Unit 2-13: Examples: The Specific Heat of Solids, Curie Paramagnetism

Here we will apply what we have learned to consider two well know problems from condensed matter physics. What is the contribution of elastic vibrations to the specific heat of a solid, and what is the paramagnetic susceptibility of magnetic moments at finite temperature.

Elastic Vibrations of a Solid

We can imagine the Hamiltonian for the periodic array of atoms in a crystalline solid to be,

$$\mathcal{H} = \sum_i \frac{p_i^2}{2M} + \frac{1}{2} \sum_{i \neq j} U(\mathbf{r}_i - \mathbf{r}_j) \tag{2.13.1}$$

The first term is the kinetic energy of the atomic motion, and the second term is a pairwise atomic interaction.

The position of atom i can be written as,

$$\mathbf{r}_i = \mathbf{R}_i + \mathbf{u}_i \tag{2.13.2}$$

where $\mathbf{R}_i$ is the atom's position in the perfect periodic array of the crystal, and $\mathbf{u}_i$ is a small displacement from this position due to thermal fluctuations.

Then we can expand U to second order in the small $\mathbf{u}_i$,

$$U(\mathbf{r}_i - \mathbf{r}_j) = U(\mathbf{R}_i - \mathbf{R}_j + \mathbf{u}_i - \mathbf{u}_j) = U(\mathbf{R}_i - \mathbf{R}_j) + \nabla U \cdot (\mathbf{u}_i - \mathbf{u}_j) + \frac{1}{2} \sum_{\alpha, \beta = 1}^{3} \frac{\partial^2 U}{\partial r_{i\alpha} r_{j\beta}} (u_{i\alpha} - u_{j\alpha})(u_{i\beta} - u_{j\beta}) \tag{2.13.3}$$

where α, β label the coordinate directions x, y, z.

Now assuming the position $\mathbf{R}_i$ describe a stable mechanical equilibrium (i.e. the positions $\{\mathbf{R}_i\}$ give a local minimum of U, and so the net force on each atom is zero when each atom is at $\mathbf{R}_i$), then the linear term in the expansion of $\mathcal{H}$ must vanish,

$$\sum_{i \neq j} \nabla U \cdot (\mathbf{u}_i - \mathbf{u}_j) = 0 \tag{2.13.4}$$

otherwise there would be some set of displacements that would lower the energy U.

The Hamiltonian is then,

$$\mathcal{H} = \sum_i \frac{p_i^2}{2M} + \frac{1}{2} \sum_{i \neq j} \sum_{\alpha, \beta = 1}^{3} \frac{\partial^2 U}{\partial r_{i\alpha} r_{j\beta}} (u_{i\alpha} - u_{j\alpha})(u_{i\beta} - u_{j\beta}) + \text{constant} \tag{2.13.5}$$

We see that $\mathcal{H}$ is *quadratic* in the displacements $\mathbf{u}_i$. We can rewrite the above as,

$$\mathcal{H} = \sum_i \frac{p_i^2}{2M} + \sum_{i \neq j} \sum_{\alpha, \beta} \mathbb{D}_{ij}^{\alpha\beta} u_{i\alpha} u_{j\beta} \tag{2.13.6}$$

where the *dynamical matrix* $\mathbb{D}_{ij}^{\alpha\beta}$ is an appropriate linear combination of the $\dfrac{\partial^2 U}{\partial r_{i\alpha} \partial r_{j\beta}}$.

One can show that it is always possible to choose *normal coordinate*, $\tilde{u}_{i\alpha} = \sum_{j\beta} C_{ij}^{\alpha\beta} u_{j\beta}$ such that the above quadratic form is diagonalized,

$$\sum_{i \neq j} \sum_{\alpha, \beta} \mathbb{D}_{ij}^{\alpha\beta} u_{i\alpha} u_{j\beta} = \sum_{i\alpha} \tilde{\mathbb{D}}_i^{\alpha} \tilde{u}_{i\alpha}^2 \tag{2.13.7}$$

The $\tilde{\mathbb{D}}_i^\alpha$ are just the eigenvalues of $\mathbb{D}_{ij}^{\alpha\beta}$, and the normal coordinates $\tilde{u}_{i\alpha}$ are the corresponding eigenvectors. By transforming to the normal coordinates, the $\tilde{u}_{i\alpha}$ are decoupled from one another.

So now $\mathcal{H}$ is quadratic in each of the $3N$ momenta $p_{i\alpha}$, and is quadratic in each of the $3N$ normal coordinates $\tilde{u}_{i\alpha}$. By the equipartition theorem we thus conclude that the average energy due to the thermal vibrations of the solid is,

$$E = \langle \mathcal{H} \rangle = (3N + 3N)\frac{1}{2}k_B T = \boxed{3Nk_B T = E} \tag{2.13.8}$$

The contribution to the specific heat of the solid, due to these atomic vibrations, is therefore,

$$\boxed{C_V = \left(\frac{\partial E}{\partial T}\right)_{V,N} = 3Nk_B} \qquad \text{the Law of Dulong and Petit} \tag{2.13.9}$$

This is the Law of Dulong and Petit, proposed in 1819 by Pierre Louis Dulong and Alexis Thérèse Petit.

This classical result predicts a C_V that is a constant *independent* of temperature. In real life, however, one finds a C_V as shown in the sketch to the right. As T decreases, C_V decreases below the Dulong and Petit value and goes to zero as $T \to 0$. This decrease is noticeable already at room temperatures. This experimental observation is unexplainable in the context of our classical model.
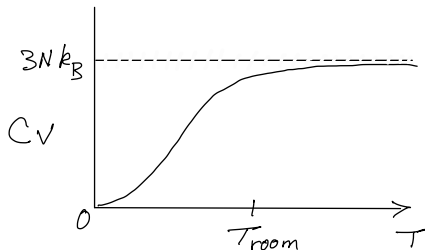
It was one of the early successes of *quantum mechanics* to explain why the Law of Dulong and Petit fails as T decreases. Usually we think of quantum mechanics as something that is important for atomic phenomena at the microscopic scale. When quantum effects are observed in macroscopic systems, like superfluids and superconductors, we usually think this happens only at very low temperatures. The failure of the Law of Dulong and Petit is an example where the effects of quantum mechanics can be observed in a macroscopic system at room temperature!

We will see the quantum solution to this problem later when we discuss the statistics of *bosons*.

Paramagnetism of Classical Spins

Imagine that we have N *distinguishable* spins $\boldsymbol{\mu}_i$ in our system. We will ignore any interactions between the spins, and only consider the interaction of each spin with an external magnetic field $\mathbf{h}$.

This might be a model for a solid in which there are a set of atomic impurities in the crystalline lattice at fixed spatial positions, such that the impurities each possess a net magnetic moment $\boldsymbol{\mu}_i$. The magnetic moment on each impurity is modeled as a "spin." The spins are *distinguishable* because they are each attached to a particular impurity, and that impurity is confined to a particular position within the crystal lattice of the solid, so we can identify which spin is which.

The Hamiltonian of the N-spin system is,

$$\mathcal{H} = \sum_{i=1}^{N} \mathcal{H}^{(1)}(\boldsymbol{\mu}_i) \qquad \text{with} \qquad \mathcal{H}^{(1)}(\boldsymbol{\mu}_i) = -\boldsymbol{\mu}_i \cdot \mathbf{h} \tag{2.13.10}$$

where $\boldsymbol{\mu}_i$ is the spin of impurity i. The minus sign is because the energy is lowest when $\boldsymbol{\mu}_i$ is parallel to $\mathbf{h}$. The Hamiltonian $\mathcal{H}$ is the sum of single-spin terms, because the spins are assumed to be non-interacting. This means that the N-particle partition function will factor into the product of single-particle partition functions.

If we take $\mu = |\boldsymbol{\mu}_i|$ as the magnitude of the spin, and θ_i as the angle of $\boldsymbol{\mu}_i$ with respect to $\mathbf{h}$, then,

$$\mathcal{H}^{(1)}(\boldsymbol{\mu}_i) = -\mu h \cos\theta_i \tag{2.13.11}$$

To evaluate the partition function, we integrate the Boltzmann factor $e^{-\beta\mathcal{H}}$ over the orientations (θ_i, φ_i) of each spin, doing the integration in spherical coordinates where $\mathbf{h}$ is along the $\hat{\mathbf{z}}$ axis,

$$Q_N = \left(\prod_{i=1}^{N} \int_0^{2\pi} d\varphi_i \int_0^{\pi} d\theta_i \sin\theta_i\right) e^{-\beta\mathcal{H}} = \left(\prod_{i=1}^{N} \int_0^{2\pi} d\varphi_i \int_0^{\pi} d\theta_i \sin\theta_i\right) e^{-\beta\sum_i \mathcal{H}^{(1)}(\boldsymbol{\mu}_i)} \tag{2.13.12}$$

$$= \prod_{i=1}^{N} \left(\int_0^{2\pi} d\varphi_i \int_0^{\pi} d\theta_i \sin\theta_i\, e^{-\beta\mathcal{H}^{(1)}(\boldsymbol{\mu}_i)}\right) = (Q_1)^N \tag{2.13.13}$$

where the single-particle partition function is,

$$Q_1 = \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta\, e^{-\beta\mathcal{H}^{(1)}(\boldsymbol{\mu})} = \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta\, e^{\beta\mu h \cos\theta} = 2\pi \int_0^{\pi} d\theta \sin\theta\, e^{\beta\mu h \cos\theta} \tag{2.13.14}$$

Note, here we have $Q_N = (Q_1)^N$ rather than $Q_N = \frac{1}{N!}(Q_1)^N$ as we saw before. This is because in this case the spins are *distinguishable*, and so there is no Gibbs factor of $1/N!$ when writing Q_N.

We can proceed to evaluate Q_1 by making a substitution of variables, $x = -\cos\theta$ so $dx = d\theta \sin\theta$,

$$Q_1 = 2\pi \int_0^{\pi} d\theta \sin\theta\, e^{\beta\mu h \cos\theta} = 2\pi \int_{-1}^{1} dx\, e^{-\beta\mu h x} = \frac{2\pi}{-\beta\mu h}\left[e^{-\beta\mu h} - e^{+\beta\mu h}\right] = \frac{4\pi}{\beta\mu h}\sinh(\beta\mu h) \tag{2.13.15}$$

Here sinh is the hyperbolic sine, $\sinh x = (e^x - e^{-x})/2$.

The average total magnetization of the system $\mathbf{M}$ is oriented parallel to $\mathbf{h}$. If we choose $\mathbf{h} = h\hat{\mathbf{z}}$ then $\mathbf{M} = M\hat{\mathbf{z}}$, and,

$$M = N\langle\mu\cos\theta\rangle = N\,\frac{\displaystyle\int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta\, e^{\beta\mu h \cos\theta}\mu\cos\theta}{\displaystyle\int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta\, e^{\beta\mu h \cos\theta}} \tag{2.13.16}$$

$$= \frac{N}{\beta}\,\frac{\dfrac{\partial}{\partial h}\left[\displaystyle\int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta\, e^{\beta\mu h \cos\theta}\right]}{\displaystyle\int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta\, e^{\beta\mu h \cos\theta}} \tag{2.13.17}$$

$$= \frac{N}{\beta}\frac{1}{Q_1}\left(\frac{\partial Q_1}{\partial h}\right) = Nk_BT\frac{\partial}{\partial h}[\ln Q_1] = \frac{\partial}{\partial h}\left[k_BT\ln Q_1^N\right] = \frac{\partial}{\partial h}[k_BT\ln Q_N] \tag{2.13.18}$$
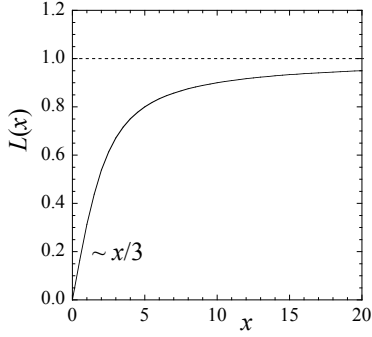
$$= -\left(\frac{\partial A}{\partial h}\right)_{T,h} \tag{2.13.19}$$

When we apply the magnetic field $\mathbf{h} = h\hat{\mathbf{z}}$, then h is a new thermodynamic variable. The above shows that the magnetization M is the thermodynamic conjugate variable to the magnetic field h.

Using our result $Q_1 = \dfrac{4\pi}{\beta\mu h}\sinh(\beta\mu h)$, we can now evaluate M,

$$\frac{M}{N} = \frac{1}{\beta Q_1}\left(\frac{\partial Q_1}{\partial h}\right) = \frac{4\pi\left[\dfrac{\cosh(\beta\mu h)}{h} - \dfrac{\sinh(\beta\mu h)}{\beta\mu h^2}\right]}{\dfrac{4\pi\sinh(\beta\mu h)}{\mu h}} = \mu h\left[\frac{\coth(\beta\mu h)}{h} - \frac{1}{\beta\mu h^2}\right] \tag{2.13.20}$$

$$\frac{M}{N} = \mu\left[\coth(\beta\mu h) - \frac{1}{\beta\mu h}\right] \tag{2.13.21}$$

The function,

$$L(x) = \coth x - \frac{1}{x} \qquad \text{is called the Langevin function.} \qquad (2.13.22)$$

For large x, $L(x) = \dfrac{1 + \mathrm{e}^{-2x}}{1 - \mathrm{e}^{-2x}} - \dfrac{1}{x} \approx 1 - \dfrac{1}{x} \to 1.$

For small x,

$$L(x) = \frac{\cosh x}{\sinh x} - \frac{1}{x} \approx \frac{1 + \dfrac{x^2}{2}}{x + \dfrac{x^3}{6}} - \frac{1}{x} = \frac{1 + \dfrac{x^2}{2}}{x\left(1 + \dfrac{x^2}{6}\right)} - \frac{1}{x} \approx \frac{\left(1 + \dfrac{x^2}{2}\right)\left(1 - \dfrac{x^2}{6}\right)}{x} - \frac{1}{x} \qquad (2.13.23)$$

$$\approx \frac{1 + \dfrac{x^2}{2} - \dfrac{x^2}{6}}{x} - \frac{1}{x} = \frac{1}{x} + \frac{x}{2} - \frac{x}{6} - \frac{1}{x} = \frac{x}{3} \qquad (2.13.24)$$

So as $x \to 0$, $L(x) \to x/3$.

In our problem, $x = \beta\mu h$.

At large h or large β (small T), we thus have,

$$\frac{M}{N} = \mu L(\beta\mu h) \approx \mu - \frac{1}{\beta h} \to \mu \qquad (2.13.25)$$

and all the spins approach perfect alignment with $\mathbf{h}$.

At small h or small β (large T), we have,

$$\frac{M}{N} = \mu L(\beta\mu h) \approx \frac{\mu^2 h}{3k_B T} \qquad (2.13.26)$$

The magnetic susceptibility is then,

$$\boxed{\chi \equiv \lim_{h \to 0}\left(\frac{\partial M}{\partial h}\right) = \frac{N\mu^2}{3k_B T} \sim \frac{1}{T}} \qquad \text{the Curie Law of Paramagnetism} \qquad (2.13.27)$$

This $\chi \sim 1/T$ is known as the Curie law of paramagnetism, discovered experimentally by Pierre Curie in ~ 1895.