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

Consider a chain of N particles of mass m. Every particle except those at the ends is coupled to its two nearest neighbors by springs of the same force constant κ. For convenience, we shall impose the periodic boundary conditions so that every particle is coupled to its two nearest neighbors [see Fig.7.22]

Fig.7.22. Chain of N particles (red dots) with periodic boundary conditions.

At equilibrium, the particles sit in a 1-D lattice of spacing a and the distance between the end particles is $L = N a$. Let q_j be the position of the j^{th} particle as measured from particle 0. The Hamiltonian of the system is

$$H = \sum_{j=1}^{N} \frac{p_j^2}{2m} + \frac{1}{2}\kappa \sum_{j=1}^{N} (q_{j+1} - q_j - a)^2 \tag{7.179}$$

where, owing to the periodic boundary conditions,

$$q_{N+1} = q_1$$

which can be accomplished by merging particles 0 & N to make a ring.

Using the displacement from the equilibrium position

$$u_j = q_j - j a \tag{7.179a}$$

we can write (7.179) as

$$H = \sum_{j=1}^{N} \frac{p_j^2}{2m} + \frac{1}{2}\kappa \sum_{j=1}^{N} (u_{j+1} - u_j)^2 \tag{7.180}$$

with

$$u_{N+1} = u_1 \tag{7.180a}$$

For both classical & quantum mechanics, the Hamilton's equations are

$$\dot{u}_j = \frac{\partial H}{\partial p_j} = \frac{p_j}{m} \tag{7.180b}$$

$$\dot{p}_j = -\frac{\partial H}{\partial u_j}$$

$$= -\frac{1}{2}\kappa \begin{cases} -2(u_2 - u_1) + 2(u_1 - u_N) & \text{if } j = 1 \\ 2(u_j - u_{j-1}) - 2(u_{j+1} - u_j) & \text{if } j \neq 1 \text{ or } N \\ 2(u_N - u_{N-1}) - 2(u_1 - u_N) & \text{if } j = N \end{cases} \qquad [\text{ (7.180a) used. }]$$

$$= -\kappa \begin{cases} 2u_1 - u_2 - u_N & \text{if } j = 1 \\ -u_{j-1} + 2u_j - u_{j+1} & \text{if } j \neq 1 \text{ or } N \\ -u_{N-1} + 2u_N - u_1 & \text{if } j = N \end{cases} \tag{7.180b}$$

$$= m\ddot{u}_j \qquad [\text{ (7.180a) used. }]$$

Using

$$\boldsymbol{u}^T = (u_1, \; \ldots, \; u_N)$$

and

$$\mathbb{V}_N = \begin{pmatrix} 2 & -1 & 0 & \cdots & 0 & -1 \\ -1 & 2 & -1 & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & 2 & -1 \\ -1 & 0 & 0 & \cdots & -1 & 2 \end{pmatrix}_N \tag{7.181}$$

we can write (7.180b) as a matrix equation

$$\ddot{\boldsymbol{u}} = -\frac{\kappa}{m}\,\mathbb{V}\cdot\boldsymbol{u} = -\omega_0^2\,\mathbb{V}\cdot\boldsymbol{u} \qquad [\,\omega_0^2 = \frac{\kappa}{m}\,] \qquad (7.182)$$

The normal modes are solutions of (7.182) where every particle is vibrating with the same frequency. Thus

$$\boldsymbol{u}(t) = \boldsymbol{u}(0)\,e^{-i\,\omega\,t} \qquad (7.182a)$$

so that (7.182) becomes

$$\omega^2\,\boldsymbol{u}(0) = \omega_0^2\,\mathbb{V}_N\cdot\boldsymbol{u}(0) \qquad (7.182b)$$

Since the sum of each row in $\mathbb{V}_N$ is zero, there is always a static solution

$$\omega = 0 \qquad \boldsymbol{u}(0) = (1,\ \ldots,\ 1) \qquad (7.182c)$$

Since $\mathbb{V}_N$ is real & symmetric, its eigenvalues are real, i.e., ω^2 is real. By the same token, $\mathbb{V}_N$ can be diagonalized by an orthogonal transform

$$\mathbb{O}^T\cdot\mathbb{V}_N\cdot\mathbb{O} = \mathbb{D}_N = \operatorname{diag}\Big(\lambda_N(1),\ \ldots,\ \lambda_N(N)\Big) \qquad (7.183)$$

where $\mathbb{O}$ is an orthogonal matrix and $\lambda_N(j) = \dfrac{\omega(j)^2}{\omega_0^2}$ is the j^{th} eigenvalue of $\mathbb{V}_N$. Since

$$\sum_{j=1}^{N}\lambda_N(j) = \operatorname{Tr}\mathbb{V}_N = 2\,N > 0 \qquad \forall\ N$$

we must have $\lambda_N(j) \geq 0$ so that $\omega(j)$ are also real.

We now proceed to find $\lambda_N(j)$. To begin, let $\mathbb{U}_N$ be the $N\times N$ tridiagonal matrix

$$\mathbb{U}_N = \begin{pmatrix} 2 & -1 & 0 & \cdots & 0 & 0 \\ -1 & 2 & -1 & \cdots & 0 & 0 \\ 0 & -1 & 2 & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & 2 & -1 \\ 0 & 0 & 0 & \cdots & -1 & 2 \end{pmatrix}_N \qquad (7.183a)$$

In general, the determinant of an $n\times n$ tridiagonal matrix

$$f_n = \det\begin{vmatrix} a_1 & b_1 & 0 & \cdots & 0 & 0 \\ c_1 & a_2 & b_2 & \cdots & 0 & 0 \\ 0 & c_2 & a_3 & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & a_{n-1} & b_{n-1} \\ 0 & 0 & 0 & \cdots & c_{n-1} & a_n \end{vmatrix} \qquad (7.183b)$$

obeys the recurrence relation

$$f_n = a_n\,f_{n-1} - b_{n-1}\,c_{n-1}\,f_{n-2} \qquad (7.183c)$$

where

$$f_{-1} = 0 \qquad f_0 = 1$$

A tridiagonal matrix is Toeplitz if

$$a_j = a \qquad b_j = b \qquad c_j = c$$

In which case, its eigenvalues are simply [see any textbook on matrices]

$$\lambda_k = a + 2\sqrt{b\,c}\,\cos\frac{k\,\pi}{n+1} \qquad k = 1,\ \ldots,\ n \qquad (7.183d)$$

Thus, the eigenvalues of $\mathbb{U}_N$ are

$$\mu_N(k) = 2 + 2\cos\frac{k\,\pi}{N+1} \qquad k = 1,\ \ldots,\ N$$

$$= 4\cos^2 \frac{k\pi}{2(N+1)} \tag{7.185}$$

Hence,

$$\det \mathbb{U}_N = \prod_{k=1}^{N} \mu_N(k) = \prod_{k=1}^{N} \left[4\cos^2 \frac{k\pi}{2(N+1)} \right] \tag{7.185a}$$

Meanwhile,

$$\det \mathbb{V}_N = \det \begin{vmatrix} 2 & -1 & 0 & 0 & \cdots & 0 & 0 & 0 & -1 \\ -1 & 2 & -1 & 0 & \cdots & 0 & 0 & 0 & 0 \\ 0 & -1 & 2 & -1 & \cdots & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 2 & \cdots & 0 & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & \cdots & 2 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & \cdots & -1 & 2 & -1 & 0 \\ 0 & 0 & 0 & 0 & \cdots & 0 & -1 & 2 & -1 \\ -1 & 0 & 0 & 0 & \cdots & 0 & 0 & -1 & 2 \end{vmatrix}_N$$

Using the Laplace expansion on the 1st row, we have

$$\det \mathbb{V}_N = 2\det \mathbb{U}_N + \det \begin{vmatrix} -1 & -1 & 0 & \cdots & 0 & 0 & 0 & 0 \\ 0 & 2 & -1 & \cdots & 0 & 0 & 0 & 0 \\ 0 & -1 & 2 & \cdots & 0 & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & 2 & -1 & 0 & 0 \\ 0 & 0 & 0 & \cdots & -1 & 2 & -1 & 0 \\ 0 & 0 & 0 & \cdots & 0 & -1 & 2 & -1 \\ -1 & 0 & 0 & \cdots & 0 & 0 & -1 & 2 \end{vmatrix}_{N-1} \tag{a}$$

$$-(-)^{N+1} \det \begin{vmatrix} -1 & 2 & -1 & 0 & \cdots & 0 & 0 & 0 \\ 0 & -1 & 2 & -1 & \cdots & 0 & 0 & 0 \\ 0 & 0 & -1 & 2 & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & \cdots & 2 & -1 & 0 \\ 0 & 0 & 0 & 0 & \cdots & -1 & 2 & -1 \\ 0 & 0 & 0 & 0 & \cdots & 0 & -1 & 2 \\ -1 & 0 & 0 & 0 & \cdots & 0 & 0 & -1 \end{vmatrix}_{N-1}$$

For the 2nd term on the R.H.S. of (a), Laplace expansion on the 1st column gives

$$-\det \mathbb{U}_{N-2} - (-)^N \det \begin{vmatrix} -1 & 0 & \cdots & 0 & 0 & 0 & 0 \\ 2 & -1 & \cdots & 0 & 0 & 0 & 0 \\ -1 & 2 & \cdots & 0 & 0 & 0 & 0 \\ \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & \cdots & 2 & -1 & 0 & 0 \\ 0 & 0 & \cdots & -1 & 2 & -1 & 0 \\ 0 & 0 & \cdots & 0 & -1 & 2 & -1 \end{vmatrix}_{N-2}$$

$$= -\det \mathbb{U}_{N-2} - (-)^N (-)^{N-2}$$

$$= -\det \mathbb{U}_{N-2} - 1 \tag{b}$$

where we have used the fact that for a triangular matrix $\mathbb{T}$,

$$\det \mathbb{T} = \prod_j T_{jj}$$

For the last term on the R.H.S. of (a), Laplace expansion on the 1st column gives

$$-(-)^{N+1} \left(-\det \begin{vmatrix} -1 & 2 & -1 & \cdots & 0 & 0 & 0 \\ 0 & -1 & 2 & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & 2 & -1 & 0 \\ 0 & 0 & 0 & \cdots & -1 & 2 & -1 \\ 0 & 0 & 0 & \cdots & 0 & -1 & 2 \\ 0 & 0 & 0 & \cdots & 0 & 0 & -1 \end{vmatrix}_{N-2} - (-)^N \det \mathbb{U}_{N-2} \right)$$

$= -(-)^{N+1} \left[-(-)^{N-2} - (-)^N \det \mathbb{U}_{N-2} \right]$

$= -1 - \det \mathbb{U}_{N-2}$ (c)

Putting (b) & (c) into (a) gives

$$\det \mathbb{V}_N = 2 \det \mathbb{U}_{N-1} - 2 \det \mathbb{U}_{N-2} - 2$$

$$= \det \mathbb{U}_N - \det \mathbb{U}_{N-2} - 2 \qquad \text{[(7.183c) used.]}$$

$$= \prod_{k=1}^{N} \left[4 \cos^2 \frac{k\pi}{2(N+1)} \right] - \prod_{k=1}^{N-2} \left[4 \cos^2 \frac{k\pi}{2(N-1)} \right] - 2 \qquad (7.185b)$$

On the other hand, (7.182b) can be written in component form as

$$\omega^2 u_j(0) = \omega_0^2 \left[-u_{j-1}(0) + 2 u_j(0) - u_{j+1}(0) \right] \qquad j = 1, \ldots, N \qquad (7.186a)$$

with the periodic boundary conditions

$$u_0(0) = u_N(0) \qquad u_{N+1}(0) = u_1(0) \qquad (7.186b)$$

The solutions to (7.186a) then takes the form

$$u_j(0) = C e^{i\alpha j} \qquad [\, C = \text{const} \,] \qquad (7.186c)$$

where (7.186b) is satisfied by setting

$$\alpha N = 2\pi k \qquad k \in \mathcal{I}_N \qquad (7.186d)$$

where

$$\mathcal{I}_N = \begin{cases} \left\{ -\frac{N}{2}, \ldots, \frac{N}{2} - 1 \right\} & \text{if } N \text{ is even} \\ \left\{ -\frac{N-1}{2}, \ldots, \frac{N-1}{2} \right\} & \text{if } N \text{ is odd} \end{cases}$$

Note that there are only N independent solutions (modes) since there are N degrees of freedom.

Putting (7.186c) into (7.186a) gives

$$\omega^2 e^{i\alpha j} = \omega_0^2 \left[-e^{i\alpha(j-1)} + 2 e^{i\alpha j} - e^{i\alpha(j+1)} \right]$$

$$\to \quad \omega^2 = \omega_0^2 \left(-e^{-i\alpha} + 2 - e^{i\alpha} \right)$$

$$= 2\omega_0^2 (1 - \cos\alpha)$$

$$= 4\omega_0^2 \sin^2 \frac{\alpha}{2}$$

$$= 4\omega_0^2 \sin^2 \frac{\pi k}{N} \qquad \text{[(7.186d) used.]} \qquad (7.186e)$$

$$= \omega(k)^2$$

The eigenvalues of $\mathbb{V}_N$ are therefore

$$\lambda_N(k) = 4 \sin^2 \frac{\pi k}{N} \qquad k \in \mathcal{I}_N \qquad (7.186f)$$

$$= \frac{\omega^2(k)}{\omega_0^2}$$

The dispersion relation is given by

$$\omega(k) = 2\omega_0 \left| \sin \frac{\pi k}{N} \right|$$

where, by convention [see (7.189a)], $\omega(k) \ge 0$.

Note that $\omega(0) = 0$, in agreement with (7.182c).

Comparing (7.186f) with (7.185b), we arrive at the amazing identity

$$\prod_{k \in \mathcal{I}_N} \left[4 \sin^2 \frac{\pi k}{N} \right] = 0$$

$$= \prod_{k=1}^{N} \left[4\cos^2 \frac{k\pi}{2(N+1)} \right] - \prod_{k=1}^{N-2} \left[4\cos^2 \frac{k\pi}{2(N-1)} \right] - 2 \qquad (7.186g)$$

See §Code for numerical test of (7.186g).

The eigenvector for $\lambda_N(k)$ is given by (7.186c) as

$$u_j(k,0) = C\, e^{i 2\pi k j / N} \qquad j = 1, \ldots, N \qquad k \in \mathcal{I}_N \qquad (7.186h)$$

so that

$$u_j(k,t) = C\, e^{i 2\pi k j / N}\, e^{i\omega(k) t} \qquad (7.186i)$$

where C is determined by the normalization

$$\boldsymbol{u}^T(k,0) \cdot \boldsymbol{u}(k,0) = 1$$

Since

$$\mathbb{V}_N \cdot \boldsymbol{u}(k,0) = \lambda_N(k)\, \boldsymbol{u}(k,0)$$

the orthogonal matrix $\mathbb{O}$ in (7.183) is given by

$$\mathbb{O} = \left(\boldsymbol{u}(0,0), \ \ldots, \boldsymbol{u}(N-1,0) \right) \qquad (7.186j)$$

so that

$$O_{jk} = u_j(k,0) \qquad (7.186k)$$

Thus,

$$\mathbb{O}^T \cdot \mathbb{V}_N \cdot \mathbb{O} = \begin{pmatrix} \boldsymbol{u}^T(0,0) \\ \vdots \\ \boldsymbol{u}^T(N-1,0) \end{pmatrix} \cdot \mathbb{V}_N \cdot \left(\boldsymbol{u}(0,0), \ \ldots, \boldsymbol{u}(N-1,0) \right)$$

$$= \begin{pmatrix} \boldsymbol{u}^T(0,0) \\ \vdots \\ \boldsymbol{u}^T(N-1,0) \end{pmatrix} \cdot \left(\lambda_N(0)\, \boldsymbol{u}(0,0), \ \ldots, \lambda_N(N-1)\, \boldsymbol{u}(N-1,0) \right)$$

$$= \text{diag}\left(\lambda_N(0), \ \ldots, \ \lambda_N(N-1) \right) \qquad [\ \boldsymbol{u}^T(k,0) \cdot \boldsymbol{u}(k',0) = \delta_{k,k'} \text{ used.}]$$

as claimed.

Writing the Hamiltonian (7.180) in matrix notations, we have, for both classical & Heisenberg picture,

$$H = \frac{1}{2m} \left(\boldsymbol{p}^T \cdot \boldsymbol{p} + \omega_0^2\, \boldsymbol{u}^T \cdot \mathbb{V}_N \cdot \boldsymbol{u} \right)$$

$$= \frac{1}{2m} \left[\left(\mathbb{O}^T \cdot \boldsymbol{p} \right)^T \cdot \left(\mathbb{O}^T \cdot \boldsymbol{p} \right) + \omega_0^2 \left(\mathbb{O}^T \cdot \boldsymbol{u} \right)^T \cdot \mathbb{O}^T \cdot \mathbb{V}_N \cdot \mathbb{O} \cdot \left(\mathbb{O}^T \cdot \boldsymbol{u} \right) \right] \qquad [\ \mathbb{O}^T \cdot \mathbb{O} = \mathbb{O} \cdot \mathbb{O}^T = \mathbb{I}\ ]$$

$$= \frac{1}{2m} \left(\boldsymbol{P}^T \cdot \boldsymbol{P} + \omega_0^2\, \boldsymbol{Q}^T \cdot \mathbb{D}_N \cdot \boldsymbol{Q} \right) \qquad [\ (7.183) \text{ used.}] \qquad (7.187a)$$

where

$$\boldsymbol{P} = \mathbb{O}^T \cdot \boldsymbol{p} \qquad \boldsymbol{Q} = \mathbb{O}^T \cdot \boldsymbol{u}$$

$$P_k = \sum_{j=1}^{N} O_{jk}\, p_j \qquad Q_k = \sum_{j=1}^{N} O_{jk}\, u_j \qquad (7.187b)$$

In component form, (7.187a) becomes

$$H = \sum_{k \in \mathcal{I}_N} \left[\frac{P_k^2}{2m} + \frac{1}{2} m\, \omega^2(k)\, Q_k^2 \right] \qquad [\ (7.183) \text{ used.}] \qquad (7.187)$$

From now on, we shall consider only the quantum case. To begin,

$$\left[\hat{Q}_k, \hat{P}_{k'} \right] = \sum_{j,j'=1}^{N} O_{jk}\, O_{j'k'} \left[\hat{u}_j, \hat{p}_{j'} \right]$$

$$= \sum_{j,j'=1}^{N} O_{jk} O_{j'k'} \, i\hbar \delta_{jj'}$$
$$= \sum_{j=1}^{N} O_{jk} O_{jk'} \, i\hbar$$
$$= i\hbar \delta_{kk'} \qquad [\ \mathbb{O}^T \cdot \mathbb{O} = \mathbb{O} \cdot \mathbb{O}^T = \mathbb{I} \text{ used. }] \qquad (7.187c)$$

so that $\hat{Q}_k$ & $\hat{P}_k$ is a conjugate pair.

Setting

$$\hat{a}_k = \sqrt{\frac{m\,\omega(k)}{2\hbar}} \left(\hat{Q}_k + \frac{i}{m\,\omega(k)} \hat{P}_k \right)$$
$$\rightarrow \quad \hat{a}_k^+ = \sqrt{\frac{m\,\omega(k)}{2\hbar}} \left(\hat{Q}_k - \frac{i}{m\,\omega(k)} \hat{P}_k \right) \qquad (7.188)$$

we have

$$\hat{a}_k^+ \hat{a}_k = \frac{m\,\omega(k)}{2\hbar} \left(\hat{Q}_k - \frac{i}{m\,\omega(k)} \hat{P}_k \right)\left(\hat{Q}_k + \frac{i}{m\,\omega(k)} \hat{P}_k \right)$$
$$= \frac{m\,\omega(k)}{2\hbar} \left(\hat{Q}_k^2 + \frac{1}{m^2\,\omega(k)^2} \hat{P}_k^2 + \frac{i}{m\,\omega(k)} [\hat{Q}_k, \hat{P}_k] \right)$$
$$= \frac{m\,\omega(k)}{2\hbar} \left(\hat{Q}_k^2 + \frac{1}{m^2\,\omega(k)^2} \hat{P}_k^2 - \frac{\hbar}{m\,\omega(k)} \right) \qquad [\ (7.187c) \text{ used. }]$$
$$= \frac{1}{\hbar\,\omega(k)} \left(\frac{1}{2} m\,\omega(k)^2 \hat{Q}_k^2 + \frac{1}{2m} \hat{P}_k^2 - \frac{\hbar}{2} \right)$$

so that (7.187) becomes

$$\hat{H} = \sum_{k \in \mathcal{I}_N} \hbar\,\omega(k) \left(\hat{a}_k^+ \hat{a}_k + \frac{1}{2} \right) \qquad (7.189a)$$

It is well known that the energy eigenvalues of a single harmonic oscillator of frequency ω is given by [see any textbook on quantum mechanics]

$$E_n = \hbar\,\omega \left(n + \frac{1}{2} \right) \qquad n = 0, 1, 2, \ldots \qquad (7.189b)$$

Comparing (7.189a & b) suggests that we define

$$\hat{n}_k = \hat{a}_k^+ \hat{a}_k = \text{ number operator for mode } k. \qquad (7.189c)$$

so that (7.189a) becomes

$$\hat{H} = \sum_{k \in \mathcal{I}_N} \hbar\,\omega(k) \left(\hat{n}_k + \frac{1}{2} \right) \qquad (7.189)$$

while the eigenstates for the mode k are eigenstates of $\hat{n}_k$ with

$$\hat{n}_k \mid n_k \rangle = n_k \mid n_k \rangle \qquad n_k = 0, 1, 2, \ldots \qquad (7.189d)$$

For the sake of clarity, we shall drop the mode index k in the following discussion. Thus, (7.188) gives

$$[\hat{a}, \hat{a}^+] = \frac{m\,\omega}{2\hbar} \left[\hat{Q} + \frac{i}{m\,\omega} \hat{P}, \hat{Q} - \frac{i}{m\,\omega} \hat{P} \right]$$
$$= \frac{m\,\omega}{2\hbar} \left\{ \left[\hat{Q}, -\frac{i}{m\,\omega} \hat{P} \right] + \left[\frac{i}{m\,\omega} \hat{P}, \hat{Q} \right] \right\}$$
$$= \frac{i}{2\hbar} \left\{ -[\hat{Q}, \hat{P}] + [\hat{P}, \hat{Q}] \right\}$$

$= 1$ [(7.187c) used.] (7.189e)

which is easily generalized to

$$[\hat{a}_k, \hat{a}^+_{k'}] = \delta_{k k'} \qquad (7.189f)$$

The Hilbert space spanned by the orthonormal states $\{ \mid n \rangle \}$ in (7.189d) are called the number space. Thus,

$$\langle n \mid m \rangle = \delta_{n m} \qquad \sum_{n=0}^{\infty} \mid n \rangle \langle n \mid = 1 \qquad \hat{n} \mid n \rangle = n \mid n \rangle \qquad (7.189g)$$

(7.189f) then gives

$$\left\langle n \middle| \hat{a}\hat{a}^+ - \hat{n} \middle| m \right\rangle = 1 \quad \to \quad \left\langle n \middle| \hat{a}\hat{a}^+ \middle| m \right\rangle = n\,\delta_{n m} + 1 \qquad (7.189h)$$

A set S of operators is complete over a Hilbert space if every state is connected to any other state by the action of a combination of operators in S alone. Let $S = \{\hat{a}, \hat{a}^+, \hat{n}\}$ be complete over the number space, then $\hat{a}$ & $\hat{a}^+$ must handle all the transformations between different number states. The simplest scenario is to allow $\hat{a}$ ($\hat{a}^+$) displace every eigenstate by a fixed amount α (β), i.e.

$$\hat{a} \mid n \rangle = c_n \mid n - \alpha \rangle \quad \to \quad \langle n \mid \hat{a}^+ = c_n^* \langle n - \alpha \mid \qquad (A)$$

$$\hat{a}^+ \mid n \rangle = d_n \mid n - \beta \rangle \quad \to \quad \langle n \mid \hat{a} = d_n^* \langle n - \beta \mid \qquad (B)$$

where c_n & d_n are normalization constants. Thus,

$$\left\langle n \middle| \hat{a}^+\hat{a} \middle| n \right\rangle = c_n^* c_n \langle n - \alpha \mid n - \alpha \rangle = c_n^* c_n \qquad \text{[(A) used.]}$$

$$= \langle n \mid \hat{n} \mid n \rangle = n \qquad \text{[(7.189c) used.]}$$

$$= c_n \langle n \mid \hat{a}^+ \mid n - \alpha \rangle = c_n d_{n-\alpha} \langle n \mid n - \alpha - \beta \rangle \qquad \text{[(A), then (B) used.]}$$

$$= c_n^* \langle n - \alpha \mid \hat{a} \mid n \rangle = c_n^* d_{n-\alpha}^* \langle n - \alpha - \beta \mid n \rangle$$

$$\to \quad \alpha + \beta = 0 \quad \& \quad c_n^* c_n = n = c_n d_{n-\alpha} = c_n^* d_{n-\alpha}^* \qquad (C)$$

Similarly,

$$\left\langle n \middle| \hat{a}\hat{a}^+ \middle| n \right\rangle = d_n^* d_n \langle n - \beta \mid n - \beta \rangle = d_n^* d_n \qquad \text{[(B) used.]}$$

$$= \left\langle n \middle| \hat{n} + 1 \middle| n \right\rangle = n + 1 \qquad \text{[(7.189h) used.]}$$

$$= d_n \langle n \mid \hat{a} \mid n - \beta \rangle = d_n c_{n-\beta} \langle n \mid n - \beta - \alpha \rangle \qquad \text{[(B), then (A) used.]}$$

$$= d_n^* \langle n - \beta \mid \hat{a}^+ \mid n \rangle = d_n^* c_{n-\beta}^* \langle n - \beta - \alpha \mid n \rangle$$

$$\to \quad \beta + \alpha = 0 \quad \& \quad d_n^* d_n = n + 1 = d_n c_{n-\beta} = d_n^* c_{n-\beta}^* \qquad (D)$$

Solutions to (C) & (D) are easily obtained if we set all constants to be real, giving

$$\beta = -\alpha \qquad c_n = \sqrt{n} = d_{n-\alpha} \qquad d_n = \sqrt{n+1} = c_{n-\beta} = c_{n+\alpha} \qquad (E)$$

So far, there seems to be no restriction on the value of α. However, since a state $\mid n \rangle$ can be connected only to states in the set $\{ \mid n \pm m\,\alpha \rangle;\ m = 1, 2, \ldots \}$, we must set $\alpha = \pm 1$ to make S complete. However, since

$$\hat{a}\hat{a}^+ \mid 0 \rangle = (\hat{n} + 1) \mid 0 \rangle = \mid 0 \rangle$$

the only choice is $\alpha = +1$.

Putting everything together, we have

$$\hat{a} \mid n \rangle = \sqrt{n} \mid n - 1 \rangle \qquad \hat{a}^+ \mid n \rangle = \sqrt{n+1} \mid n + 1 \rangle \qquad (7.189i)$$

With respect to the product basis

$$\{ \mid n_0 \rangle \otimes \ldots \otimes \mid n_{N-1} \rangle \}$$

the partition function for (7.189) is easily evaluated:

$$\begin{aligned}Z_N(T) &= \mathrm{Tr}_N \exp\left[-\beta \sum_{k=0}^{N-1} \hbar\,\omega(k)\left(\hat{n}_k + \frac{1}{2}\right)\right] \\ &= \prod_{k\in\mathcal{I}_N} \mathrm{Tr}_1 \exp\left[-\beta\,\hbar\,\omega(k)\left(\hat{n}_k + \frac{1}{2}\right)\right] \\ &= \prod_{k\in\mathcal{I}_N} \left\{\sum_{n_k=0}^{\infty} \exp\left[-\beta\,\hbar\,\omega(k)\left(n_k + \frac{1}{2}\right)\right]\right\} \\ &= \prod_{k\in\mathcal{I}_N} \frac{e^{-\beta\hbar\omega(k)/2}}{1 - e^{-\beta\hbar\omega(k)}}\end{aligned} \tag{7.191}$$

The thermodynamic internal energy is

$$\begin{aligned}U = \langle H\rangle &= -\frac{\partial \ln Z_N}{\partial \beta} \\ &= -\frac{\partial}{\partial \beta}\sum_{k\in\mathcal{I}_N} \ln\left[\frac{e^{-\beta\hbar\omega(k)/2}}{1 - e^{-\beta\hbar\omega(k)}}\right] = \frac{\partial}{\partial \beta}\sum_{k\in\mathcal{I}_N} \ln\left(e^{\beta\hbar\omega(k)/2} - e^{-\beta\hbar\omega(k)/2}\right) \\ &= \sum_{k\in\mathcal{I}_N} \frac{\hbar\,\omega(k)}{2}\left(\frac{e^{\beta\hbar\omega(k)/2} + e^{-\beta\hbar\omega(k)/2}}{e^{\beta\hbar\omega(k)/2} - e^{-\beta\hbar\omega(k)/2}}\right) \\ &= \sum_{k\in\mathcal{I}_N} \frac{\hbar\,\omega(k)}{2}\left(\frac{e^{\beta\hbar\omega(k)} + 1}{e^{\beta\hbar\omega(k)} - 1}\right) \\ &= \sum_{k\in\mathcal{I}_N} \frac{\hbar\,\omega(k)}{2}\left(1 + \frac{2}{e^{\beta\hbar\omega(k)} - 1}\right) \\ &= \sum_{k\in\mathcal{I}_N} \frac{\hbar\,\omega(k)}{2} + \sum_{k\in\mathcal{I}_N} \frac{\hbar\,\omega(k)}{e^{\beta\hbar\omega(k)} - 1} \\ &= \sum_{k\in\mathcal{I}_N} \hbar\,\omega(k)\left(\langle n_k\rangle + \frac{1}{2}\right)\end{aligned} \tag{7.192}$$

where [see Planck's formula (7.65)]

$$\langle n_k\rangle = \frac{1}{e^{\beta\hbar\omega(k)} - 1} \tag{7.193}$$

The heat capacity is therefore

$$\begin{aligned}C_N = \left(\frac{\partial U}{\partial T}\right)_N &= \sum_{k\in\mathcal{I}_N} \frac{\partial}{\partial T}\left(\frac{\hbar\,\omega(k)}{e^{\beta\hbar\omega(k)} - 1}\right) \\ &= \sum_{k\in\mathcal{I}_N} \frac{\hbar\,\omega(k)\,e^{\beta\hbar\omega(k)}}{(e^{\beta\hbar\omega(k)} - 1)^2}\,\frac{\hbar\,\omega(k)}{k_B\,T^2} \\ &= k_B \sum_{k\in\mathcal{I}_N} \frac{\left[\beta\,\hbar\,\omega(k)\right]^2 e^{\beta\hbar\omega(k)}}{(e^{\beta\hbar\omega(k)} - 1)^2}\end{aligned} \tag{7.194}$$

Code

```
tri[i_, j_] := { 2    i == j
               { -1   i == j - 1 || i == j + 1
tri[i_, j_, λ_] := { 2 - λ   i == j
                   { -1      i == j - 1 || i == j + 1
U[n_] := Table[tri[i, j], {i, n}, {j, n}]
U[n_, λ_] := Table[tri[i, j, λ], {i, n}, {j, n}]

V[n_] := ReplacePart[ ReplacePart[U[n], {1, n} → -1], {n, 1} → -1]
```

```
In[∘]:= V[n_, λ_] := ReplacePart[ReplacePart[U[n, λ], {1, n} → -1], {n, 1} → -1]

(* (7.163g) *)
Veq[n_] := Det[U[n, λ]] - Det[U[n - 2, λ]] - 2

(* comparing solutions of (7.163g) with the eigenvalues of V *)
Table[{λ /. NSolve[Veq[n] == 0, λ, Reals], Eigenvalues[V[n]] // N}, {n, 4, 10}]

Out[∘]= {{{0, 2., 2., 4.}, {4., 2., 2., 0.}},
 {{0, 1.38197, 1.38197, 3.61803, 3.61803}, {3.61803, 3.61803, 1.38197, 1.38197, 0.}},
 {{0, 1., 1., 3., 3., 4.}, {4., 3., 3., 1., 1., 0.}},
 {{0, 0.75302, 0.75302, 2.44504, 2.44504, 3.80194, 3.80194},
  {3.80194, 3.80194, 2.44504, 2.44504, 0.75302, 0.75302, 0.}},
 {{0, 0.585786, 0.585786, 2., 2., 3.41421, 3.41421, 4.},
  {4., 3.41421, 3.41421, 2., 2., 0.585786, 0.585786, 0.}},
 {{0, 0.467911, 0.467911, 1.6527, 1.6527, 3., 3., 3.87939, 3.87939},
  {3.87939, 3.87939, 3., 3., 1.6527, 1.6527, 0.467911, 0.467911, 0.}},
 {{0, 0.381966, 0.381966, 1.38197, 1.38197, 2.61803, 2.61803, 3.61803, 3.61803, 4.},
  {4., 3.61803, 3.61803, 2.61803, 2.61803, 1.38197, 1.38197, 0.381966, 0.381966, 0.}}}

(* Test on (7.186g) *)
Table[Times @@ Table[4 Cos[k π/(2 (n + 1))]^2, {k, n}] -
  Times @@ Table[4 Cos[k π/(2 (n - 1))]^2, {k, n - 2}] // N, {n, 3, 30}]

Out[∘]= {2., 2., 2., 2., 2., 2., 2., 2., 2., 2., 2., 2.,
 2., 2., 2., 2., 2., 2., 2., 2., 2., 2., 2., 2., 2., 2., 2., 2.}
```

S7.A.1. Exact Expression -- Large N

In the limit of large N, summations over k can be approximated by integrals. For periodic boundary conditions, (7.186f) gives the dispersion relation as

$$\omega(k) = 2\,\omega_0 \left|\sin\frac{\pi k}{N}\right| \qquad k \in \mathcal{I}_N \qquad (7.195)$$

so that

$$\begin{aligned}\sum_{k\in\mathcal{I}_N} f(k) = \sum_{k\in\mathcal{I}_N} \Delta k\, f(k) \xrightarrow[N\gg 1]{} \int_{-[N/2]}^{[N/2]} dk\, f(k) &= \left(\int_{-[N/2]}^{0} + \int_{0}^{[N/2]}\right) dk\, f(k) \\ &= \int_{[N/2]}^{0} d(-k)\, f(-k) + \int_0^{[N/2]} dk\, f(k) \\ &= \int_0^{[N/2]} dk\,[f(k) + f(-k)] \\ &= \int_0^{\omega_L} d\omega\, g(\omega)\, f(\omega) \qquad (7.196a)\end{aligned}$$

where $\left[\frac{N}{2}\right]$ is the nearest integer to $\frac{N}{2}$,

$$\omega_L = \omega\left(\left[\frac{N}{2}\right]\right) = 2\,\omega_0 = \max \omega(k) \qquad (7.196b)$$

and the density of states is defined as

$$g(\omega) = 2\left|\frac{dk}{d\omega}\right| \qquad (7.197a)$$

Now, $\frac{d}{d\omega}$(7.195) gives

$$1 = 2\,\omega_0\,\frac{\pi}{N}\,\frac{dk}{d\omega}\cos\frac{\pi k}{N}$$

$$\rightarrow \quad g(\omega) = \frac{N}{\pi\,\omega_0\left|\cos\frac{\pi k}{N}\right|} = \frac{N}{\pi\,\omega_0\sqrt{1-\frac{\omega^2}{4\,\omega_0^2}}} \qquad \text{[(7.195) used.]}$$

$$= \frac{2N}{\pi\sqrt{\omega_L^2-\omega^2}} \qquad (7.197)$$

If one chooses to follow Reichl and use the fixed boundary conditions, one should start by replacing Reichl's erroneous (7.185) with ours. The scenario in k-space is quite different from the periodic boundary case since the spacing between k points are now halved and runs from 1 to N, while the maximum of $\omega(k)$ occurs at $k = 0$. However, $g(\omega)$ remains the same for $N \gg 1$, which is what really matters. Actual derivation of the results will be left as an exercise.

Using

$$\sum_{k\in\mathcal{I}_N} 1 = N$$

(7.196a) gives

$$N = \int_0^{\omega_L} d\omega\, g(\omega) \qquad (7.196c)$$

$$= \int_0^{\omega_L} d\omega\,\frac{2N}{\pi\sqrt{\omega_L^2-\omega^2}} \qquad \text{[(7.197) used.]}$$

$$= \frac{2N}{\pi}\tan^{-1}\frac{\omega}{\sqrt{\omega_L^2-\omega^2}}\Bigg|_0^{\omega_L} = N$$

which legitimizes (7.197).

(7.192) now becomes

$$U = \int_0^{\omega_L} d\omega\; g(\omega)\;\hbar\,\omega\left(\langle n(\omega)\rangle + \frac{1}{2}\right) \qquad (7.198a)$$

where

$$\langle n(\omega)\rangle = \frac{1}{e^{\beta\hbar\omega}-1} \qquad (7.198b)$$

Using

$$\int_0^{\omega_L} d\omega\; g(\omega)\;\hbar\,\omega = \int_0^{\omega_L} d\omega\;\frac{2N}{\pi\sqrt{\omega_L^2-\omega^2}}\;\hbar\,\omega \qquad \text{[(7.197) used.]}$$

$$= -\frac{2N}{\pi}\,\hbar\sqrt{\omega_L^2-\omega^2}\,\Bigg|_0^{\omega_L}$$

$$= \frac{2N}{\pi}\,\hbar\,\omega_L \qquad (7.198c)$$

we can write (7.198a) as

$$U = U_0 + \int_0^{\omega_L} d\omega\; g(\omega)\;\hbar\,\omega\,\langle n(\omega)\rangle \qquad (7.198)$$

where

$$U_0 = \frac{N}{\pi}\,\hbar\,\omega_L = \text{(average) zero-point energy}$$

(7.198b) gives

$$\langle n(\omega)\rangle\Big|_{T=0} = 0 \qquad \to \qquad U\Big|_{T=0} = U_0$$

Note that

$$U_0 \xrightarrow[N\to\infty]{} \infty$$

so that $U \to \infty$ in the thermodynamic limit. Luckily, U_0 is a constant so that we can get rid of this singularity by simply shifting the origin of the energy to U_0.

The heat capacity is

$$C_N = \left(\frac{\partial U}{\partial T}\right)_N = \int_0^{\omega_L} d\omega\, g(\omega)\, \hbar\omega \left(-k_B \beta^2 \frac{\partial \langle n(\omega)\rangle}{\partial \beta}\right) \qquad \left[\ \frac{\partial \beta}{\partial T} = -\frac{1}{k_B T^2} = -k_B \beta^2\ \right]$$

$$= k_B \int_0^{\omega_L} d\omega\, g(\omega)\, (\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega} - 1\right)^2} \qquad \left[\ \frac{\partial \langle n(\omega)\rangle}{\partial \beta} = -\frac{\hbar\omega\, e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega} - 1\right)^2}\ \right]$$

$$= k_B \frac{2N}{\pi} \int_0^{\omega_L} d\omega \frac{1}{\sqrt{\omega_L^2 - \omega^2}} (\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega} - 1\right)^2} \qquad \text{[(7.197) used.]} \qquad (7.199)$$

$$= k_B \frac{2N}{\pi} \int_0^{x_L} dx \frac{1}{\sqrt{x_L^2 - x^2}} x^2 \frac{e^x}{(e^x - 1)^2} \qquad (7.200)$$

where

$$x = \beta\hbar\omega \qquad x_L = \beta\hbar\omega_L = \frac{T_L}{T} \qquad T_L = \frac{\hbar\omega_L}{k_B} \qquad (7.200a)$$

For $T \to 0$, (7.200) becomes

$$C_N \approx k_B \frac{2N}{\pi} \int_0^\infty dx \frac{1}{x_L}\left(1 - \frac{x^2}{x_L^2}\right)^{-1/2} x^2 \frac{e^x}{(e^x - 1)^2}$$

$$= k_B \frac{2N}{\pi x_L} \int_0^\infty dx\, x^2 \frac{e^x}{(e^x - 1)^2}\left(1 + \frac{x^2}{2x_L^2} + \ldots\right)$$

$$= k_B \frac{2N}{\pi x_L}\left(\frac{\pi^2}{3} + \frac{2\pi^4}{15 x_L^2} + \ldots\right) \qquad \text{[See §Code.]}$$

$$= k_B \frac{2NT}{\pi T_L}\left(\frac{\pi^2}{3} + \frac{2\pi^4}{15 T_L^2} T^2 + \ldots\right) \qquad (7.201)$$

We have evaluated the integrals using *Mathematica*. Alternatively, one can also use the formula

$$I_n = \int_0^\infty dx\, x^n \frac{e^x}{(e^x - 1)^2} = \sum_{\alpha=1}^{\infty} \frac{n!}{\alpha^n} = \zeta(n)\, n! \qquad (7.202)$$

Derivation of (7.202) is a simpler version of that used to derive (7.173) for the Fermi integrals. Details are left for those interested.

Code

```
(* (7.196c) *)
∫ 1/Sqrt[a^2 - ω^2] dω
```

Out[ ]= $\text{ArcTan}\left[\frac{\omega}{\sqrt{a^2 - \omega^2}}\right]$

```
(* (7.198c) *)
```
$$\int \frac{\omega}{\sqrt{a^2-\omega^2}}\, d\omega$$

Out[ ]= $-\sqrt{a^2-\omega^2}$

In[ ]:=
```
(* (7.198c) *)
```
$$\left\{\int_0^\infty \frac{x^2 e^x}{(e^x-1)^2}\, dx,\ \int_0^\infty \frac{x^4 e^x}{(e^x-1)^2}\, dx\right\}$$

Out[ ]= $\left\{\frac{\pi^2}{3}, \frac{4\pi^4}{15}\right\}$

In[ ]:=
```
{2! Zeta[2], 4! Zeta[4]}
```

Out[ ]= $\left\{\frac{\pi^2}{3}, \frac{4\pi^4}{15}\right\}$

In[ ]:=
```
{2! PolyLog[2, 1], 4! PolyLog[4, 1]}
```

Out[ ]= $\left\{\frac{\pi^2}{3}, \frac{4\pi^4}{15}\right\}$

S7.A.2. Continuum Approximation -- Large N

Ref: §12-1, H.Goldstein, “Classical Mechanics”, 2nd ed. (1980).

In the continuum limit, the chain of particles becomes an elastic string of length $L = N a$ with

mass density $\rho = \frac{m}{a}$

and

Young’s modulus $Y = k a$

so that the Euler-Lagrange equation becomes the wave equation

$$\rho \frac{\partial^2 u}{\partial t^2} - Y \frac{\partial^2 u}{\partial x^2} = 0 \tag{7.203a}$$

Solutions to (7.203a) are plane waves $e^{i k x - i \omega t}$ with dispersion

$$\omega = \sqrt{\frac{Y}{\rho}}\, k = c\, k \tag{7.203b}$$

where

$$c = \sqrt{\frac{Y}{\rho}} = \text{phase velocity}$$

With the periodic boundary conditions, we have

$$k = \frac{2\pi}{L} n = \frac{2\pi}{N a} n \qquad n = 0, \pm 1, \ \ldots, \left[\frac{N}{2}\right]$$

The maximum $|k|$ is called the Debye wave-vector

$$k_D = \frac{\pi}{a} = \frac{\pi}{L} N$$

so that the correspond Debye frequency is

$$\omega_D = c\, k_D = c \frac{\pi}{L} N \tag{7.203c}$$

$$\sum_{n=-[N/2]}^{[N/2]} f(n)\,\Delta n = \frac{L}{2\pi} \sum_{k=-k_D}^{k_D} f(k)\,\Delta k$$
$$\approx \frac{L}{2\pi}\int_{-k_D}^{k_D} dk\, f(k) = \int_0^{\omega_D} d\omega\, g(\omega)\, f(\omega) \qquad (7.203d)$$

Putting (7.203b) into (7.197a) then gives

$$g(\omega) = \frac{L}{2\pi}\frac{2}{\left|\frac{d\omega}{dk}\right|} = \frac{L}{\pi c} = \frac{N}{\omega_D} \qquad \text{[(7.203c) used.]} \qquad (7.204)$$

so that

$$\int_0^{\omega_D} d\omega\, g(\omega) = N \qquad (7.203)$$

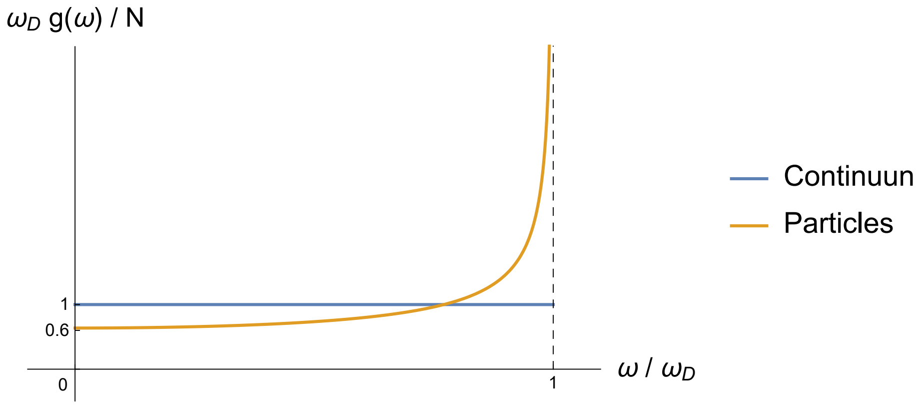

Fig.7.23. Plots of the Debye (continuum) & particles density of states.

With ω_L replaced by ω_D and $g(\omega)$ given by (7.204), the internal energy (7.198) becomes

$$U = \frac{N}{\pi}\hbar\omega_D + \frac{N}{\omega_D}\int_0^{\omega_D} d\omega\, \hbar\omega\, \langle n(\omega)\rangle \qquad (7.205)$$

so that the heat capacity (7.199) becomes

$$C_N = k_B \frac{N}{\omega_D}\int_0^{\omega_D} d\omega\, (\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega}-1\right)^2}$$
$$= k_B \frac{N k_B T}{\hbar\omega_D}\int_0^{x_D} dx\; x^2 \frac{e^x}{(e^x-1)^2} \qquad x_D = \beta\hbar\omega_D$$
$$= k_B \frac{N T}{T_D}\int_0^{T_D/T} dx\; x^2 \frac{e^x}{(e^x-1)^2} \qquad T_D = \frac{\hbar\omega_D}{k_B} \qquad (7.206)$$

For $T \to 0$,

$$C_N = k_B \frac{N T}{T_D}\int_0^{\infty} dx\, x^2 \frac{e^x}{(e^x-1)^2} - k_B \frac{N T}{T_D}\int_{T_D/T}^{\infty} dx\, x^2 \frac{e^x}{(e^x-1)^2}$$
$$\approx k_B \frac{N T}{T_D}\int_0^{\infty} dx\, x^2 \frac{e^x}{(e^x-1)^2} + \ldots$$
$$= k_B \frac{N T}{T_D}\frac{\pi^2}{3} + \ldots \qquad \text{[(7.202) used.]} \qquad (7.207)$$

Code

```
(* Fig.7.23 *)
Plot[{1, 2/(π Sqrt[1 - ω^2])}, {ω, 0, 1},
        PlotRange → {{- .1, 1.1}, {- .5, 5}},
        AxesLabel → {"ω / ωD", "ωD g(ω) / N"},
        Ticks → {{0, 1}, {0, 0.6, 1}},
        PlotLegends → {"Continuun", "Particles"},
        Epilog → {Text["0", - .05 {.5, 5}],
                Dashed, Line[{{1, 0}, {1, 5}}] }
]
```