} = \left. \frac{d \operatorname{Im} \chi_{\mathbf{q}}^{\alpha}(\varepsilon)}{d\varepsilon} \right|_{\varepsilon=0}. \quad (40)$$

The approximation (38) not only reproduces the behaviour of the Bose function $B(\varepsilon)$ with respect to thermal energies, but also has the same first moment $\int_0^{\infty} \varepsilon B(\varepsilon) d\varepsilon = (\pi T)^2/6$, which essentially defines the upper bound ε_0 . Thus, the approximation (38) is well justified. Its other advantage is the possibility of the straightforward proceeding to the static limit at high temperatures, when the argument of the arctangent in (39) is much larger than unity.

The function $\lambda_{\mathbf{q}}^{\alpha}$ is calculated using the expansion for the static susceptibility:

$$\chi_{\mathbf{q}}^{\alpha}(0) \approx \chi_0^{\alpha}(0) + B^{\alpha} q^2, \quad (41)$$

where $\chi_0^{\alpha}(0)$ is the static uniform susceptibility, and the coefficient B^{α} is obtained from the local susceptibility $\chi_L^{\alpha}(0) = N_a^{-1} \sum_{\mathbf{q}} \chi_{\mathbf{q}}^{\alpha}(0)$. Substituting (41) in the first equality (40), we get

$$\lambda_{\mathbf{q}}^{\alpha} = \lambda_0^{\alpha} + (\lambda_L^{\alpha} - \lambda_0^{\alpha}) q^2 / \bar{q}^2, \quad (42)$$

where $\lambda_0^{\alpha} = 1 - u\chi_0^{\alpha}(0)$, $\lambda_L^{\alpha} = 1 - u\chi_L^{\alpha}(0)$ and $\bar{q}^2 = N_a^{-1} \sum_{\mathbf{q}} q^2$. The function $\varphi_{\mathbf{q}}^{\alpha}$ is approximated by its mean value:

$$\varphi_{\mathbf{q}}^{\alpha} \approx N_a^{-1} \sum_{\mathbf{q}} \varphi_{\mathbf{q}}^{\alpha} = \varphi_L^{\alpha}. \quad (43)$$

The summation over \mathbf{q} is carried out by the integration over the Brillouin zone, approximated for simplicity by the sphere of the same volume. Using (39), (42) and (43) for the local fluctuation (36), we finally obtain

$$\zeta^{\alpha} \equiv \langle \Delta V_{\alpha}^2 \rangle = \frac{uT}{2\lambda_L^{\alpha}} \int_0^1 \frac{1}{a_{\alpha}^2 + b_{\alpha}^2 k^2} \frac{2}{\pi} \arctan \frac{c_{\alpha}}{a_{\alpha}^2 + b_{\alpha}^2 k^2} 3k^2 dk, \quad (44)$$

where

$$a_{\alpha}^2 = \lambda_0^{\alpha} / \lambda_L^{\alpha}, \quad b_{\alpha}^2 = (1 - a_{\alpha}^2) / 0.6, \quad c_{\alpha} = u\varphi_L^{\alpha} \pi^2 T / (6\lambda_L^{\alpha}).$$

Relation (44) is obtained using the integration over the Brillouin zone with the Bose distribution and a simple dispersion relation, whose parameters are chosen to give a correct value of the local susceptibility. Thus, expression (44) for the mean square of the spin fluctuations is self-consistent and does not contain any free parameters.

3.3. Mean single-site Green's function

To calculate the local susceptibility $\chi_L^{\alpha}(\varepsilon) = \chi_L^{\alpha}(0) + i\varphi_L^{\alpha}\varepsilon$, we replace the mean Green's function \bar{G} in (33) by its site-diagonal part:

$$\bar{G}_{jj'n} = \bar{G}_{j-j',n} \approx \bar{G}_{0n} \delta_{jj'} \equiv g_n \delta_{jj'}, \quad (45)$$

so that the Fourier transform is \mathbf{k} -independent: $\bar{G}_{\mathbf{kn}} = g_n$. Thus, we rewrite (33) as

$$\chi_L^{\alpha}(i\omega_m) = -\frac{N_d}{2} (1 + 3\eta) T \sum_n \sum_{\gamma_1 \gamma_2} g^{\gamma_1}(i\omega_n) g^{\gamma_2}(i\omega_n - i\omega_m) \operatorname{Sp}(\sigma^{\gamma_1} \sigma^{\alpha} \sigma^{\gamma_2} \sigma^{\alpha}).$$

Using analytic continuation first from points $i\omega_n$ and then from $i\omega_m$, we replace the sum over 'frequencies' by the integral over the energy variable:

$$\chi_L^{\alpha}(z) = -\frac{N_d}{2\pi} (1 + 3\eta) \sum_{\gamma_1 \gamma_2} \int \operatorname{Im}(g^{\gamma_1}(\varepsilon)[g^{\gamma_2}(\varepsilon - z) + g^{\gamma_2}(\varepsilon + z)] \operatorname{Sp}(\sigma^{\gamma_1} \sigma^{\alpha} \sigma^{\gamma_2} \sigma^{\alpha})) f(\varepsilon) d\varepsilon,$$

where $f(\varepsilon) = [\exp((\varepsilon - \mu)/T) + 1]^{-1}$ is the Fermi function, and $g(\varepsilon) = g(\varepsilon - i0)$. The 2×2 matrix $g(\varepsilon)$ is spin-diagonal: $g^x(\varepsilon) = g^y(\varepsilon) = 0$, same as $\bar{G}_{\mathbf{kn}}$ (see (22)). Denoting the diagonal elements of $g(\varepsilon)$ by $g_{\uparrow}(\varepsilon)$ and $g_{\downarrow}(\varepsilon)$, we have $g^0(\varepsilon) = \frac{1}{2}[g_{\uparrow}(\varepsilon) + g_{\downarrow}(\varepsilon)]$ and $g^z(\varepsilon) = \frac{1}{2}[g_{\uparrow}(\varepsilon) - g_{\downarrow}(\varepsilon)]$. Hence,⁵

$$\chi_L^x(0) = -\frac{N_d(1+3\eta)}{\pi} \int \text{Im}(g_{\uparrow}g_{\downarrow}) f \, d\varepsilon, \quad (46)$$

$$\varphi_L^x = \frac{N_d(1+3\eta)}{\pi} \int \text{Im} g_{\uparrow} \text{Im} g_{\downarrow} \left(-\frac{\partial f}{\partial \varepsilon}\right) d\varepsilon, \quad (47)$$

$$\chi_L^z(0) = -\frac{N_d(1+3\eta)}{2\pi} \int (\text{Im} g_{\uparrow}^2 + \text{Im} g_{\downarrow}^2) f \, d\varepsilon, \quad (48)$$

$$\varphi_L^z = \frac{N_d(1+3\eta)}{2\pi} \int [(\text{Im} g_{\uparrow})^2 + (\text{Im} g_{\downarrow})^2] \left(-\frac{\partial f}{\partial \varepsilon}\right) d\varepsilon. \quad (49)$$

Similarly, in equations for the mean field (29) and chemical potential (30), we use the mean single-site Green's function (45) and replace the sum over 'frequencies' by the integral over the energy variable. Thus, we rewrite equation (29) as

$$\bar{V}_z = -u(1+\eta) \frac{N_d}{2\pi} \int \text{Im}(g_{\uparrow} - g_{\downarrow}) f \, d\varepsilon \quad (50)$$

and equation (30) as

$$N_e = N_a \frac{N_d}{\pi} \int \text{Im}(g_{\uparrow} + g_{\downarrow}) f \, d\varepsilon. \quad (51)$$

In formulae (46)–(51), the mean single-site Green's function is given by

$$g_{\sigma}(\varepsilon) = \int \frac{v(\varepsilon')}{\varepsilon - \sigma \bar{V}_z - \Delta \Sigma_{\sigma}(\varepsilon) - \varepsilon'} d\varepsilon',$$

where $\sigma = \uparrow, \downarrow$ or ± 1 is the spin index, $v(\varepsilon)$ is the non-magnetic DOS and $\Delta \Sigma_{\sigma}(\varepsilon)$ is the fluctuational contribution to the self-energy part, calculated by the formula

$$\Delta \Sigma_{\sigma}(\varepsilon) = \frac{g_{\sigma}(\varepsilon) \zeta^z}{1 + 2\sigma \bar{V}_z g_{\sigma}(\varepsilon)} + 2g_{\bar{\sigma}}(\varepsilon) \zeta^x, \quad \bar{\sigma} \equiv -\sigma.$$

The latter is obtained from the coherent potential equation

$$\Delta \Sigma = \langle \Delta V [1 - g(\Delta V - \Delta \Sigma)]^{-1} \rangle$$

in the second order with respect to the fluctuations ΔV [9].

3.4. Correction coefficient

Final computational formulae of the extended SFT differ from the ones in [9] by the renormalization of susceptibility (46)–(49) and the mean field (50) that depend on the coefficient η defined in (21) (with $\eta = 0$, the system of equations reduces to the one in [9]). Using the single-site and quasi-static approximations, we come to the following expression for η (see appendix D):

$$\eta \approx \frac{1}{\pi T} \left[2\zeta^x \int (\text{Re} g_{\uparrow} \text{Im} g_{\downarrow} + \text{Re} g_{\downarrow} \text{Im} g_{\uparrow}) f \, d\varepsilon + \zeta^z \int (\text{Re} g_{\uparrow} \text{Im} g_{\uparrow} + \text{Re} g_{\downarrow} \text{Im} g_{\downarrow}) f \, d\varepsilon \right]. \quad (52)$$

⁵ Recall that $\chi_{\mathbf{qm}}^x = \chi_{\mathbf{qm}}^y$ due to axial symmetry (for details see appendix C).

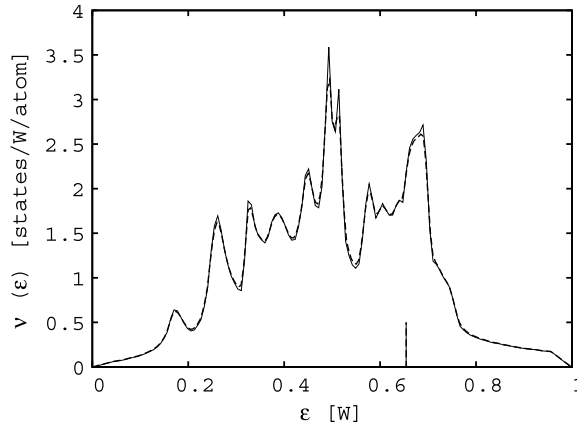


Figure 2. The DOS of the d band of non-magnetic $\text{Fe}_{0.65}\text{Ni}_{0.35}$, obtained from [26] (—), and the one smoothed out by convolution with the Lorentz function of the half-width $\Gamma = 0.001$ (---). The energy ϵ and half-width Γ are in the units of the bandwidth $W = 9.70$ eV. The vertical line indicates the position of the Fermi level ϵ_F .

The impact of the corrections due to the third- and fourth-order terms becomes critical at high temperatures. Therefore, the coefficient η can be estimated by the reduced formula

$$\eta \approx \frac{6\bar{\zeta}}{\pi T} \int \text{Re } g^0 \text{Im } g^0 f \, d\epsilon \equiv \frac{c}{T} \bar{\zeta}, \quad (53)$$

where $\bar{\zeta} = (2\zeta^x + \zeta^z)/3$ is the mean fluctuation, and $g^0 = (g_\uparrow + g_\downarrow)/2$. In the ferromagnetic region, formula (53) follows from the initial formula (52) in the approximation $g_\uparrow = g_\downarrow$. In the paramagnetic region, formulae (52) and (53) coincide.

4. Numerical results

The extended SFT is investigated by the example of the Invar alloy $\text{Fe}_{0.65}\text{Ni}_{0.35}$. The initial non-magnetic DOS $\nu(\epsilon)$ (see figure 2) is obtained from the two spin-polarized densities that are obtained from the self-consistent calculation for the completely disordered $\text{Fe}_{0.65}\text{Ni}_{0.35}$ alloy [26]. The experimental value of the spin magnetic moment per atom $m_0^{\text{exp}} = 1.70 \mu_B$ (where μ_B is the Bohr magneton), used to determine the effective interaction constant u , is taken from [27].

Note that we neglect here the fine effects of atomic and/or magnetic short-range order (see, e.g., [20, 28] and references therein). Moreover, the magnetic moment m_0^{exp} and the DOS $\nu(\epsilon)$ represent the values per *averaged* atom. However, as stated in the introduction, even with these initial data one can calculate the temperature dependence of magnetic properties of an alloy in the SFT.

Figure 3 presents the basic magnetic characteristics for $\text{Fe}_{0.65}\text{Ni}_{0.35}$ Invar calculated within the Gaussian SFT [9]. Clearly, at high temperatures, the calculated magnetization curve does not fit well enough the experimental one. For the Curie temperature, we obtain $T_C = 0.83 T_C^{\text{exp}}$. But most important, the calculated curve $m(T)$ has the inflection (see the discussion in [10]).

In [13], we took into account the higher terms in the expansion of the free energy $F(V)$ by using the simplified expression (53) for the correction coefficient η with $c = -0.015W^{-1}$ ($W = 9.70$ eV is the bandwidth). The calculation showed nearly full agreement with experiment for

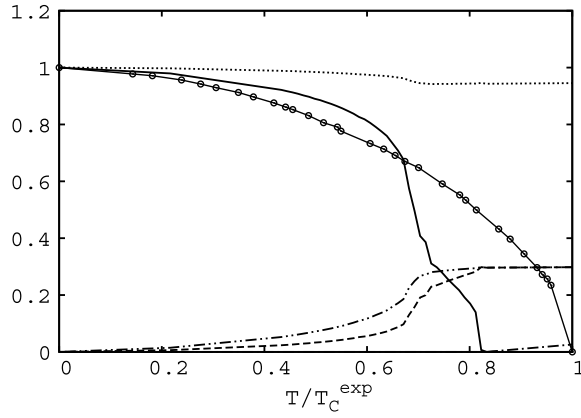


Figure 3. The magnetization $m(T)/m(0)$ (— calculation, $\circ\circ\circ\circ$ experiment [27]), the mean square of spin fluctuations ζ^x ($\cdots\cdots$) and ζ^z ($-\cdots-$) in units of $um(0)/(2\mu_B)$, the reciprocal paramagnetic susceptibility $\chi^{-1}(T)$ ($-\cdot-\cdot-$) in units of T_C^{exp}/μ_B^2 , and the local magnetic moment $m_L(T)/m(0)$ ($\cdots\cdots$) of Invar $\text{Fe}_{0.65}\text{Ni}_{0.35}$ calculated in the Gaussian SFT as functions of the reduced temperature T/T_C^{exp} .

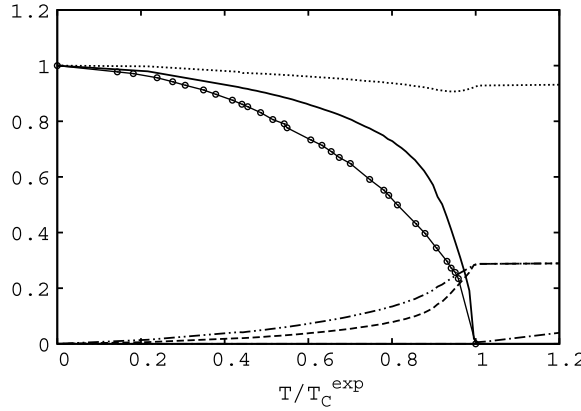


Figure 4. As figure 3, but calculated in the extended SFT with expression (52) for η .

the Curie temperature: $T_C = 1.02T_C^{\text{exp}}$ ($T_C^{\text{exp}} = 520$ K [27]), for the paramagnetic Curie point: $\Theta_C = 1.06T_C^{\text{exp}}$, for the effective magnetic moment: $m_{\text{eff}} = 0.90m_{\text{eff}}^{\text{exp}}$ ($m_{\text{eff}}^{\text{exp}} = 3.3 \mu_B$ [29]) and for the local magnetic moment $m_L(T)$ (see the discussion in [22]). As can be seen from figure 1 in [13], a sharp increase of the fluctuations and a sharp decrease in magnetization at high temperatures, which occurred in [10], disappear in the extended SFT.

On the whole, the curve for the magnetization in [13] fits the experimental one well enough. However, the inflection in the temperature dependence, reported in [10], does not vanish entirely. Therefore, in the present paper, we apply expression (52), which alternates with T in a self-consistent way. This finally gives a smooth curve without the inflection (figure 4).

A qualitative analysis of our equations explains the mechanism that leads to a jump transition of magnetization in the simple Gaussian theory and its elimination in the extended

SFT. Indeed, in the presence of the external magnetic field h , the mean-field equation (29) takes the form

$$\bar{V}_z(h) = -u(1 + \eta)s_z(\bar{V}_z(h) + h).$$

Hence, for the enhanced magnetic susceptibility, we get

$$-\frac{ds_z}{dh} = \frac{\chi_0}{1 - u(1 + \eta)\chi_0}, \quad (54)$$

where $\chi_0 = -\partial s_z / \partial h$ is the unenhanced (with constant \bar{V}_z) susceptibility of non-interacting electrons. The fluctuation (44) is proportional to

$$\langle \Delta V_\alpha^2 \rangle \propto \frac{1}{1 - u(1 + 3\eta)\chi_0}. \quad (55)$$

The enhanced susceptibility (54) diverges at the critical temperature (the condition of the transition from the ferromagnetic to paramagnetic state). If, at the same time, the fluctuations also increase sharply, i.e. the derivative tends to infinity, then there exists an extra (unstable) solution and hence a jump transition to the paramagnetic state. Such a scenario takes place in the Gaussian approach ($\eta = 0$), where the susceptibility (54) and the amplitude of the fluctuations (55) diverge simultaneously. In the present variant of the theory ($\eta < 0$), the fluctuations are weakened, and as a result, we observe a continuous magnetic transition.

There are different ways to go beyond the approximation of the non-interacting spin fluctuations. In this respect, our approach can be treated as a variant of the SCR theory. Formulae (54) and (55), together with (53), schematically demonstrate the character of our renormalizations.

5. Conclusions

We have developed an approximation to the SFT that describes the thermodynamics of magnetic characteristics. Our approach takes into account both dynamics and non-locality of thermal spin fluctuations, as well as their mode–mode ‘frequency’ interactions. As the initial data, the calculation employs the value of the magnetic moment and *ab initio* DOS, calculated at zero temperature. Further self-consistent treatment of thermal fluctuations, including ‘large’ non-Gaussian fluctuations, makes the approximation of the SFT applicable for all temperatures. Particularly, the present theory yields a proper second-order phase transition from the ferromagnetic to paramagnetic state.

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Appendix A. Relation between the free energy and Green’s function

In this section, we derive the relation between the free energy of electrons in the external field and the Green’s function used in the main text⁶. Exact expression for the constant term of the

⁶ The relation between the thermodynamic potential $\Omega_1(V)$ and the Green’s function $G(V)$, in the case of an *arbitrary* perturbation V , was obtained in [30]. Without a proof the formula analogous to (A.12) was presented in [31].

free energy allows us to obtain the equation on the chemical potential as the conservation of the number of the particles condition in the next appendix.

The thermodynamic potential of non-interacting electrons in the external field V is defined as

$$\Omega_1(V) = -T \ln \text{Tr} \left[T_\tau \exp \left(- \int_0^{1/T} H'(V) d\tau \right) \right], \quad (\text{A.1})$$

where the Hamiltonian corresponding to the grand canonical ensemble,

$$H'(V) = H'_0 + V(\tau),$$

consists of the Hamiltonian $H'_0 = H_0 - \mu N_e$ and the external field

$$V(\tau) = \sum_{j\sigma\sigma'} V_{j\sigma\sigma'}(\tau) a_{j\sigma}^+(\tau) a_{j\sigma'}(\tau) = \sum_j \text{Sp}(V_j(\tau) \rho_j(\tau)); \quad (\text{A.2})$$

the interaction representation of an operator \mathcal{O} is defined as

$$\mathcal{O}(\tau) = e^{\tau H'_0} \mathcal{O} e^{-\tau H'_0}.$$

Here, T_τ stands for the ‘time’-ordering operator and Tr contains the summation over states with any number of particles. Note that in $H'(V)$, μ is the chemical potential, $N_e = \sum_{j\sigma} a_{j\sigma}^+(\tau) a_{j\sigma}(\tau)$ is the number of the particles operator, $a_{j\sigma}^+$ and $a_{j\sigma}$ are the creation/annihilation operators for Wannier states, and ρ_j is the local spin density matrix, with elements

$$\rho_{j\sigma\sigma'} = a_{j\sigma'}^+ a_{j\sigma}. \quad (\text{A.3})$$

The method to relate the thermodynamic potential $\Omega_1(V)$ to the Green’s function

$$G(V) = (z - H'(V))^{-1} \quad (\text{A.4})$$

is to vary the strength of the external field from 0 to V . To this end, we consider

$$H'(\lambda) = H'_0 + \lambda V, \quad (\text{A.5})$$

so that $H'(0) = H'_0$ and $H'(1) = H'(V)$. The thermodynamic potential corresponding to $H'(\lambda)$ is

$$\Omega_1(\lambda) = -T \ln \text{Tr} \left[T_\tau \exp \left(- \int_0^{1/T} H'(\lambda) d\tau \right) \right].$$

Using formula (A.5), we find the derivative of $\Omega_1(\lambda)$ with respect to λ (cf [30]):

$$\frac{\partial \Omega_1(\lambda)}{\partial \lambda} = \left\langle T \int_0^{1/T} V(\tau) d\tau \right\rangle_\lambda, \quad (\text{A.6})$$

where the averaging $\langle \cdot \cdot \cdot \rangle_\lambda$ of an arbitrary operator \mathcal{O} is defined as

$$\langle \mathcal{O} \rangle_\lambda \equiv \frac{\text{Tr}(\mathcal{O} T_\tau \exp(-\int_0^{1/T} H'(\lambda) d\tau))}{\text{Tr}(T_\tau \exp(-\int_0^{1/T} H'(\lambda) d\tau))}. \quad (\text{A.7})$$

The general formula (A.6) holds for any perturbation V , not necessarily one-particle operator. For a non-interacting system, substituting (A.2) for V in (A.6) and rearranging, we write

$$\frac{\partial \Omega_1(\lambda)}{\partial \lambda} = T \int_0^{1/T} \sum_j \text{Sp}(V_j(\tau) \langle \rho_j(\tau) \rangle_\lambda) d\tau. \quad (\text{A.8})$$

The average of the spin density matrix in the interaction representation is related to the Green’s function:

$$\langle \rho_{j\sigma\sigma'}(\tau) \rangle_\lambda = - \langle T_\tau a_{j\sigma}(\tau) a_{j\sigma'}^+(\tau + 0) \rangle_\lambda \equiv G_{j\sigma\sigma'}^\lambda(\tau, \tau). \quad (\text{A.9})$$

Substituting (A.9) into (A.8), we come to

$$\frac{\partial \Omega_1(\lambda)}{\partial \lambda} = T \operatorname{Tr}(V G^\lambda).$$

Integration over λ between 0 and 1 yields

$$\Omega_1(1) - \Omega_1(0) = \int_0^1 T \operatorname{Tr}(V G^\lambda) d\lambda, \quad (\text{A.10})$$

where $\Omega_1(1) = \Omega_1(V)$ and $\Omega_1(0) = -T \ln \operatorname{Tr} \exp(-H'_0/T)$.

The Green's function G^λ of non-interacting electrons satisfies the equation

$$G^\lambda = G_0 + \lambda G_0 V G^\lambda, \quad (\text{A.11})$$

where G_0 corresponds to H_0 . Express G^λ from equation (A.11) and substitute to the right-hand side of (A.10). Using the cyclic property of trace, we get

$$\begin{aligned} \Omega_1(1) - \Omega_1(0) &= T \operatorname{Tr} \int_0^1 (1 - \lambda G_0 V)^{-1} G_0 V d\lambda \\ &= -T \operatorname{Tr} \int_0^1 \frac{d}{d\lambda} \ln(1 - \lambda G_0 V) d\lambda = -T \operatorname{Tr} \ln(1 - G_0 V). \end{aligned}$$

Using equation (A.11) and the fact that $G^1 = G(V)$, we come to⁷

$$\Omega_1(V) = -T \ln \operatorname{Tr} \exp(-H'_0/T) - T \operatorname{Tr} \ln G_0 + T \operatorname{Tr} \ln G(V). \quad (\text{A.12})$$

The free energy $F_1(V)$ is related to the thermodynamic potential $\Omega_1(V)$ by the formula

$$F_1(V) = -T \ln \operatorname{Tr} \left[T_\tau \exp \left(- \int_0^{1/T} H(V) d\tau \right) \right] = \Omega_1(V) + \mu N_e,$$

where $H(V) = H_0 + V$ is the Hamiltonian corresponding to the canonical ensemble, and the number of electrons N_e is fixed. Hence, formula (A.12) can be rewritten as

$$F_1(V) = -T \ln \operatorname{Tr} \exp(-H_0/T) - T \operatorname{Tr} \ln G_0 + T \operatorname{Tr} \ln G(V). \quad (\text{A.13})$$

Omitting the first and second terms, that do not depend on V , we come to formula (4) of the main text. The matrix of the Green's function (A.4) for the system with N_e electrons reduces to (see formula (5) in the main text)

$$G(V) = (z + \mu - H_0 - V)^{-1}. \quad (\text{A.14})$$

Appendix B. Formulae for the total charge and spin moment

In this section, we express the mean spin moment and total number of electrons in terms of the mean Green's function.

The Green's function $G(V)$ is related to the spin density matrix ρ by formula (A.9):

$$\langle \rho(\tau) \rangle_V = G(\tau, \tau),$$

where we write $\langle \cdot \cdot \cdot \rangle_V$ instead of $\langle \cdot \cdot \cdot \rangle_1$ defined by (A.7). As any Hermitian 2×2 matrix, the local spin density matrix (A.3) can be expressed as

$$\rho_j = \rho_j^0 \sigma^0 + \rho_j \sigma = \sum_{\mu} \rho_j^{\mu} \sigma^{\mu},$$

with the coefficients

$$\rho_j^{\mu} = \frac{1}{2} \operatorname{Sp}(\sigma^{\mu} \rho_j), \quad \mu = 0, x, y, z. \quad (\text{B.1})$$

⁷ Recall the formula $\operatorname{Tr} \ln(AB) = \operatorname{Tr} \ln A + \operatorname{Tr} \ln B$, which is valid for the arbitrary matrices A and B .

Here, σ^0 is the 2×2 unity matrix, and σ^α ($\alpha = x, y, z$) are the Pauli matrices. Formulae (A.3) and (B.1) yield that the scalar component ρ_j^0 is equal to one half of the local charge:

$$\rho_j^0 = \frac{1}{2}(a_{j\uparrow}^\dagger a_{j\uparrow} + a_{j\downarrow}^\dagger a_{j\downarrow}) = \frac{1}{2}(n_{j\uparrow} + n_{j\downarrow}) = \frac{1}{2}n_j, \quad (\text{B.2})$$

and the vector component ρ_j is equal to the local spin $s_j = (s_j^x, s_j^y, s_j^z)$. Indeed, writing the operator s_j in the second-quantization form, from (A.3), we find

$$s_j^\alpha = \sum_{\sigma\sigma'} s_{\sigma\sigma'}^\alpha a_{j\sigma}^\dagger a_{j\sigma'} = \sum_{\sigma\sigma'} s_{\sigma\sigma'}^\alpha \rho_{j\sigma'\sigma} = \text{Sp}(s^\alpha \rho_j).$$

Since the spin operator can be represented by the Pauli matrices: $s = \frac{1}{2}\sigma$, using (B.1), we obtain

$$s_j^\alpha = \frac{1}{2}\text{Sp}(\sigma^\alpha \rho_j) = \rho_j^\alpha. \quad (\text{B.3})$$

Relations (A.3), (B.2) and (B.3) lead to

$$\frac{1}{2}\langle n_j(\tau) \rangle_V = \bar{G}_j^0(\tau, \tau), \quad \langle s_j^\alpha(\tau) \rangle_V = \bar{G}_j^\alpha(\tau, \tau),$$

where $\langle \dots \rangle$ is the averaging over all configurations of the field V with the probability density $p(V) \propto \exp(-\Omega(V)/T)$. Introduce the Fourier transform

$$G_j(\tau, \tau') = T \sum_{nn'} G_j(i\omega_n, i\omega'_n) e^{-i\omega_n \tau} e^{i\omega'_n \tau'}.$$

Using the ‘time’-invariance of the mean Green’s function, we have

$$\bar{G}_j(\tau, \tau) = T \sum_n \bar{G}_j(i\omega_n) \equiv T \sum_n \bar{G}_{jn}.$$

Hence, summing over the sites and bands, we come to the expressions for the total number of electrons:

$$N_e = N_d \sum_j \langle n_j \rangle_V = 2N_d T \sum_{jn} \bar{G}_{jn}^0 = N_d T \sum_{jn} \text{Sp} \bar{G}_{jn} = T \text{Tr} \bar{G}$$

and the total z -projection of spin moment:

$$S^z = N_d \sum_j \langle s_j^z \rangle_V = T \text{Tr} \bar{G}^z, \quad (\text{B.4})$$

S^x and S^y being equal to zero in the ferromagnetic case, since $\bar{G}^x = 0$ and $\bar{G}^y = 0$. Analogously, for the non-interacting electrons, we have

$$N_e = T \text{Tr} G_0. \quad (\text{B.5})$$

Now consider the total free energy $\mathcal{F} = -T \ln Z$, where the partition function Z is defined by (2). Since μ is the Lagrange multiplier in the expression for the free energy, $\mathcal{F} = \Omega + \mu N_e$, the equation on μ follows from the extremum condition:

$$\frac{\partial \mathcal{F}}{\partial \mu} = 0.$$

The latter is exactly the conservation of the electrons condition. Since $F_0(V)$ does not depend on μ , differentiation of \mathcal{F} with respect to μ yields

$$\frac{\partial \mathcal{F}}{\partial \mu} = \frac{1}{Z} \left(\frac{\int e^{-F_0(V)/T} e^{-F_1(V)/T} \frac{\partial F_1(V)}{\partial \mu} \text{D}V(\tau)}{\int e^{-F_0(V)/T} \text{D}V(\tau)} \right) \equiv \left\langle \frac{\partial F_1(V)}{\partial \mu} \right\rangle = 0.$$

Using formulae (A.13) and (A.14), we come to

$$\left\langle \frac{\partial F_1(V)}{\partial \mu} \right\rangle = -T \text{Tr}(G) + T \text{Tr} G_0 = 0.$$

Due to (B.5), we finally obtain

$$\left\langle \frac{\partial F_1(V)}{\partial \mu} \right\rangle = -T \text{Tr} \bar{G} + N_e = 0.$$

The latter is the equation for the chemical potential (30) of the main text.

Appendix C. Axial symmetry relations

In this section, we prove the axial symmetry of the magnetic susceptibility in the ferromagnetic state: $\chi^x = \chi^y$ (with the z -axis chosen along the field), and hence the axial symmetry of the fluctuations: $\zeta^x = \zeta^y$.

For given \mathbf{q} and m , calculate the susceptibilities

$$\begin{aligned} \chi_{\mathbf{q}m}^{\alpha\beta} &\equiv -\frac{1}{2} \frac{\partial^2 F_1^{(2)}}{\partial (\Delta V_{\mathbf{q}m}^\alpha) \partial (\Delta V_{-\mathbf{q}-m}^\beta)} \\ &= -\frac{N_d}{2} (1 + 3\eta) T \sum_{\mathbf{k}n} \sum_{\gamma_1 \gamma_2} \bar{G}_{\mathbf{k}n}^{\gamma_1} \bar{G}_{\mathbf{k}-\mathbf{q},n-m}^{\gamma_2} \text{Sp}(\sigma^{\gamma_1} \sigma^\alpha \sigma^{\gamma_2} \sigma^\beta), \end{aligned}$$

where $\gamma_1, \gamma_2 = 0, z$. First, using the properties of the Pauli matrices, we find

$$\chi_{\mathbf{q}m} = \begin{vmatrix} \chi_{\mathbf{q}m}^{xx} & \chi_{\mathbf{q}m}^{xy} & 0 \\ -\chi_{\mathbf{q}m}^{xy} & \chi_{\mathbf{q}m}^{xx} & 0 \\ 0 & 0 & \chi_{\mathbf{q}m}^{zz} \end{vmatrix} \quad (\text{C.1})$$

where

$$\begin{aligned} \chi_{\mathbf{q}m}^{xx} &= -N_d(1 + 3\eta) T \sum_{\mathbf{k}n} (\bar{G}_{\mathbf{k}n}^0 \bar{G}_{\mathbf{k}-\mathbf{q},n-m}^0 - \bar{G}_{\mathbf{k}n}^z \bar{G}_{\mathbf{k}-\mathbf{q},n-m}^z), \\ \chi_{\mathbf{q}m}^{zz} &= -N_d(1 + 3\eta) T \sum_{\mathbf{k}n} (\bar{G}_{\mathbf{k}n}^0 \bar{G}_{\mathbf{k}-\mathbf{q},n-m}^0 + \bar{G}_{\mathbf{k}n}^z \bar{G}_{\mathbf{k}-\mathbf{q},n-m}^z) \end{aligned}$$

and

$$\chi_{\mathbf{q}m}^{xy} = iN_d(1 + 3\eta) T \sum_{\mathbf{k}n} (\bar{G}_{\mathbf{k}n}^0 \bar{G}_{\mathbf{k}-\mathbf{q},n-m}^z - \bar{G}_{\mathbf{k}n}^z \bar{G}_{\mathbf{k}-\mathbf{q},n-m}^0). \quad (\text{C.2})$$

Next, we prove that the non-diagonal elements (C.2) of the matrix (C.1) are equal to zero. Introducing the new indices, we rewrite the second part of the sum (C.2) as

$$\sum_{\mathbf{k}n} \bar{G}_{\mathbf{k}n}^z \bar{G}_{\mathbf{k}-\mathbf{q},n-m}^0 = \sum_{\mathbf{k}'n'} \bar{G}_{-\mathbf{k}'+\mathbf{q},-n'+m}^z \bar{G}_{-\mathbf{k}'-n'}^0.$$

Using the property $\bar{G}_{\mathbf{k}n}^\alpha = (\bar{G}_{-\mathbf{k}-n}^\alpha)^*$ of the Fourier transformation $\bar{G}_{\mathbf{k}n}^\alpha$ of the real function $\bar{G}_j^\alpha(\tau)$, we have

$$\sum_{\mathbf{k}n} \bar{G}_{\mathbf{k}n}^z \bar{G}_{\mathbf{k}-\mathbf{q},n-m}^0 = \sum_{\mathbf{k}'n'} (\bar{G}_{\mathbf{k}'n'}^0 \bar{G}_{\mathbf{k}'-\mathbf{q},n'-m}^z)^*.$$

Hence, for the non-diagonal element (C.2), we get

$$\chi_{\mathbf{q}m}^{xy} = -2N_d(1 + 3\eta) T \sum_{\mathbf{k}n} \text{Im}(\bar{G}_{\mathbf{k}n}^0 \bar{G}_{\mathbf{k}-\mathbf{q},n-m}^z).$$

Since η is real, the latter is also real. On the other hand, matrix (C.1) is Hermitian; hence, $\chi_{\mathbf{q}m}^{xy}$ must be imaginary. Thus, $\chi_{\mathbf{q}m}^{xy} = 0$, and the susceptibility χ is diagonal in the momentum-‘frequency’ representation. Formula (36) yields the required relation for the fluctuations: $\zeta^x = \zeta^y$.

Appendix D. Derivation of formula (52) for the correction coefficient η

To calculate the correction coefficient (21),

$$\eta = (\text{Tr}(\mathbf{1}))^{-1} \text{Tr}(\bar{G} \Delta V \bar{G} \Delta V), \quad (\text{D.1})$$

where $\text{Tr}(\mathbf{1}) = 2N_a N_d$, we introduce the Gaussian susceptibility

$$\tilde{\chi}_{\mathbf{q}m}^\alpha = -\frac{N_d}{2} T \sum_{\mathbf{k}n} \sum_{\gamma_1 \gamma_2} \bar{G}_{\mathbf{k}n}^{\gamma_1} \bar{G}_{\mathbf{k}-\mathbf{q}, n-m}^{\gamma_2} \text{Sp}(\sigma^{\gamma_1} \sigma^\alpha \sigma^{\gamma_2} \sigma^\alpha), \quad (\text{D.2})$$

i.e. the susceptibility $\chi_{\mathbf{q}m}^\alpha$ with no account of high-order terms ($\eta = 0$). Then formula (D.1) can be rewritten as

$$\eta = -\frac{1}{N_a N_d T} \sum_{\mathbf{q}m\alpha} \Delta V_{\mathbf{q}m}^\alpha \tilde{\chi}_{\mathbf{q}m}^\alpha \Delta V_{-\mathbf{q}-m}^\alpha = -\frac{1}{N_a N_d T} \sum_{\mathbf{q}m\alpha} \tilde{\chi}_{\mathbf{q}m}^\alpha \langle |\Delta V_{\mathbf{q}m}^\alpha|^2 \rangle. \quad (\text{D.3})$$

We approximate (D.2) using the single-site Green's function (45) and the quasi-static approximation (which implies that the main impact to (D.2) is due to the terms with $n-m \approx n$):

$$\tilde{\chi}_{\mathbf{q}m}^\alpha \approx \tilde{\chi}_{00}^\alpha = -\frac{N_d}{2} T \sum_n \sum_{\gamma_1 \gamma_2} g_{0n}^{\gamma_1} g_{0n}^{\gamma_2} \text{Sp}[\sigma^{\gamma_1} \sigma^\alpha \sigma^{\gamma_2} \sigma^\alpha]. \quad (\text{D.4})$$

Using (D.4), we rewrite (D.3) as

$$\eta \approx -\frac{1}{N_d N_a T} \sum_{\alpha} \tilde{\chi}_{00}^\alpha \sum_{\mathbf{q}m} \langle |\Delta V_{\mathbf{q}m}^\alpha|^2 \rangle = -\frac{1}{N_d T} \sum_{\alpha} \tilde{\chi}_{00}^\alpha \zeta^\alpha. \quad (\text{D.5})$$

Due to the cyclic property of trace and the anticommutation relations for the Pauli matrices, $\sigma^\alpha \sigma^\beta = (2\delta_{\alpha\beta} - 1) \sigma^\beta \sigma^\alpha$, we obtain

$$\tilde{\chi}_{00}^\alpha = -N_d T \sum_n \left((g_{0n}^0)^2 + (2\delta_{\alpha z} - 1) (g_{0n}^z)^2 \right).$$

Replacing the summation over 'frequencies' by the integration over the energy variable, we come to

$$\tilde{\chi}_{00}^\alpha = -\frac{N_d}{\pi} \int \text{Im}((g^0)^2 + (2\delta_{\alpha z} - 1)(g^z)^2) f \, d\varepsilon. \quad (\text{D.6})$$

Substituting (D.6) in (D.5) and using the axial symmetry ($\zeta^x = \zeta^y$), we get

$$\eta = \frac{1}{\pi T} \left(2\zeta^x \int \text{Im}((g^0)^2 - (g^z)^2) \, d\varepsilon + \zeta^z \int \text{Im}((g^0)^2 + (g^z)^2) \, d\varepsilon \right).$$

Recalling that $g^0(\varepsilon) = \frac{1}{2}[g_\uparrow(\varepsilon) + g_\downarrow(\varepsilon)]$ and $g^z(\varepsilon) = \frac{1}{2}[g_\uparrow(\varepsilon) - g_\downarrow(\varepsilon)]$, we finally obtain

$$\eta \approx \frac{1}{\pi T} \left[2\zeta^x \int (\text{Re } g_\uparrow \text{Im } g_\downarrow + \text{Re } g_\downarrow \text{Im } g_\uparrow) f \, d\varepsilon + \zeta^z \int (\text{Re } g_\uparrow \text{Im } g_\uparrow + \text{Re } g_\downarrow \text{Im } g_\downarrow) f \, d\varepsilon \right]$$

(see formula (52) of the main text).

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