Special Section 7

S7.A. Heat Capacity of Lattice Vibrations on a 1-D Lattice – Exact Solution

S7.A.0. Preliminary

Consider a 1-D chain of N atoms of mass m linked together with harmonic springs of force constant κ and equilibrium length a. [see Fig.7.22] The end atoms 1 and N are linked by springs to rigid walls at distance $L = \left(N+1\right)a$ apart. Let the position of the jth atom be q_j from the wall to which atom 1 is joined. The potential energy of the spring joining interior atoms j and j+1 is then

$$\phi_j = \frac{1}{2}\kappa\left(q_{j+1} - q_j - a\right)^2 \qquad \text{where} \quad j = 1,\cdots,N-1$$

For the end atoms, we can treat the walls as atoms at fixed positions $q_0 = 0$ and $q_{N+1} = \left(N+1\right)a$ so that

$$\phi_0 = \frac{1}{2}\kappa\left(q_1 - a\right)^2$$

and

$$\phi_N = \frac{1}{2}\kappa\left[\left(N+1\right)a - q_N - a\right]^2 = \frac{1}{2}\kappa\left(Na - q_N\right)^2$$

The Hamiltonian is therefore

$$H = \sum_{j=1}^{N}\frac{1}{2m}p_j^2 + \frac{1}{2}\kappa\sum_{j=0}^{N}\phi_j$$

$$= \sum_{j=1}^{N}\frac{1}{2m}p_j^2 + \frac{1}{2}\kappa\left[\sum_{j=1}^{N-1}\left(q_{j+1} - q_j - a\right)^2 + \left(q_1 - a\right)^2 + \left(Na - q_N\right)^2\right] \qquad (7.179)$$

For a quantum system, we have

$$\left[q_i, p_j\right] = i\hbar\delta_{ij} \qquad \left[p_i, p_j\right] = \left[q_i, q_j\right] = 0$$

Shifting to the displacement variables $u_j = q_j - ja$, eq(7.179) becomes

$$H = \sum_{j=1}^{N}\frac{1}{2m}p_j^2 + \frac{1}{2}\kappa\left[\sum_{j=1}^{N-1}\left(u_{j+1} - u_j\right)^2 + u_1^2 + u_N^2\right] \qquad (7.180)$$

$$= \sum_{j=1}^{N}\frac{1}{2m}p_j^2 + \frac{1}{2}\kappa\left[\sum_{j=1}^{N-1}\left(u_{j+1}^2 + u_j^2 - 2u_{j+1}u_j\right) + u_1^2 + u_N^2\right]$$

$$= \sum_{j=1}^{N}\frac{1}{2m}p_j^2 + \frac{1}{2}\kappa\left[2\sum_{j=1}^{N}u_j^2 - \sum_{j=1}^{N-1}\left(u_j u_{j+1} + u_{j+1}u_j\right)\right]$$

which can be put in matrix form as

$$H = \frac{1}{2m}\mathbf{p}^T \cdot \mathbf{I} \cdot \mathbf{p} + \frac{1}{2} m \mathbf{u}^T \cdot \mathbf{V} \cdot \mathbf{u} \qquad (7.182)$$

where

$$\mathbf{p}^T = \left(p_1, \cdots, p_N \right) \qquad \mathbf{u}^T = \left(u_1, \cdots, u_N \right)$$

$$\mathbf{V} = \frac{\kappa}{m} \begin{pmatrix} 2 & -1 & 0 & \cdots & 0 & 0 \\ -1 & 2 & -1 & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & 2 & -1 \\ 0 & 0 & 0 & \cdots & -1 & 2 \end{pmatrix} \qquad (7.181)$$

Since **V** is real and symmetric, it is normal. Therefore, it can be diagonalized by a similarity, or more precisely, orthogonal, transformation. Thus, there is an **X** with $\mathbf{X} \cdot \mathbf{X}^T = \mathbf{X}^T \cdot \mathbf{X} = \mathbf{I}$ so that

$$\mathbf{X}^T \cdot \mathbf{V} \cdot \mathbf{X} = \qquad (7.183)$$

with

$$\mathbf{\Lambda} = \begin{pmatrix} \omega_1^2 & 0 & \cdots & 0 \\ 0 & \omega_2^2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \omega_N^2 \end{pmatrix} \qquad (7.184)$$

where ω_α^2, with $\alpha = 1, \cdots, N$, are the eigenvalues of **V**. To find ω_α^2, we can treat the walls as immobile atoms. Thus, we can try a spatially periodic solution for N+2 atoms so that for the α mode,

$$u_{j\alpha} = u_\alpha \sin \frac{j\,\pi\,\alpha}{N+1} \qquad j = 0, \cdots, N+1$$

where u_α is a constant and $u_0 = u_{N+1} = 0$. Now,

$$u_{j+1,\alpha} - u_{j\alpha} = u_\alpha \left[\sin \frac{\left(j+1 \right) \pi\alpha}{N+1} - \sin \frac{j\pi\alpha}{N+1} \right]$$

$$= 2u_\alpha \sin \frac{\pi\alpha}{2\left(N+1 \right)} \cos \frac{\left(2j+1 \right) \pi\alpha}{2\left(N+1 \right)}$$

Thus, (7,182) can be written as

$$
\begin{aligned}
H &= \frac{1}{2m}\mathbf{p}^T \cdot \mathbf{X} \cdot \mathbf{X}^T \cdot \mathbf{p} + \frac{1}{2} m\mathbf{u}^T \cdot \mathbf{X} \cdot \quad \cdot \quad {}^{T} \cdot \\
&= \frac{1}{2m}\mathbf{P}^T \cdot \mathbf{I} \cdot \mathbf{P} + \frac{1}{2} m\mathbf{Q}^T \cdot \quad \cdot \\
&= \sum_{\alpha=1}^{N} \left(\frac{1}{2m} P_\alpha^2 + \frac{1}{2} m\omega_\alpha^2 Q_\alpha^2 \right)
\end{aligned}
\qquad (7.187)
$$

where $\mathbf{P} = \mathbf{X}^T \cdot \mathbf{p}$ and $\mathbf{Q} = \mathbf{X}^T \cdot \mathbf{u}$. Note that (7.187) represents N decoupled oscillators.

S7.A.1. Exact Expression – Large N

S7.A.2. Continuum Approximation – Large N

S7.B. Momentum Condensation in an Interacting Fermi Liquid

S7.C. The Yang-Lee Theory of Phase Transitions

S7.C.1. Configuration Integral

Consider a classical system of particles interacting via a hard core potential

$$\Phi\left(\left|\mathbf{q}_{ij}\right|\right)=\begin{cases}\infty & \\ -\varepsilon_{ij} & \text{if} \\ 0 & \end{cases}\qquad \begin{matrix}\left|\mathbf{q}_{ij}\right|<a \\ a\le\left|\mathbf{q}_{ij}\right|\le b \\ b<\left|\mathbf{q}_{ij}\right|\end{matrix} \qquad (7.255)$$

where $\mathbf{q}_{ij}=\mathbf{q}_i-\mathbf{q}_j$. Since each particle has an infinite hard core, there is a maximum number M of particles that can fit in a given volume V. Thus, the grand partition function must have the form

$$Z_\mu\left(T,V\right)=\sum_{N=0}^{M}\frac{\exp\left(\beta\mu' N\right)}{N!\,h^{3N}}\int d^{3N}p\int d^{3N}q\,\exp\left\{-\beta\left[\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m}+\sum_{i<j=1}^{N(N-1)/2}\Phi\left(\left|\mathbf{q}_{ij}\right|\right)\right]\right\}$$

$$=\sum_{N=0}^{M}\frac{\exp\left(\beta\mu' N\right)}{N!\,\lambda_T^{3N}}\int d^{3N}q\,\exp\left[-\beta\sum_{i<j=1}^{N(N-1)/2}V\left(\left|\mathbf{q}_{ij}\right|\right)\right]$$

$$=\sum_{N=0}^{M}\frac{\exp\left(\beta\mu' N\right)}{N!\,\lambda_T^{3N}}Q_N\left(T,V\right) \qquad (7.256)$$

where λ_T is the thermal wavelength [see Exercise 7.3]. Deviation from the ideal gas behavior is contained in the **configuration integral** Q_N defined by

$$Q_N\left(T,V\right)=\int d^{3N}q\,\exp\left[-\beta\sum_{i<j=1}^{N(N-1)/2}\Phi\left(\left|\mathbf{q}_{ij}\right|\right)\right] \qquad (7.257)$$

Note that we must have $Q_N\left(T,V\right)=0$ for $N>M$ so that such impossible configurations do not contribute to Z_μ.

S7.C.2. Roots of Z_μ

We now introduce a new variable

$$y = \frac{\exp(\beta\mu')}{\lambda_T^3} \tag{7.258a}$$

so that (7.256) becomes

$$Z_\mu(T,V) = \sum_{N=0}^{M} \frac{y^N}{N!} Q_N(T,V) \tag{7.258}$$

Thus, for a finite volume V, the grand partition function Z_μ is a polynomial of finite order M in y. Therefore, we can write Z_μ as

$$Z_\mu(T,V) = \prod_{i=1}^{M} \left(1 - \frac{y}{y_i}\right) \tag{7.259}$$

where y_i are the roots of Z_μ. We have also made use of the fact that the constant ($N = 0$) term in (7.258) must equal to 1. This is due to the fact that the partition function Z_N is equal to 1 for $N = 0$ so that $F = -k_B T \ln Z_N = 0$, as expected for a vacuum. Since e^x is real and positive for all real x, we see from (7.257) that Q_N is real and positive. The coefficients of y^N in (7.258) are therefore all real and positive. Hence, Z_μ has no root on the positive real axis and y_i must either be negative or occur in complex conjugate pairs.

For an infinite volume, $M \to \infty$ and a root, say y_0, may be squeezed onto the positive real axis [see Fig.7.27]. In which case, a phase transition occurs since the system can have different properties for $y > y_0$ and $y < y_0$. In general, Z_μ, Ω, and hence P will be continuous across y_0 but derivatives of Ω such as $n = \frac{\langle N \rangle}{V} = \frac{1}{v}$ can be discontinuous. By definition,

$$\frac{P}{k_B T} = \lim_{V\to\infty} \left\{ \frac{1}{V} \ln\left[Z_\mu(T,V) \right] \right\} \tag{7.260}$$

$$\frac{1}{v} = \lim_{V\to\infty} \frac{\langle N \rangle}{V} = \lim_{V\to\infty} \left\{ y \frac{\partial}{\partial y} \left(\frac{1}{V} \ln\left[Z_\mu(T,V) \right] \right) \right\} \tag{7.261}$$

where (7.261) made use of $\langle N \rangle = -\left(\frac{\partial \Omega}{\partial \mu'} \right)_{TV}$ and (7.258a) so that

$$1 = \frac{\exp(\beta\mu')}{\lambda_T^3} \beta \left(\frac{\partial \mu'}{\partial y} \right)_T$$

$$\Rightarrow \qquad \left(\frac{\partial}{\partial\mu'}\right)_T = \left(\frac{\partial y}{\partial\mu'}\right)_T \left(\frac{\partial}{\partial y}\right)_T = \frac{\beta\exp(\beta\mu')}{\lambda_T^3}\left(\frac{\partial}{\partial y}\right)_T = \beta\left(y\frac{\partial}{\partial y}\right)_T$$

or
$$\left(y\frac{\partial}{\partial y}\right)_T = k_B T\left(\frac{\partial}{\partial\mu'}\right)_T$$

so that

$$\langle N\rangle = k_B T\left(\frac{\partial}{\partial\mu'}\ln Z_{\mu'}\right)_{TV} = \left(y\frac{\partial}{\partial y}\ln Z_{\mu'}\right)_{TV}$$

$$\langle N^2\rangle - \langle N\rangle^2 = (k_B T)^2\left(\frac{\partial^2}{\partial\mu'^2}\ln Z_{\mu'}\right)_{TV} = \left[\left(y\frac{\partial}{\partial y}\right)^2 \ln Z_{\mu'}\right]_{TV} \qquad \text{[see (7.115)]}$$

Note that in general, the operations $\lim_{V\to\infty}$ and $y\frac{\partial}{\partial y}$ do not commute.

S7.C.3. Theorems

Theorem I

For all positive real *y*, $\lim_{V\to\infty}\left\{\frac{1}{V}\ln\left[Z_\mu\left(T,V\right)\right]\right\}$ is independent of shape of *V* and increases monotonically with *y*.

Theorem II

Let *R* be a region containing a segment of the positive real axis in the complex *y* plane. If *R* is always free of roots of Z_μ, then

$$\lim_{V\to\infty}\left\{\frac{1}{V}\ln\left[Z_\mu\left(T,V\right)\right]\right\}$$

and

$$\lim_{V\to\infty}\left\{\left(y\frac{\partial}{\partial y}\right)^n\left(\frac{1}{V}\ln\left[Z_\mu\left(T,V\right)\right]\right)\right\}\qquad \text{for}\quad n=1,2,\cdots,\infty$$

are analytic functions of *y* in *R*. Furthermore, the operations $\lim_{V\to\infty}$ and $y\frac{\partial}{\partial y}$ commute in *R* so that

$$\lim_{V\to\infty}\left\{y\frac{\partial}{\partial y}\left(\frac{1}{V}\ln\left[Z_\mu\left(T,V\right)\right]\right)\right\}=y\frac{\partial}{\partial y}\left\{\lim_{V\to\infty}\left(\frac{1}{V}\ln\left[Z_\mu\left(T,V\right)\right]\right)\right\}\qquad (7.261a)$$

S7.C.4. Corollaries

The followings are some immediate conclusions of the theorems. For convenience, we shall restrict *y* to physically meaningful values, i.e., *y* is real and positive.

Derivatives of *P*

From eqs(7.260,1,1a), we have, in *R*,

$$\frac{1}{v} = y\frac{\partial}{\partial y}\left(\frac{P}{k_B T}\right) \qquad (7.262)$$

Thus, although *P* must be continuous for all *y*, its derivatives are required to be continuous only when $Z_\mu \neq 0$. By definition, if $\frac{\partial P}{\partial y}$ is discontinuous at a root y_0, we have a 1st order phase transition at y_0. If the discontinuity involves a higher order of derivative, the transition is continuous.

1st Phase Transitions

If *v* is discontinuous at y_0, it will decrease as *y* increases.

Proof

Using eqs(7.261,1a), we have, for $y \neq y_0$,

$$\left[y\frac{\partial}{\partial y}\left(\frac{1}{v}\right)\right]_T = \lim_{V\to\infty}\left\{\left(y\frac{\partial}{\partial y}\right)^2\left[\frac{1}{V}\ln Z_\mu\left(T,V\right)\right]\right\}_T$$

$$= \lim_{V\to\infty}\frac{1}{V}\left[\left\langle N^2\right\rangle - \left\langle N\right\rangle^2\right] \qquad \text{[see S7.C.4]}$$

$$= \lim_{V\to\infty}\frac{1}{V}\left\langle\left(N-\left\langle N\right\rangle\right)^2\right\rangle \geq 0$$

Since $y > 0$, this means v^{-1} increases monotonically with *y* so that *v* decreases monotonically with *y*. QED.

2-D Ising Model

Application to the 2-D Ising model [C.N.Yang, Phys Rev 85, 809 (52); C.N.Yang, T.D.Lee, Phys Rev 87, 404 and 410 (52)] showed that the roots of Z_μ all lie on the unit circle and close on the real axis as $N \to \infty$. The point at which the roots touch the real axis exhibits a phase transition.