Velocity Correlation Function

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Power Spectra

$$u_{ls}(t) = \frac{1}{\sqrt{NM_s}} \sum_{k\sigma} e_{k\sigma}(s)\, Q_{k\sigma}(t) e^{ik\cdot R_l}$$

$$\frac{1}{N} \sum_{l} e^{i(k-k')\cdot R_l} = \delta_{k',k}$$

先取共轭 $u_{ls}^{*}(t)$

$$\left\langle \sum_i M_i v_i(t) \cdot v_i(0) \right\rangle = \left\langle \sum_{ls} \frac{1}{N} \sum_{k\sigma\, k'\sigma'} e_{k\sigma}(s) e_{k'\sigma'}^{*}(s)\, \dot{Q}_{k\sigma}(t) \dot{Q}_{k'\sigma'}^{*}(0) e^{i(k-k')\cdot R_l} \right\rangle$$

$$= \left\langle \sum_{s} \sum_{k\sigma\sigma'} e_{k\sigma}(s) e_{k\sigma'}^{*}(s)\, \dot{Q}_{k\sigma}(t) \dot{Q}_{k\sigma'}^{*}(0) \right\rangle$$

Power Spectra

$$\left\langle \sum_i M_i v_i(t) \cdot v_i(0) \right\rangle = \left\langle \sum_{ls} \frac{1}{N} \sum_{k\sigma\, k'\sigma'} e_{k\sigma}(s) e^*_{k'\sigma'}(s)\, \dot{Q}_{k\sigma}(t) \dot{Q}^*_{k'\sigma'}(0) e^{i(k-k')\cdot R_l} \right\rangle$$

$$= \left\langle \sum_s \sum_{k\sigma\sigma'} e_{k\sigma}(s) e^*_{k\sigma'}(s)\, \dot{Q}_{k\sigma}(t) \dot{Q}^*_{k\sigma'}(0) \right\rangle$$

$$\sum_s e_{k\sigma}(s) e^*_{k\sigma'}(s) = \delta_{\sigma\sigma'}$$

$$\left\langle \sum_i M_i v_i(t) \cdot v_i(0) \right\rangle = \left\langle \sum_{k\sigma} \dot{Q}_{k\sigma}(t) \dot{Q}^*_{k\sigma}(0) \right\rangle = \left\langle \sum_{k\sigma} P^*_{k\sigma}(t) P_{k\sigma}(0) \right\rangle$$

Power Spectra

$$P_{k\sigma} = i\left(\frac{\omega_{k\sigma}\hbar}{2}\right)^{\frac{1}{2}}(\mathrm{a}_{k\sigma} - \mathrm{a}^{+}_{-k\sigma}) = i\left(\frac{\omega_{k\sigma}\hbar}{2}\right)^{\frac{1}{2}}\left(\mathrm{a}_{k\sigma 0}e^{-\mathrm{i}\omega_{k\sigma}\mathrm{t}} - \mathrm{a}^{+}_{-k\sigma 0}e^{\mathrm{i}\omega_{k\sigma}\mathrm{t}}\right)$$

$$\left\langle\sum_{k\sigma} P^{*}_{k\sigma}(t)P_{k\sigma}(0)\right\rangle = \left\langle\sum_{k\sigma}\frac{\omega_{k\sigma}\hbar}{2}\left(\mathrm{a}_{-k\sigma 0}e^{\mathrm{i}\omega_{k\sigma}\mathrm{t}} - \mathrm{a}^{+}_{k\sigma 0}e^{-\mathrm{i}\omega_{k\sigma}\mathrm{t}}\right)(\mathrm{a}_{k\sigma 0} - \mathrm{a}^{+}_{-k\sigma 0})\right\rangle$$

$$= \sum_{k\sigma}\frac{\omega_{k\sigma}\hbar}{2}\left\langle\left(\mathrm{a}_{-k\sigma 0}e^{\mathrm{i}\omega_{k\sigma}\mathrm{t}} - \mathrm{a}^{+}_{k\sigma 0}e^{-\mathrm{i}\omega_{k\sigma}\mathrm{t}}\right)(\mathrm{a}_{k\sigma 0} - \mathrm{a}^{+}_{-k\sigma 0})\right\rangle$$

$$= \sum_{k\sigma}\frac{\omega_{k\sigma}\hbar}{2}\left\langle\left(\mathrm{a}_{-k\sigma 0}\mathrm{a}_{k\sigma 0}e^{\mathrm{i}\omega_{k\sigma}\mathrm{t}} + \mathrm{a}^{+}_{k\sigma 0}\mathrm{a}^{+}_{-k\sigma 0}e^{-\mathrm{i}\omega_{k\sigma}\mathrm{t}} - \mathrm{a}_{-k\sigma 0}\mathrm{a}^{+}_{-k\sigma 0}e^{\mathrm{i}\omega_{k\sigma}\mathrm{t}} - \mathrm{a}^{+}_{k\sigma 0}\mathrm{a}_{k\sigma 0}e^{-\mathrm{i}\omega_{k\sigma}\mathrm{t}}\right)\right\rangle$$

Power Spectra

Some average

$|\varphi_i> = |\{\mathrm{n}\}_\mathrm{i}>$ Fork 空间基矢

$$\mathrm{a}_{k\sigma}|\varphi_i> = \sqrt{n_{k\sigma}}|\{\mathrm{n}|n_{k\sigma}-1\}_\mathrm{i}>$$

$$\langle \mathrm{a}_{k\sigma}\mathrm{a}_{k'\sigma'}\rangle = Tr(\mathrm{a}_{k\sigma}\mathrm{a}_{k'\sigma'}\rho) = \frac{1}{Z}\sum_i \langle \varphi_i|\mathrm{a}_{k\sigma}\mathrm{a}_{k'\sigma'}\rho|\varphi_i\rangle$$

$$= \frac{1}{Z}\sum_{\{\mathrm{n}_{k\sigma}\}} e^{-\beta\sum_{k\sigma}\omega_{k\sigma}\hbar(\mathrm{n}_{k\sigma}+\frac{1}{2})} \langle \varphi_i|\mathrm{a}_{k\sigma}\mathrm{a}_{k'\sigma'}|\varphi_i\rangle = 0$$

Power Spectra Some average

$$\langle\varphi_i|\mathrm{a}^+_{k\sigma}\mathrm{a}_{k'\sigma'}|\varphi_i\rangle = \delta_{k\sigma,k'\sigma'}\, n_{k\sigma}$$

$$\langle\mathrm{a}^+_{k\sigma}\mathrm{a}_{k'\sigma'}\rangle = \frac{\delta_{k\sigma,k'\sigma'}}{Z}\sum_{\{\mathrm{n}_{k\sigma}\}} e^{-\beta\sum_{k\sigma}\omega_{k\sigma}\hbar(\mathrm{n}_{k\sigma}+\frac{1}{2})}\, n_{k\sigma}$$

$$= \frac{\delta_{k\sigma,k'\sigma'}}{Z}\prod_{k\sigma\neq k_1\sigma_1}\left(\sum_{\mathrm{n}_{k\sigma}} e^{-\beta\omega_{k\sigma}\hbar(\mathrm{n}_{k\sigma}+\frac{1}{2})}\right)\sum_{n_{k_1\sigma_1}} e^{-\beta\omega_{k_1\sigma_1}\hbar(n_{k_1\sigma_1}+\frac{1}{2})} n_{k_1\sigma_1}$$

$$= \delta_{k\sigma,k'\sigma'}\frac{\sum_{\mathrm{n}_{k\sigma}} e^{-\beta\omega_{k\sigma}\hbar\left(\mathrm{n}_{k\sigma}+\frac{1}{2}\right)}\mathrm{n}_{k\sigma}}{\sum_{\mathrm{n}_{k\sigma}} e^{-\beta\omega_{k\sigma}\hbar\left(\mathrm{n}_{k\sigma}+\frac{1}{2}\right)}}$$

$$= \delta_{k\sigma,k'\sigma'}\frac{\sum_{\mathrm{n}_{k\sigma}} e^{-\beta\omega_{k\sigma}\hbar\left(\mathrm{n}_{k\sigma}+\frac{1}{2}\right)}\mathrm{n}_{k\sigma}}{Z_{k\sigma}}$$

Power Spectra Some average

$$= \delta_{k\sigma,k'\sigma'} \frac{-\frac{dZ_{k\sigma}}{dx} - \frac{1}{2} Z_{k\sigma}}{Z_{k\sigma}} = \delta_{k\sigma,k'\sigma'} \left(-\frac{d\ln Z_{k\sigma}}{dx} - \frac{1}{2}\right)$$

设 $x = \beta\omega_{k\sigma}\hbar$

$$Z_{k\sigma} = \frac{e^{-\frac{1}{2}\beta\omega_{k\sigma}\hbar}}{1 - e^{-\beta\omega_{k\sigma}\hbar}}$$

$$\frac{d\ln Z_{k\sigma}}{dx} = \frac{d\left(-\frac{1}{2}x - \ln(1 - e^{-x})\right)}{dx} = -\frac{1}{2} - \frac{e^{-x}}{(1 - e^{-x})}$$

$$\langle \mathrm{a}_{k\sigma}^{+} \mathrm{a}_{k'\sigma'} \rangle = \delta_{k\sigma,k'\sigma'} \frac{e^{-x}}{(1 - e^{-x})} = \frac{\delta_{k\sigma,k'\sigma'}}{e^{\beta\omega_{k\sigma}\hbar} - 1}$$

$$\langle \mathrm{a}_{k\sigma} \mathrm{a}_{k'\sigma'}^{+} \rangle = \langle \delta_{k\sigma,k'\sigma'} + \mathrm{a}_{k\sigma}^{+} \mathrm{a}_{k'\sigma'} \rangle = \delta_{k\sigma,k'\sigma'} + \langle \mathrm{a}_{k\sigma}^{+} \mathrm{a}_{k'\sigma'} \rangle$$

$$\langle \mathrm{a}_{k\sigma} \mathrm{a}_{k'\sigma'} \rangle = \langle \mathrm{a}_{k\sigma 0}^{+} \mathrm{a}_{-k\sigma 0}^{+} \rangle = 0$$

Power Spectra

$$\rho = \frac{1}{Z} e^{-\beta H}$$

$$\langle \mathrm{a}_{-k\sigma 0} \mathrm{a}_{k\sigma 0} \rangle = Tr(\mathrm{a}_{-k\sigma 0} \mathrm{a}_{k\sigma 0} \rho) = 0 \quad \langle \mathrm{a}^{+}_{k\sigma 0} \mathrm{a}^{+}_{-k\sigma 0} \rangle = 0$$

$$\langle \mathrm{a}_{-k\sigma 0} \mathrm{a}^{+}_{-k\sigma 0} \rangle - 1 = \langle \mathrm{a}^{+}_{k\sigma 0} \mathrm{a}_{k\sigma 0} \rangle = f(\omega_{k\sigma}) = \frac{1}{e^{\frac{\omega_{k\sigma}\hbar}{k_B T}} - 1}$$

$$因此有 \left\langle \sum_i M_i v_i(t) \cdot v_i(0) \right\rangle = \left\langle \sum_{k\sigma} P^*_{k\sigma}(t) P_{k\sigma}(0) \right\rangle$$

$$= \sum_{k\sigma} -\omega_{k\sigma} \hbar f(\omega_{k\sigma}) \cos(\omega_{k\sigma} \mathrm{t}) - \frac{1}{2} \sum_{k\sigma} \omega_{k\sigma} \hbar e^{\mathrm{i}\omega_{k\sigma} \mathrm{t}}$$

$$= \int -\hbar\omega D(\omega) f(\omega) \cos(\omega \mathrm{t}) d\omega \ - \frac{1}{2} \int \hbar\omega D(\omega) e^{\mathrm{i}\omega \mathrm{t}}$$

Mode dependent situation

$$\langle P^*_{k\sigma}(t) P_{k\sigma}(0) \rangle = \omega_{k\sigma} \hbar \left(f(\omega_{k\sigma}) + \frac{1}{2} \right) \cos(\omega_{k\sigma} \mathrm{t})$$

Power Spectra 三角变换正交性

$$\int \cos(\omega \mathrm{t})\ \ \cos(\omega' \mathrm{t})\, dt = \int \frac{e^{i\omega \mathrm{t}} + e^{-i\omega\,\mathrm{t}}}{2}\frac{e^{i\omega' \mathrm{t}} + e^{-i\omega' \mathrm{t}}}{2} dt$$

$$= \frac{1}{4}\int e^{i(\omega+\omega')\mathrm{t}} + e^{i(\omega-\omega')\mathrm{t}} + e^{-i(\omega\,-\omega')\mathrm{t}} + e^{-i(\omega+\omega')\mathrm{t}} dt$$

$$= \frac{1}{2}\left(2\pi\delta(\omega+\omega') + 2\pi\,\delta(\omega-\omega')\right)$$

If ω>0

$$\delta(\omega+\omega') = 0$$

$$\int \cos(\omega \mathrm{t})\ \ \cos(\omega' \mathrm{t})\, dt = \pi\,\delta(\omega-\omega')$$

同理 $\int \cos(\omega t)\ \ e^{-i\omega' \mathrm{t}} dt = \pi\,\delta(\omega-\omega')$

$$\int \sin(\omega t)\cos(\omega' \mathrm{t})\, dt = 0$$

Power Spectra

$$\omega_{k\sigma}\hbar\left(f(\omega_{k\sigma})+\frac{1}{2}\right)\delta(\omega-\omega_{k\sigma})=\frac{1}{\pi}\int\langle P_{k\sigma}^{*}(t)P_{k\sigma}(0)\rangle\cos(\omega\mathrm{t})\,dt$$

$$\sum_{k\sigma}\omega_{k\sigma}\hbar\left(f(\omega_{k\sigma})+\frac{1}{2}\right)\delta(\omega-\omega_{k\sigma})=\frac{1}{\pi}\int\left\langle\sum_{i}M_{i}v_{i}(t)\cdot v_{i}(0)\right\rangle\cos(\omega\mathrm{t})\,dt$$

这就是power spectra

Phonon DOS

$$\langle v_i(t)\cdot v_i(0)\rangle = \frac{1}{NM_s}\sum_{k\sigma\, k'\sigma'} e_{k\sigma}(s)e^*_{k'\sigma'}(s)\left\langle \dot{Q}_{k\sigma}(t)\dot{Q}^*_{k'\sigma'}(0)\right\rangle e^{i(k-k')\cdot R_l}$$

$$= \frac{1}{NM_s}\sum_{k\sigma\, k'\sigma'} e_{k\sigma}(s)e^*_{k'\sigma'}(s)\,\langle P^*_{k\sigma}(t)\,P_{k'\sigma'}(0)\rangle e^{i(k-k')\cdot R_l}$$

$$\langle P^*_{k\sigma}(t)\,P_{k'\sigma'}(0)\rangle = \frac{\hbar}{2}(\omega_{k\sigma}\omega_{k'\sigma'})^{\frac{1}{2}}\left\langle\left(\mathrm{a}_{-k\sigma 0}e^{\mathrm{i}\omega_{k\sigma}\mathrm{t}} - \mathrm{a}^{+}_{k\sigma 0}e^{-\mathrm{i}\omega_{k\sigma}\mathrm{t}}\right)(\mathrm{a}_{k'\sigma' 0} - \mathrm{a}^{+}_{-k'\sigma' 0})\right\rangle$$

$$= \frac{\hbar}{2}(\omega_{k\sigma}\omega_{k'\sigma'})^{\frac{1}{2}}\left(-\delta_{k\sigma,k'\sigma'}(f(\omega_{k\sigma})+1)e^{-\mathrm{i}\omega_{k\sigma}\mathrm{t}} - \delta_{k\sigma,k'\sigma'}f(\omega_{k\sigma})e^{\mathrm{i}\omega_{k\sigma}\mathrm{t}}\right)$$

$$\langle v_i(t)\cdot v_i(0)\rangle = \frac{1}{NM_s}\sum_{k\sigma} e_{k\sigma}(s)e^*_{k\sigma}(s)\,\omega_{k\sigma}\hbar\left(f(\omega_{k\sigma})+\frac{1}{2}\right)\cos(\omega_{k\sigma}t)$$

Phonon DOS

$if\ \omega_{k\sigma}\hbar \ll k_B T$ Classical limit $60THz\,\frac{\hbar}{k_B} = 2879.4K$

$$\omega_{k\sigma}\hbar\left(f(\omega_{k\sigma}) + \frac{1}{2}\right) = \frac{\omega_{k\sigma}\hbar}{e^{\frac{\omega_{k\sigma}\hbar}{k_B T}} - 1} + \frac{1}{2}\omega_{k\sigma}\hbar \approx \frac{\omega_{k\sigma}\hbar}{1 + \frac{\omega_{k\sigma}\hbar}{k_B T} - 1} = k_B T$$

$$\langle v_i(t)\cdot v_i(0)\rangle = \frac{1}{NM_s}\sum_{k\sigma} e_{k\sigma}(s)e^*_{k\sigma}(s)\,k_B T\cos(\omega_{k\sigma}t)$$

$$\int \frac{\langle v_i(t)\cdot v_i(0)\rangle}{\langle v_i(0)\cdot v_i(0)\rangle}\cos(\omega t)\,dt = \frac{\left(\sum_{k\sigma} e_{k\sigma}(s)e^*_{k\sigma}(s)\,k_B T\delta(\omega_{k\sigma}-\omega)\right)}{\sum_{k\sigma} e_{k\sigma}(s)e^*_{k\sigma}(s)\,k_B T}$$

$$= \frac{\sum_{k\sigma} e_{k\sigma}(s)e^*_{k\sigma}(s)\,\delta(\omega_{k\sigma}-\omega)}{\sum_{k\sigma} e_{k\sigma}(s)e^*_{k\sigma}(s)} = \frac{g(\omega)}{\int g(\omega)d\omega}$$

$g(\omega)=\sum_{k\sigma} e_{k\sigma}(s)e^*_{k\sigma}(s)\,\delta(\omega_{k\sigma}-\omega)$ Atom projected DOS

Phonon DOS

$$if\ \omega_{k\sigma}\hbar \gg k_B T$$

$$\omega_{k\sigma}\hbar\left(f(\omega_{k\sigma}) + \frac{1}{2}\right) \approx \frac{\omega_{k\sigma}\hbar}{2}$$

$$\int \frac{\langle v_i(t)\cdot v_i(0)\rangle}{\langle v_i(0)\cdot v_i(0)\rangle}\cos(\omega t)\,dt = \frac{\sum_{k\sigma} e_{k\sigma}(s)e_{k\sigma}^{*}(s)\,\omega_{k\sigma}\hbar\delta(\omega_{k\sigma}-\omega)}{\sum_{k\sigma} e_{k\sigma}(s)e_{k\sigma}^{*}(s)\,\omega_{k\sigma}\hbar}$$

NOTICE:模拟是经典模拟而非量子模拟，高温极限是正确的。

Phonon DOS

$$\langle P^*_{k\sigma}(t)\, P_{k'\sigma'}(0)\rangle = \langle P^*_{k\sigma}(0)\cos(\omega_{k\sigma}t)\, P_{k'\sigma'}(0)\rangle = \langle P^*_{k\sigma}(0)P_{k'\sigma'}(0)\rangle\cos(\omega_{k\sigma}t)$$

Hamiltonian $$H = \sum_{k\sigma} \frac{P^*_{k\sigma}P_{k\sigma}}{2} + \omega^2_{k\sigma}Q^*_{k\sigma}Q_{k\sigma}$$

能量均分原理 $$\langle P^*_{k\sigma}P_{k\sigma}\rangle = \frac{1}{2}k_BT$$

$$\langle v_i(t)\cdot v_i(0)\rangle = \frac{1}{NM_s}\sum_{k\sigma} e_{k\sigma}(s)e^*_{k\sigma}(s)\, k_BT\cos(\omega_{k\sigma}t)$$

$$\int \frac{\langle v_i(t)\cdot v_i(0)\rangle}{\langle v_i(0)\cdot v_i(0)\rangle}\cos(\omega t)\, dt = \frac{\left(\sum_{k\sigma} e_{k\sigma}(s)e^*_{k\sigma}(s)\, k_BT\delta(\omega_{k\sigma}-\omega)\right)}{\sum_{k\sigma} e_{k\sigma}(s)e^*_{k\sigma}(s)\, k_BT}$$

$$= \frac{\sum_{k\sigma} e_{k\sigma}(s)e^*_{k\sigma}(s)\, \delta(\omega_{k\sigma}-\omega)}{\sum_{k\sigma} e_{k\sigma}(s)e^*_{k\sigma}(s)} = \frac{g(\omega)}{\int g(\omega)d\omega}$$

Velocity correlation function

时间关联函数的计算

$$\langle A(t)B(0)\rangle = \frac{1}{\mathrm{N}} * (\mathrm{A(t)B(0) + A(t+dt)B(dt) + A(t+2dt)B(2dt)} + \cdots)$$

$$= \frac{1}{N}\sum_{n=0}^{N}\left(A(t+ndt)B(ndt)\right)$$

实际计算使用

$$\mathrm{F}\{\langle A(t)B(0)\rangle\} = F\{A(t)\} \; * F\{B(t)\}^{*}$$

Velocity correlation function

证明：

$$\mathrm{F}\{\langle A(t)B(0)\rangle\} = \frac{1}{\mathrm{M}}\sum_{m=0}^{M}\frac{1}{N}\sum_{n=0}^{N}A(mdt+ndt)e^{-i\omega mdt}B(ndt)$$

$$=\frac{1}{N}\sum_{n=0}^{N}\frac{1}{M}\sum_{k=n}^{n+M}A(kdt)e^{-i\omega kdt}B(ndt)\,e^{i\omega ndt}$$

由于达到平衡 $$\sum_{k=n}^{n+M}A(kdt)e^{-i\omega kdt}=\sum_{k=0}^{M}A(kdt)e^{-i\omega kdt}$$

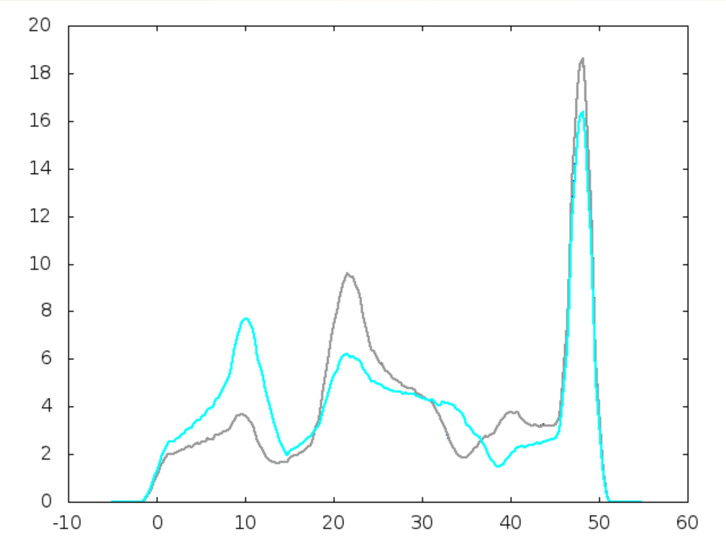
$$\mathrm{F}\{\langle A(t)B(0)\rangle\} = \frac{1}{M}\sum_{k=0}^{M}A(kdt)e^{-i\omega kdt}\frac{1}{N}\sum_{n=0}^{N}B(ndt)e^{i\omega ndt}$$

$$= F\{A(t)\} \;*\; F\{B(t)\}^{*}$$

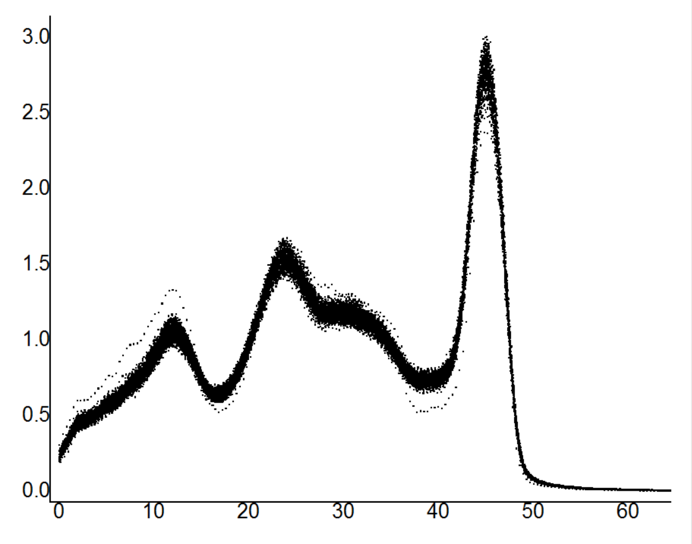
Atom projected DOS

$$g(\omega)=\sum_{k\sigma} e_{k\sigma}(s)e^{*}_{k\sigma}(s)\,\delta(\omega_{k\sigma}-\omega)$$

apdos of CN



Calculated with
frozen phonon



VCF method
A big problem
为了研究随机掺杂体系的性质

THANK YOU!

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