

Two definitions of magnetization

M represents the thermodynamic (or macroscopic) magnetization: it is a function of macrostate (e.g. $M(S, H)$ or $M(T, H)$).

\mathcal{M} represents the microscopic magnetization: it is a function of microstate (e.g. $\mathcal{M}(\mathbf{x})$).

From thermodynamics using the master function $E(S, H)$:

$$dE = T dS - M dH \quad \text{whence} \quad M(S, H) = - \left. \frac{\partial E}{\partial H} \right|_S.$$

Execute a Legendre transformation to

$$F(T, H) = E - TS,$$

giving

$$dF = -S dT - M dH \quad \text{whence} \quad M(T, H) = - \left. \frac{\partial F}{\partial H} \right|_T.$$

But the statistical mechanical magnetization is

$$\langle \mathcal{M} \rangle = \frac{\sum_{\mathbf{x}} \mathcal{M}(\mathbf{x}) e^{-\beta \mathcal{H}(\mathbf{x})}}{\sum_{\mathbf{x}} e^{-\beta \mathcal{H}(\mathbf{x})}}.$$

Here the Hamiltonian is $\mathcal{H}(\mathbf{x}) = \mathcal{H}_0(\mathbf{x}) - H \mathcal{M}(\mathbf{x})$, where $\mathcal{H}_0(\mathbf{x})$ is the part of the Hamiltonian independent of H . Thus

$$\langle \mathcal{M} \rangle = \frac{\sum_{\mathbf{x}} \mathcal{M}(\mathbf{x}) e^{-\beta \mathcal{H}_0(\mathbf{x}) + \beta H \mathcal{M}(\mathbf{x})}}{\sum_{\mathbf{x}} e^{-\beta \mathcal{H}_0(\mathbf{x}) + \beta H \mathcal{M}(\mathbf{x})}} = \frac{1}{\beta} \frac{\partial}{\partial H} \left(\ln \sum_{\mathbf{x}} e^{-\beta \mathcal{H}_0(\mathbf{x}) + \beta H \mathcal{M}(\mathbf{x})} \right),$$

where we've used the "slick trick" of parametric differentiation. (The derivative is taken with constant β , i.e. constant T , but it's clumsy to use our "subscript T " notation here.)

Thus

$$\langle \mathcal{M} \rangle = \frac{\partial}{\partial H} \left(k_B T \ln \sum_{\mathbf{x}} e^{-\beta \mathcal{H}(\mathbf{x})} \right),$$

or, because $F = -k_B T \ln(Z)$,

$$\langle \mathcal{M} \rangle = - \left. \frac{\partial F}{\partial H} \right|_T.$$

We conclude that the thermodynamic magnetization is the same as the statistical mechanical magnetization.