Anomalia da Constante Dielétrica do Gelo

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1. Introdução
2. Objetivos
3. Referencial Teórico
4. Modelo
5. Metodologia
6. Resultados
7. Conclusões
8. Referências

1 Introdução

2 Objetivos

3 Referencial Teórico

4 Modelo

5 Metodologia

6 Resultados

7 Conclusões

8 Referências

Água

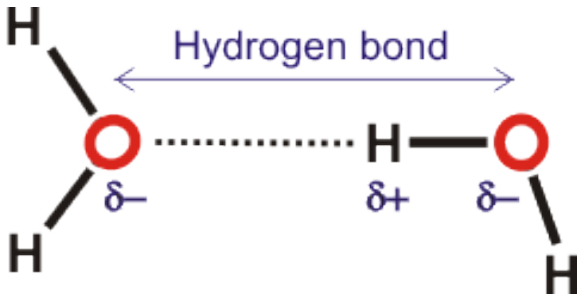


Figura 1: Ligações de hidrogênio. Fonte: [Chaplin]

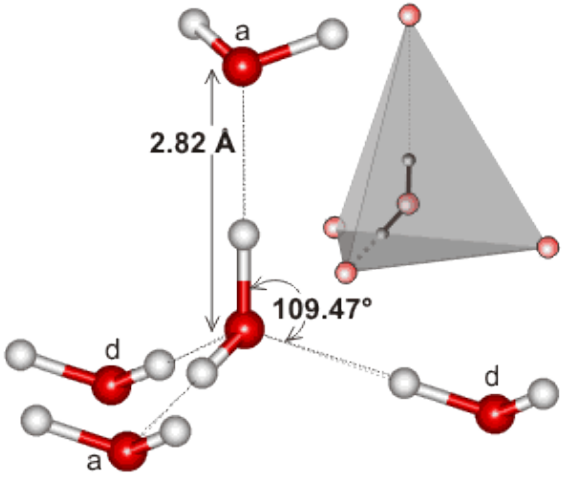


Figura 2: Estrutura tetraédrica.Fonte: [Chaplin]

Algumas anomalias da água são:

- Temperatura de máxima densidade (TMD)
- Alto valor do calor específico
- Superfluxo

Gelo

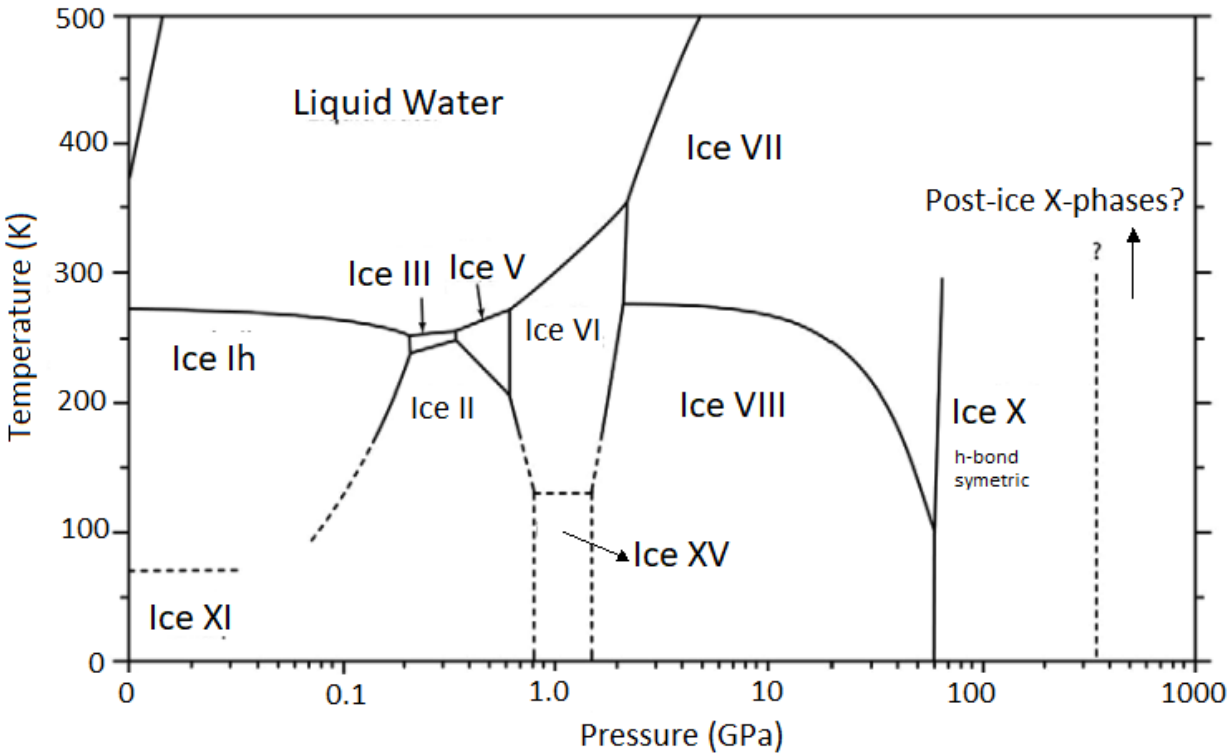


Figura 3: Diagrama de fase do gelo. Fonte: [Fuentes-Landete et al. 2015]

Regras do gelo (Bernal–Fowler)

4 ligações de hidrogênio por molécula: duas próximas e duas distantes

Constante Dielétrica

Permissividade Relativa (Constante Dielétrica) é a medida da capacidade do material de armazenar energia potencial elétrica e de ser polarizado.

$$\epsilon = \epsilon' + i\epsilon'' \tag{1}$$

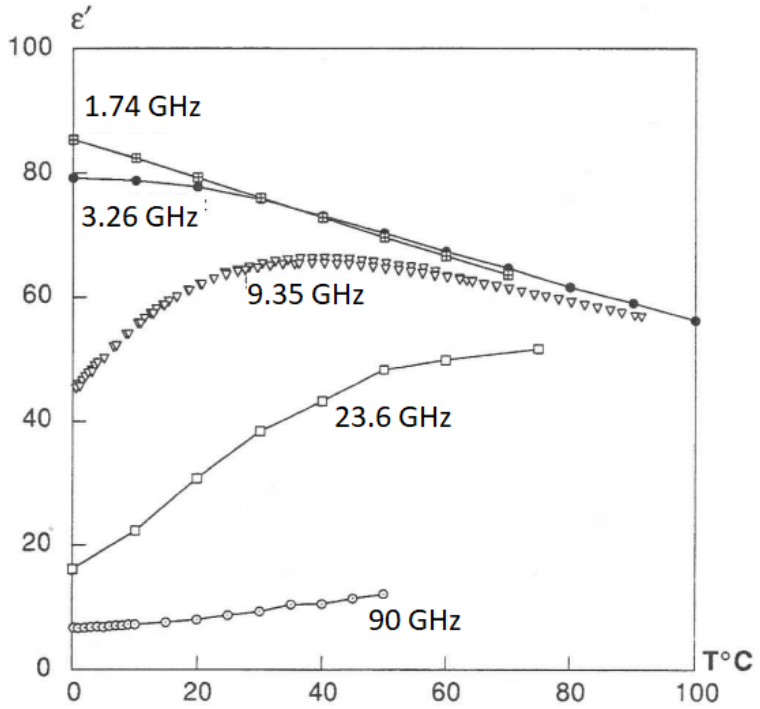


Figura 4: Parte real da permissividade elétrica. [Ellison, Lamkaouchi e Moreau 1996].

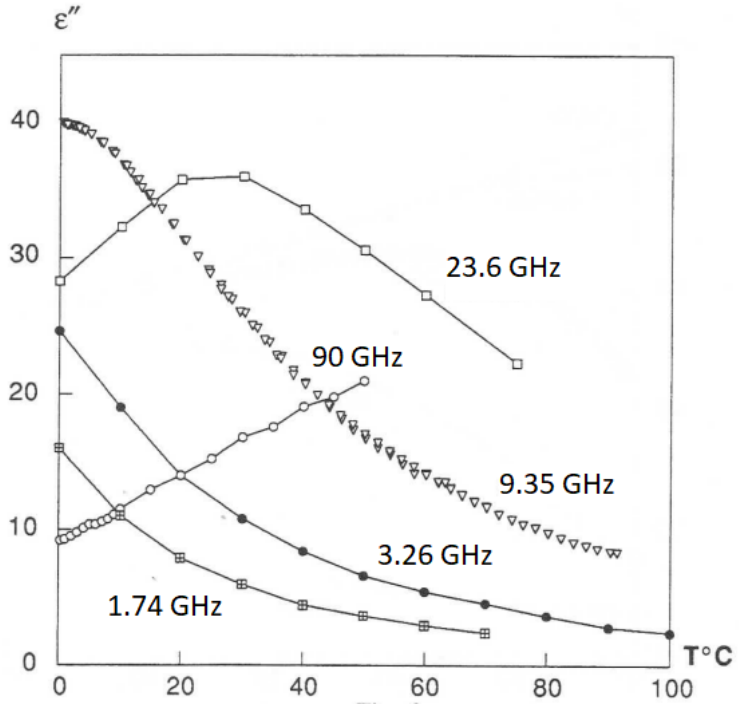


Figura 5: Parte imaginária da permissividade elétrica. [Ellison, Lamkaouchi e Moreau 1996].

Anomalia da Constante Dielétrica

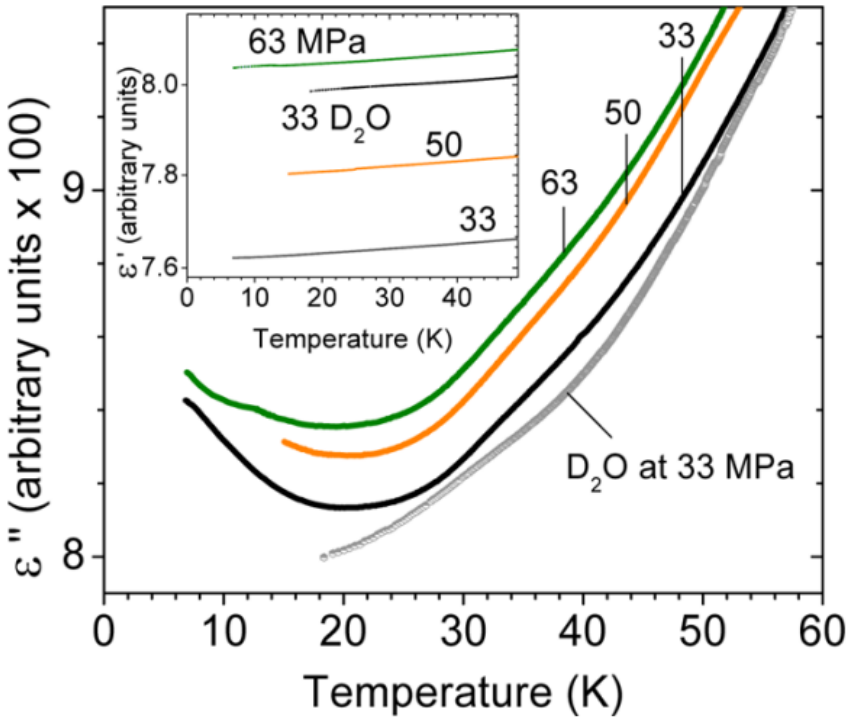


Figura 6: Resultados experimentais da permissividade relativa do gelo. [Yen e Gao 2015]

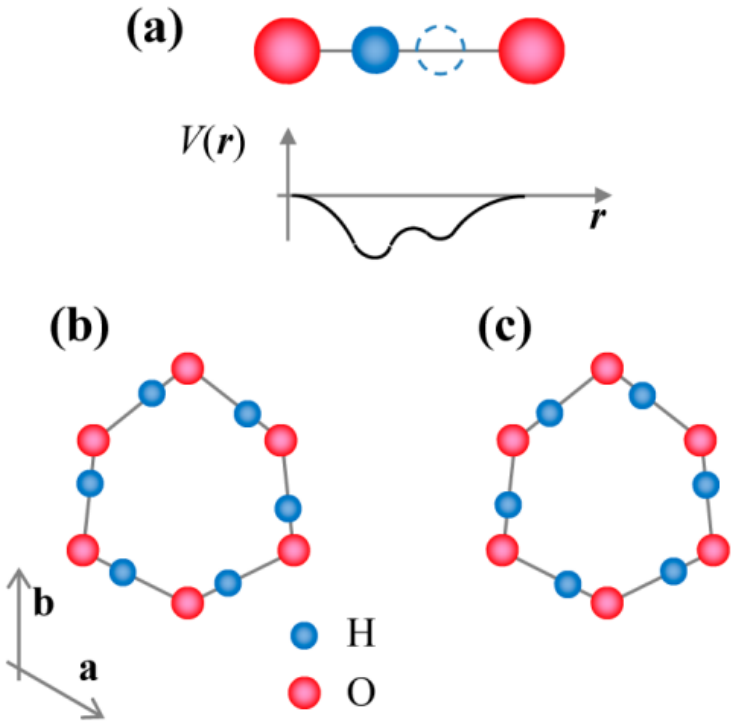


Figura 7: Hipótese de tunelamento correlacionado. [Yen e Gao 2015]

1 Introdução

2 Objetivos

3 Referencial Teórico

4 Modelo

5 Metodologia

6 Resultados

7 Conclusões

8 Referências

Objetivos

Verificar numericamente se o tunelamento correlacionado é o mecanismo fundamental da anomalia da constante dielétrica do gelo.

Objetivos específicos:

- Estudo analítico de sistema unidimensional periódico;
- Estudo numérico de sistema unidimensional periódico;
- Estudo numérico de sistema bidimensional periódico.

1 Introdução

2 Objetivos

3 Referencial Teórico

4 Modelo

5 Metodologia

6 Resultados

7 Conclusões

8 Referências

$$\epsilon = \chi + 1 \tag{2}$$

$$Im(\tilde{\chi}) = -\frac{\pi}{\hbar \mathcal{Z}} \sum_{n,m} |\langle n| P |m\rangle|^2 \left(e^{-\beta E_n} - e^{-\beta E_m}\right) \delta(w_{nm} - w) \tag{3}$$

1 Introdução

2 Objetivos

3 Referencial Teórico

4 Modelo

5 Metodologia

6 Resultados

7 Conclusões

8 Referências

Modelo do gelo

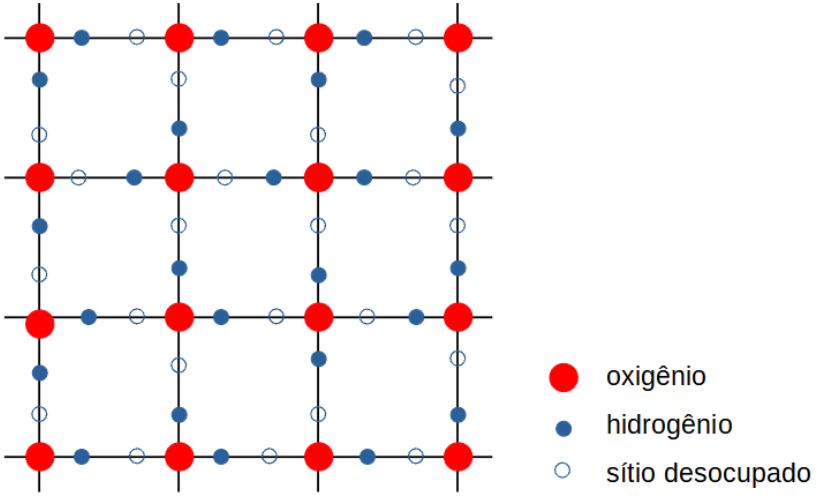


Figura 8: Ilustração do gelo quadrado.

$$\mathcal{H} = U \sum_{i}^{N} \sum_{\alpha}^{4} \sum_{\beta}^{4} \left(n_{i\alpha} - \frac{1}{2} \right) \left(n_{i\beta} - \frac{1}{2} \right) - t \sum_{i}^{N} \sum_{\alpha}^{4} (c_{j\alpha'}^{\dagger} c_{i\alpha} + c_{i\alpha}^{\dagger} c_{j\alpha'}) \quad (4)$$

$$n_{i\alpha} = c_{i\alpha}^{\dagger} c_{i\alpha} \quad (5)$$

Modelo do gelo

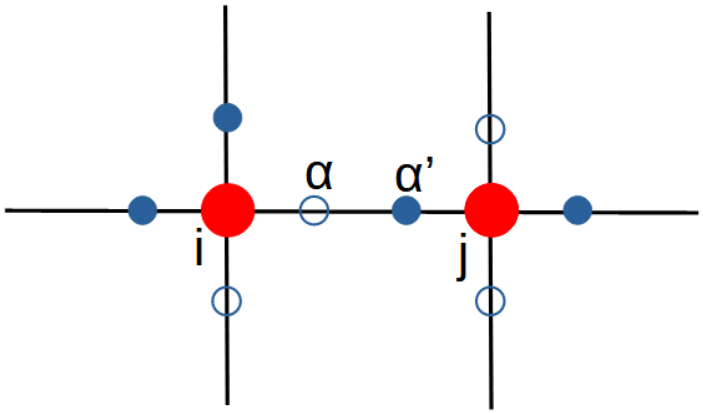


Figura 8: Ilustração dos índices do hamiltoniano.

$$\mathcal{H} = U \sum_{i}^{N} \sum_{\alpha}^{4} \sum_{\beta}^{4} \left(n_{i\alpha} - \frac{1}{2} \right) \left(n_{i\beta} - \frac{1}{2} \right) - t \sum_{i}^{N} \sum_{\alpha}^{4} (c_{j\alpha'}^{\dagger} c_{i\alpha} + c_{i\alpha}^{\dagger} c_{j\alpha'}) \quad (4)$$

$$n_{i\alpha} = c_{i\alpha}^{\dagger} c_{i\alpha} \quad (5)$$

Polarização

Sistema unidimensional:

$$\hat{P} = \mu_0 \sum_i \sigma_i = \mu_0 \sum_i (n_{i1} - n_{i2}) \tag{6}$$

Sistema bidimensional:

$$\hat{P} = \frac{\mu_0}{\sqrt{2}} \sqrt{\left(\sum_i \sigma_i^x\right)^2 + \left(\sum_i \sigma_i^y\right)^2} \tag{7}$$

1 Introdução

2 Objetivos

3 Referencial Teórico

4 Modelo

5 Metodologia

6 Resultados

7 Conclusões

8 Referências

Metodologia

1. Diagonalização exata de $\mathcal{H}$ (LAPACK e BLAS) $\rightarrow$ autovetores e autovalores
2. Cálculo da polarização de cada estado $\rightarrow \langle n| \hat{P} |m\rangle$
3. Somatório da susceptibilidade:

$$Im(\tilde{\chi}) = \frac{2\pi}{\hbar \mathcal{Z}} \sum_{n,m} |\langle n| P |m\rangle|^2 \left(e^{-\beta E_n} - e^{-\beta E_m}\right) \delta(w_{nm} - w) \tag{27}$$

1 Introdução

2 Objetivos

3 Referencial Teórico

4 Modelo

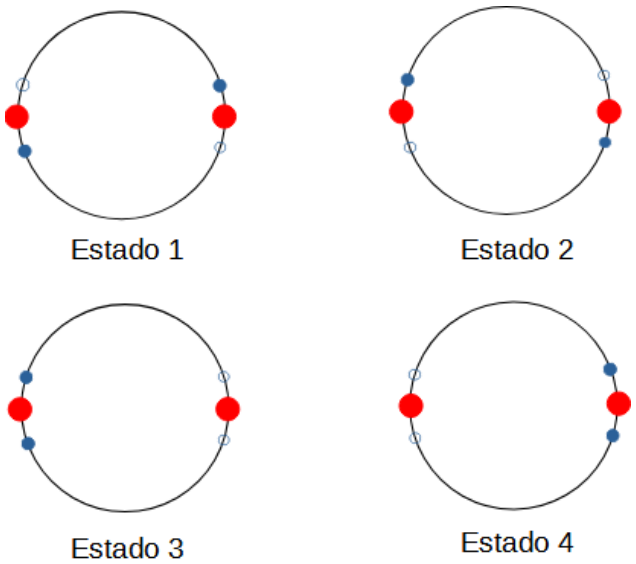
5 Metodologia

6 Resultados

7 Conclusões

8 Referências

Resultados Analíticos de Sistema Unidimensional com 2 oxigênios

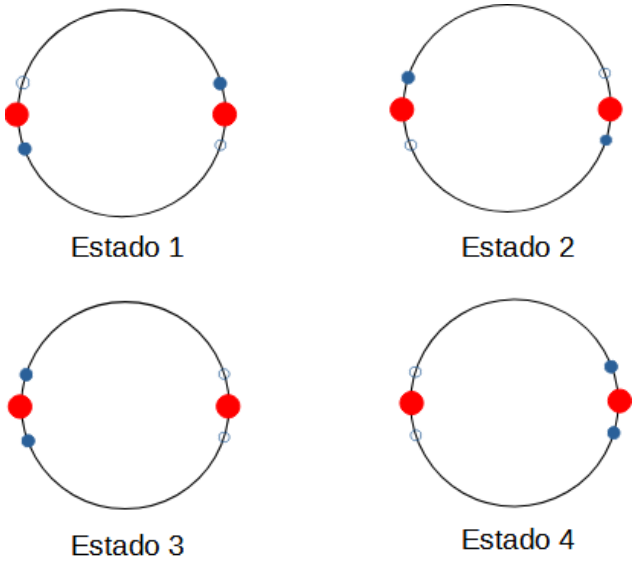


$$\mathcal{H} = \begin{pmatrix} -\frac{U}{2} & 0 & -t & -t \\ 0 & -\frac{U}{2} & -t & -t \\ -t & -t & \frac{U}{2} & 0 \\ -t & -t & 0 & \frac{U}{2} \end{pmatrix} \quad (8)$$

Sem hopping ($t = 0$)

$$E_1 = -\frac{U}{2} \qquad E_2 = -\frac{U}{2} \qquad E_3 = \frac{U}{2} \qquad E_4 = \frac{U}{2}$$

$$|\phi_1\rangle = |1\rangle \qquad |\phi_2\rangle = |2\rangle \qquad |\phi_3\rangle = |3\rangle \qquad |\phi_4\rangle = |4\rangle$$



Sem hopping ($t = 0$)

$$Im(\tilde{\chi}) = \frac{2\pi}{\hbar} \sum_{n,m} |\langle m| P |n\rangle|^2 \left(e^{-\beta E_n} - e^{-\beta E_m}\right) \delta(w_{nm} - w) \qquad (9)$$

	$\lvert\phi_1\rangle$	$\lvert\phi_2\rangle$	$\lvert\phi_3\rangle$	$\lvert\phi_4\rangle$
$\langle\phi_1\rvert$	$\frac{2\mu_0}{\sqrt{2}}$	0	0	0
$\langle\phi_2\rvert$	0	-$\frac{2\mu_0}{\sqrt{2}}$	0	0
$\langle\phi_3\rvert$	0	0	0	0
$\langle\phi_4\rvert$	0	0	0	0

Tabela 1: Resultados da polarização dada por $\langle\phi_n| \hat{P} |\phi_m\rangle$ para $t = 0$.

A parte imaginária da susceptibilidade é nula!

Com hopping ($t \neq 0$)

$$E_1 \approx -\frac{U}{2} - \frac{4t^2}{U} \qquad E_2 = -\frac{U}{2} \qquad E_3 = \frac{U}{2} \qquad E_4 \approx \frac{U}{2} - \frac{4t^2}{U}$$

$$\begin{aligned}
|\phi_1\rangle &\approx \frac{U}{2t}|1\rangle + \frac{U}{2t}|2\rangle + |3\rangle + |4\rangle \\
|\phi_2\rangle &= -|1\rangle + |2\rangle \\
|\phi_3\rangle &= -|3\rangle + |4\rangle \\
|\phi_4\rangle &\approx -\frac{2t}{U}|1\rangle - \frac{2t}{U}|2\rangle + |3\rangle + |4\rangle
\end{aligned}$$

Com hopping ($t \neq 0$)

$$Im(\tilde{\chi}) = \frac{2\pi}{\hbar} \sum_{n,m} |\langle m| P |n\rangle|^2 \left(e^{-\beta E_n} - e^{-\beta E_m}\right) \delta(w_{nm} - w) \qquad (9)$$

	$\lvert\phi_1\rangle$	$\lvert\phi_2\rangle$	$\lvert\phi_3\rangle$	$\lvert\phi_4\rangle$
$\langle\phi_1\rvert$	0	$-\frac{\mu_0 U}{2At}$	0	0
$\langle\phi_2\rvert$	$-\frac{\mu_0 U}{2At}$	0	0	$2\frac{\mu_0 t}{BU}$
$\langle\phi_3\rvert$	0	0	0	0
$\langle\phi_4\rvert$	0	$2\frac{\mu_0 t}{BU}$	0	0

Tabela 2: Resultados dos elementos da matriz de polarização dada por $\langle\phi_n| \hat{P} |\phi_m\rangle$ para $t \neq 0$.

Com hopping ($t \neq 0$)

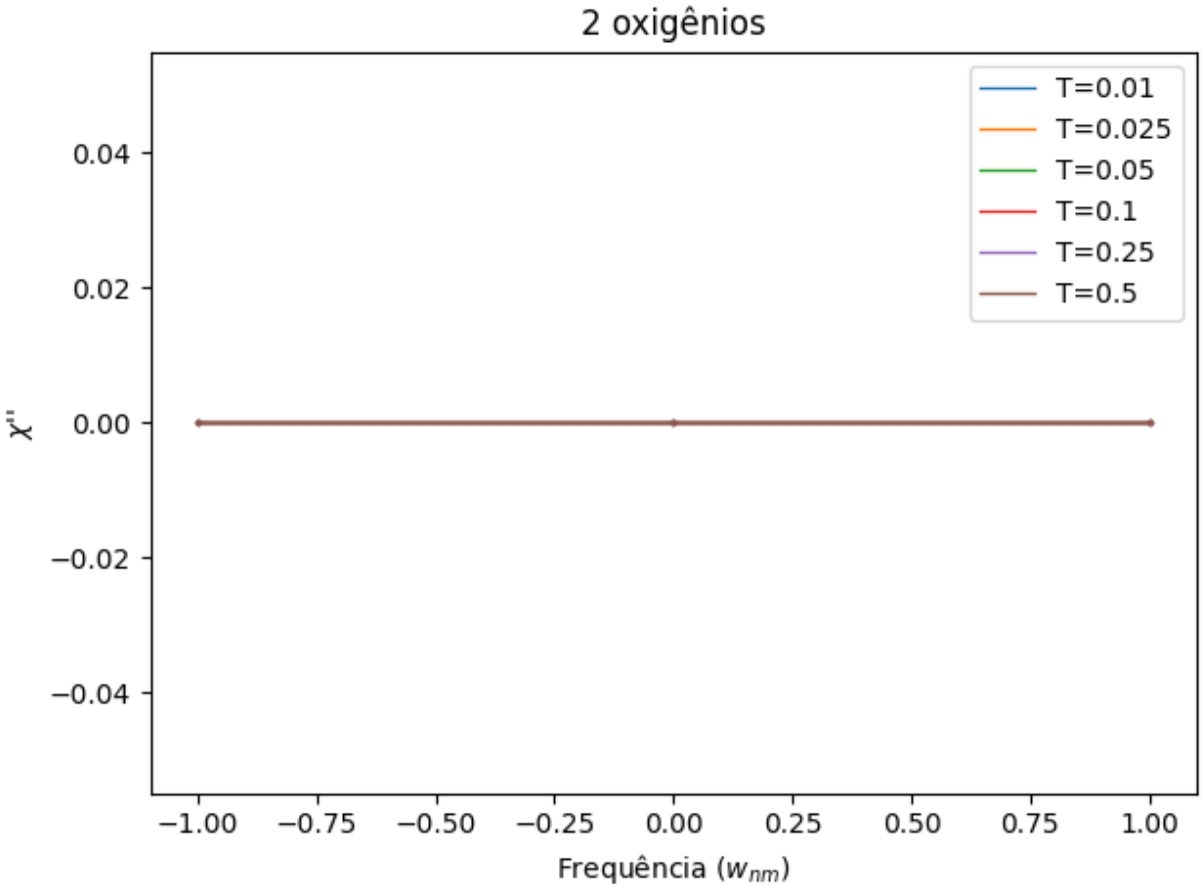
$$Im(\tilde{\chi}) = \frac{2\pi}{\hbar} \sum_{n,m} |\langle m| P |n\rangle|^2 \left(e^{-\beta E_n} - e^{-\beta E_m}\right) \delta(w_{nm} - w) \qquad (9)$$

		m			
		1	2	3	4
n	1	0	$\frac{\lvert\langle\phi_1\lvert P\rvert\phi_2\rangle\rvert^2}{Z}(e^{-\beta E_1} - e^{-\beta E_2})$	0	0
	2	$\frac{\lvert\langle\phi_2\lvert P\rvert\phi_1\rangle\rvert^2}{Z}(e^{-\beta E_2} - e^{-\beta E_1})$	0	0	$\frac{\lvert\langle\phi_2\lvert P\rvert\phi_4\rangle\rvert^2}{Z}(e^{-\beta E_2} - e^{-\beta E_4})$
	3	0	0	0	0
	4	0	$\frac{\lvert\langle\phi_4\lvert P\rvert\phi_2\rangle\rvert^2}{Z}(e^{-\beta E_4} - e^{-\beta E_2})$	0	0

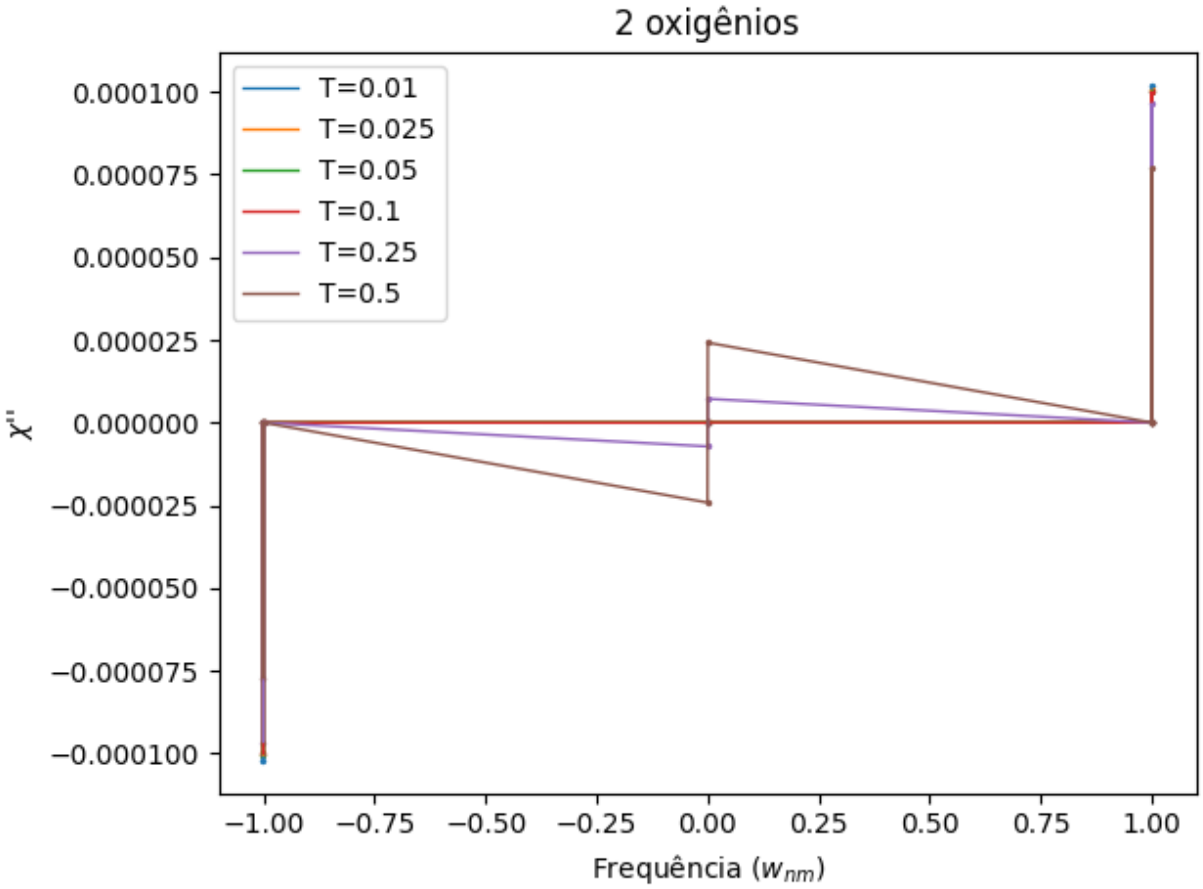
Tabela 3: Resultado da parte imaginária da susceptibilidade do sistema dada pela Equação 9 para $t \neq 0$.

Resultados Numéricos de Sistema Unidimensional com 2 oxigênios

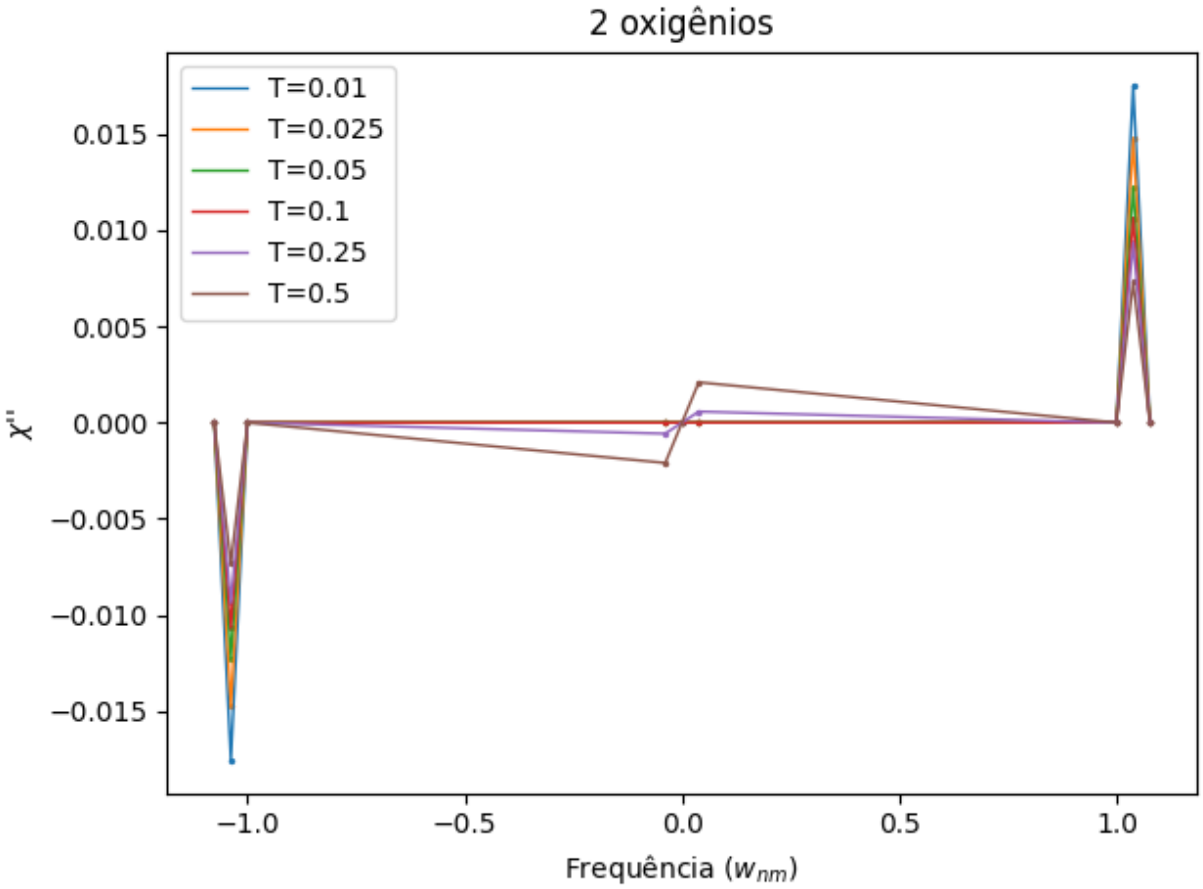
Sem hopping ($t = 0$)



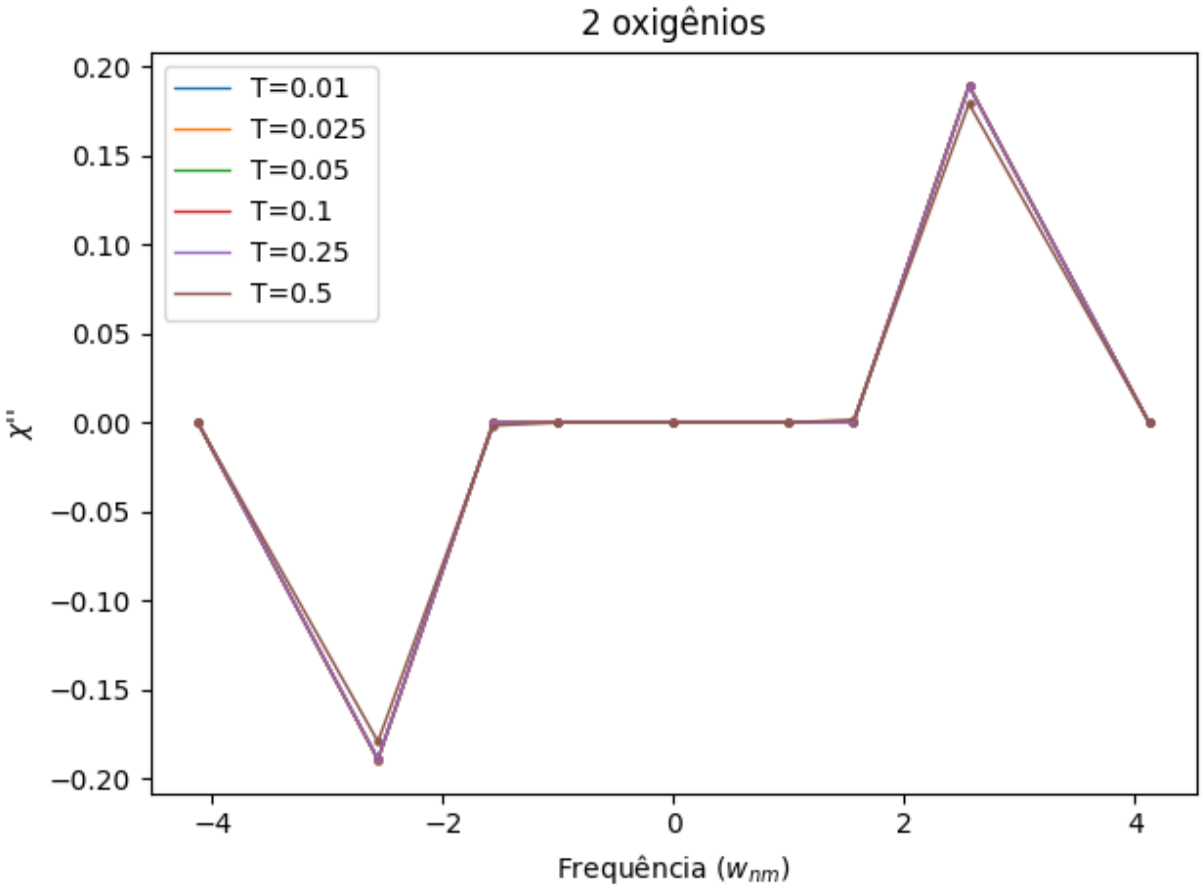
Com hopping ($t = 0.01$)

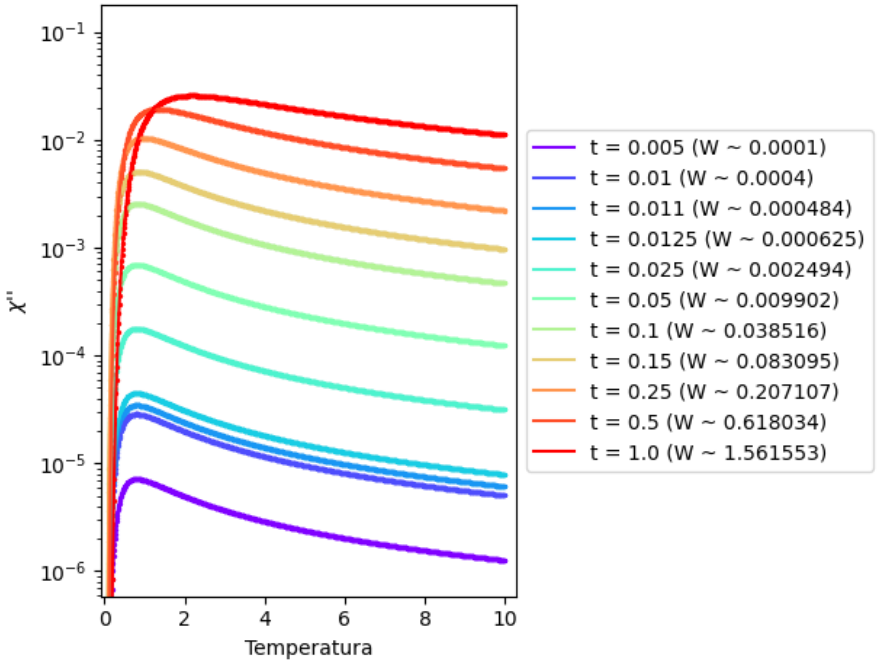


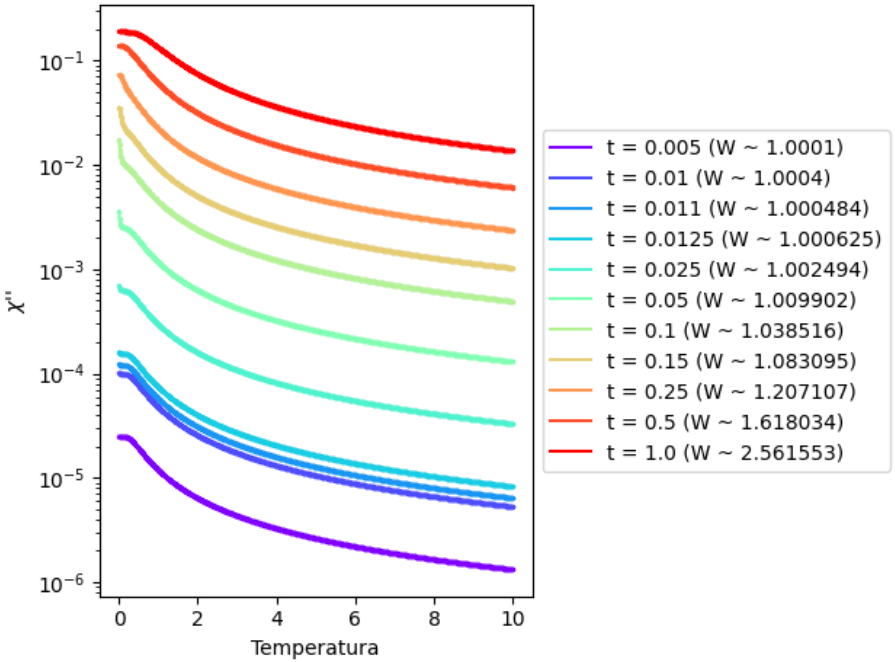
Com hopping ($t = 0.1$)

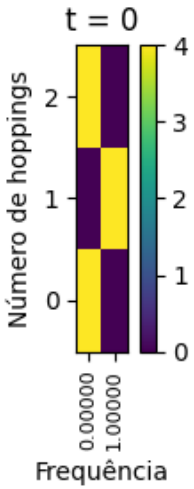


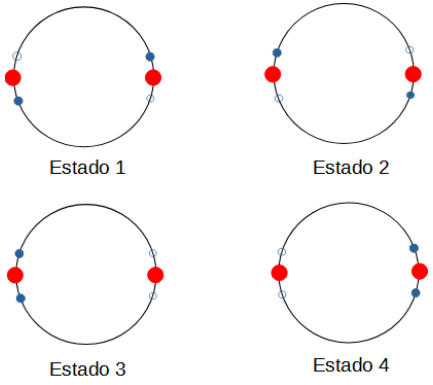
Com hopping ($t = 1.0$)

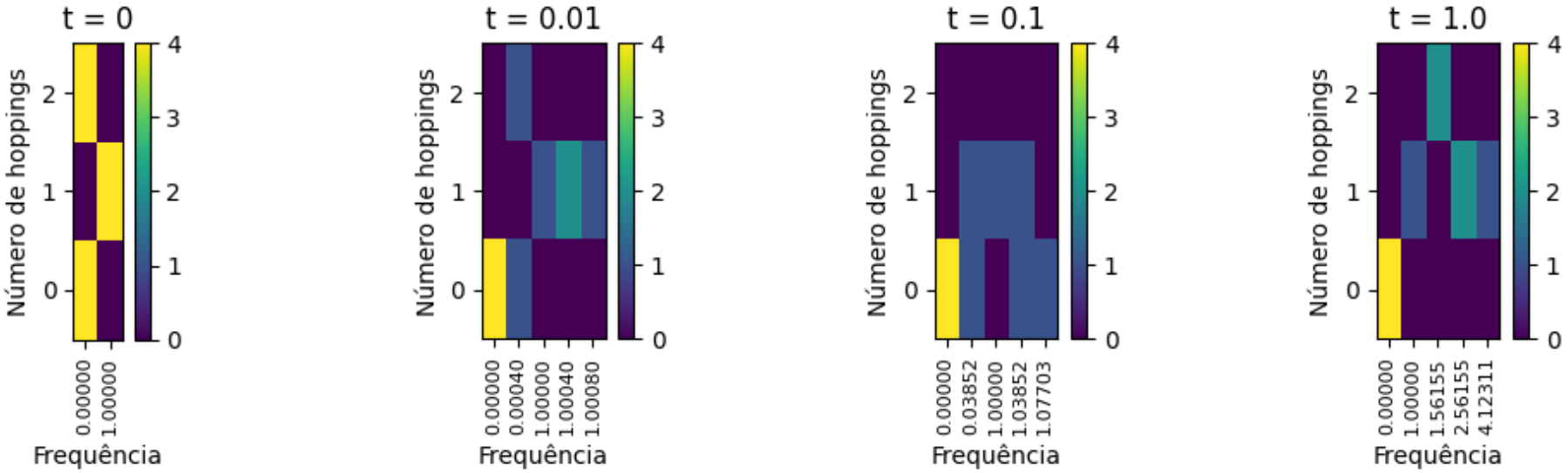



10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
χ''
0 2 4 6 8 10
Temperatura
t = 0.005 (W ~ 0.0001)
t = 0.01 (W ~ 0.0004)
t = 0.011 (W ~ 0.000484)
t = 0.0125 (W ~ 0.000625)
t = 0.025 (W ~ 0.002494)
t = 0.05 (W ~ 0.009902)
t = 0.1 (W ~ 0.038516)
t = 0.15 (W ~ 0.083095)
t = 0.25 (W ~ 0.207107)
t = 0.5 (W ~ 0.618034)
t = 1.0 (W ~ 1.561553)

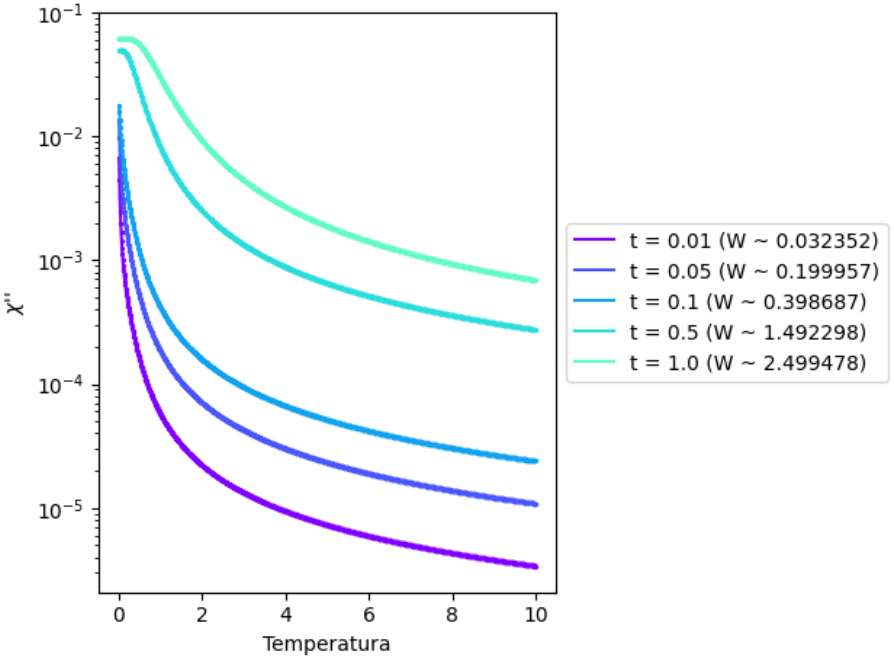

10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
χ''
0 2 4 6 8 10
Temperatura
t = 0.005 (W ~ 1.0001)
t = 0.01 (W ~ 1.0004)
t = 0.011 (W ~ 1.000484)
t = 0.0125 (W ~ 1.000625)
t = 0.025 (W ~ 1.002494)
t = 0.05 (W ~ 1.009902)
t = 0.1 (W ~ 1.038516)
t = 0.15 (W ~ 1.083095)
t = 0.25 (W ~ 1.207107)
t = 0.5 (W ~ 1.618034)
t = 1.0 (W ~ 2.561553)

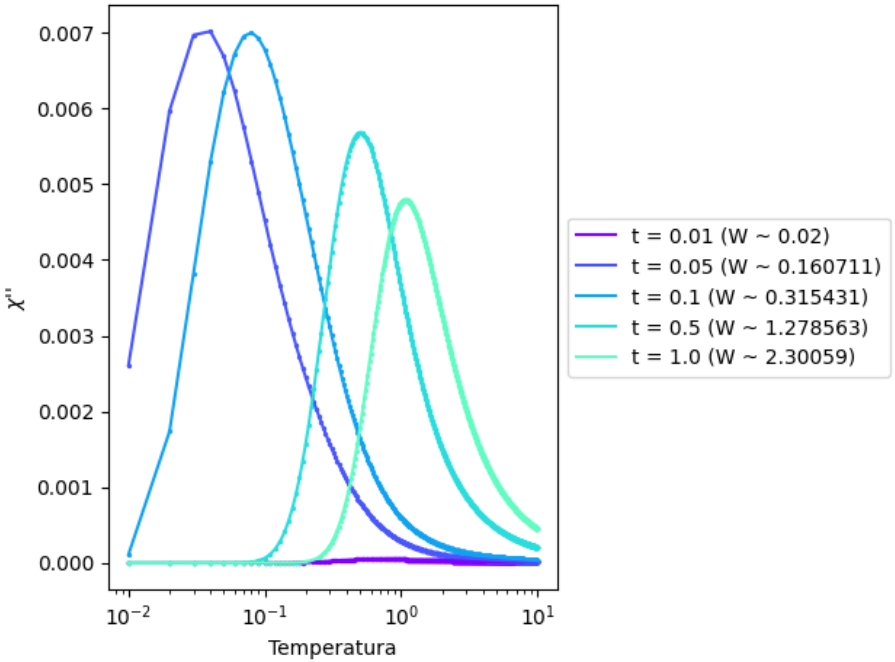

t = 0
Número de hoppings
0
1
2
0.00000
1.00000
Frequência
0
1
2
3
4

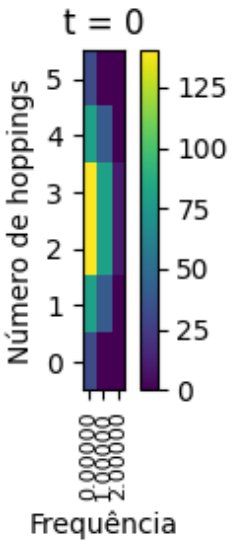

Estado 1
Estado 2
Estado 3
Estado 4

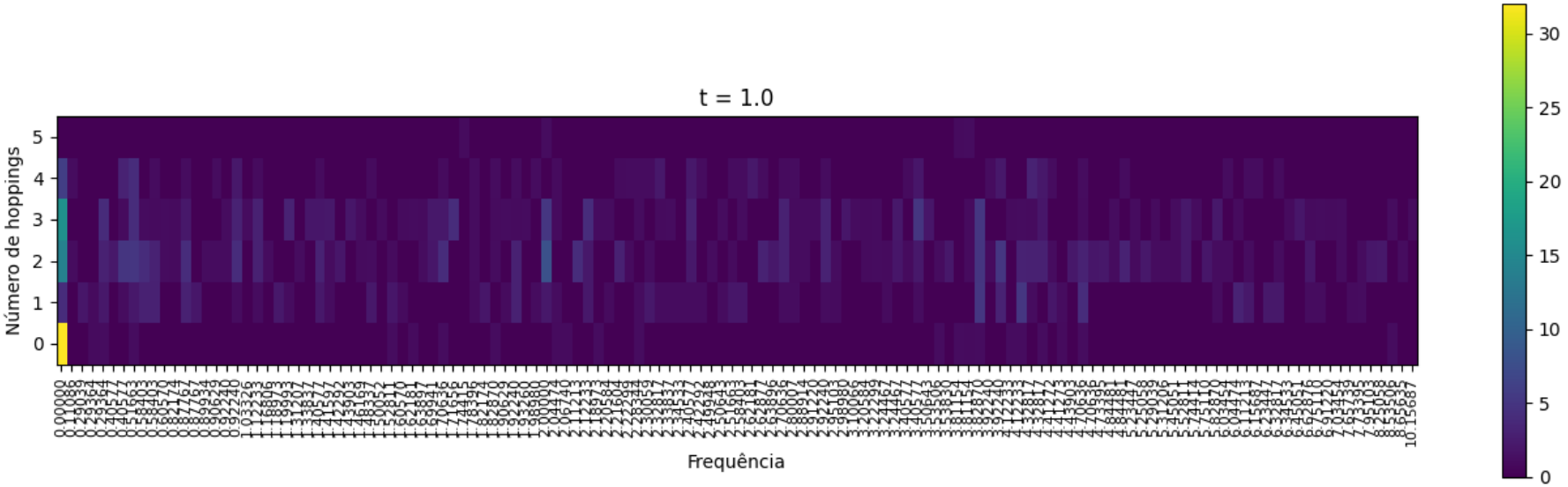

t = 0
t = 0.01
t = 0.1
t = 1.0
Número de hoppings
Frequência
0.00000
1.00000
0.00040
1.00040
1.00080
0.03852
1.03852
1.07703
1.56155
2.56155
4.12311

Resultados Numéricos de Sistema Unidimensional com 5 oxigênios

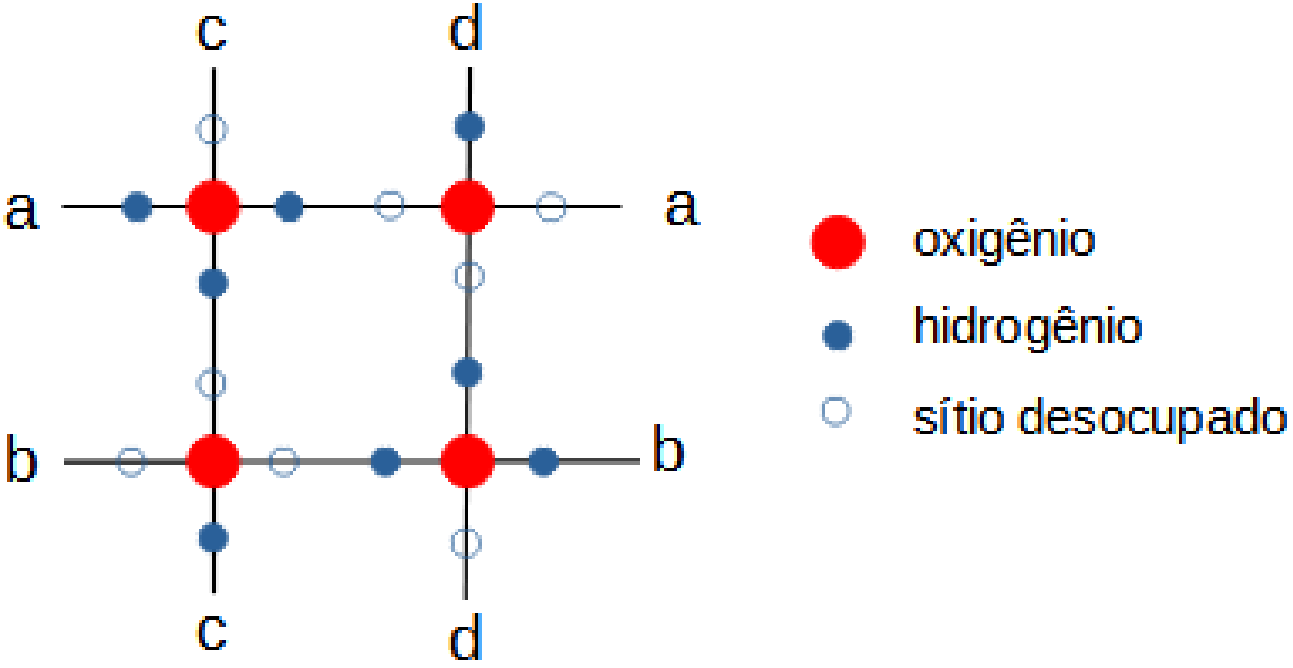

10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
χ''
0
2
4
6
8
10
Temperatura
t = 0.01 (W ~ 0.032352)
t = 0.05 (W ~ 0.199957)
t = 0.1 (W ~ 0.398687)
t = 0.5 (W ~ 1.492298)
t = 1.0 (W ~ 2.499478)

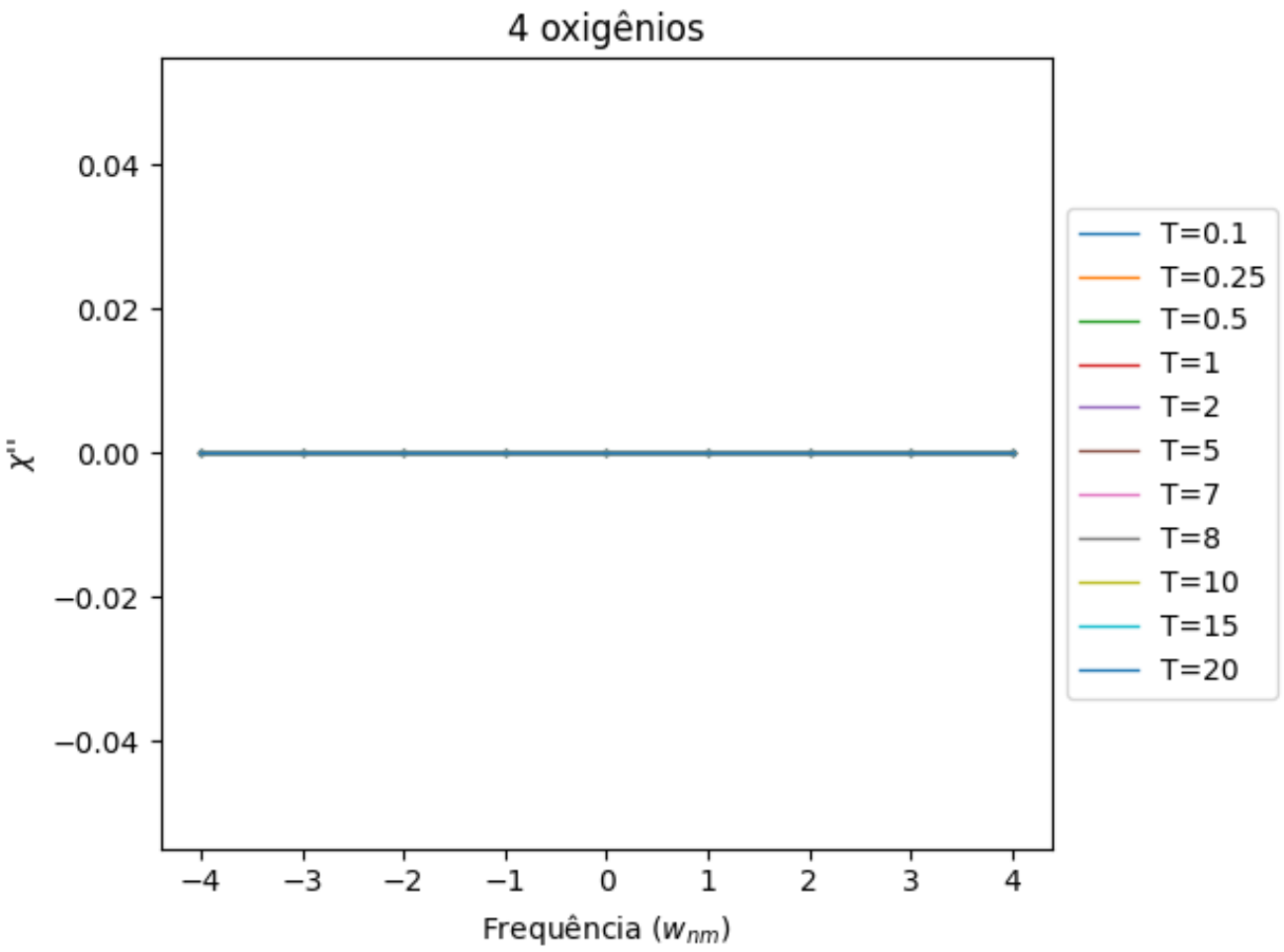

0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
χ''
10^{-2}
10^{-1}
10^{0}
10^{1}
Temperatura
t = 0.01 (W ~ 0.02)
t = 0.05 (W ~ 0.160711)
t = 0.1 (W ~ 0.315431)
t = 0.5 (W ~ 1.278563)
t = 1.0 (W ~ 2.30059)

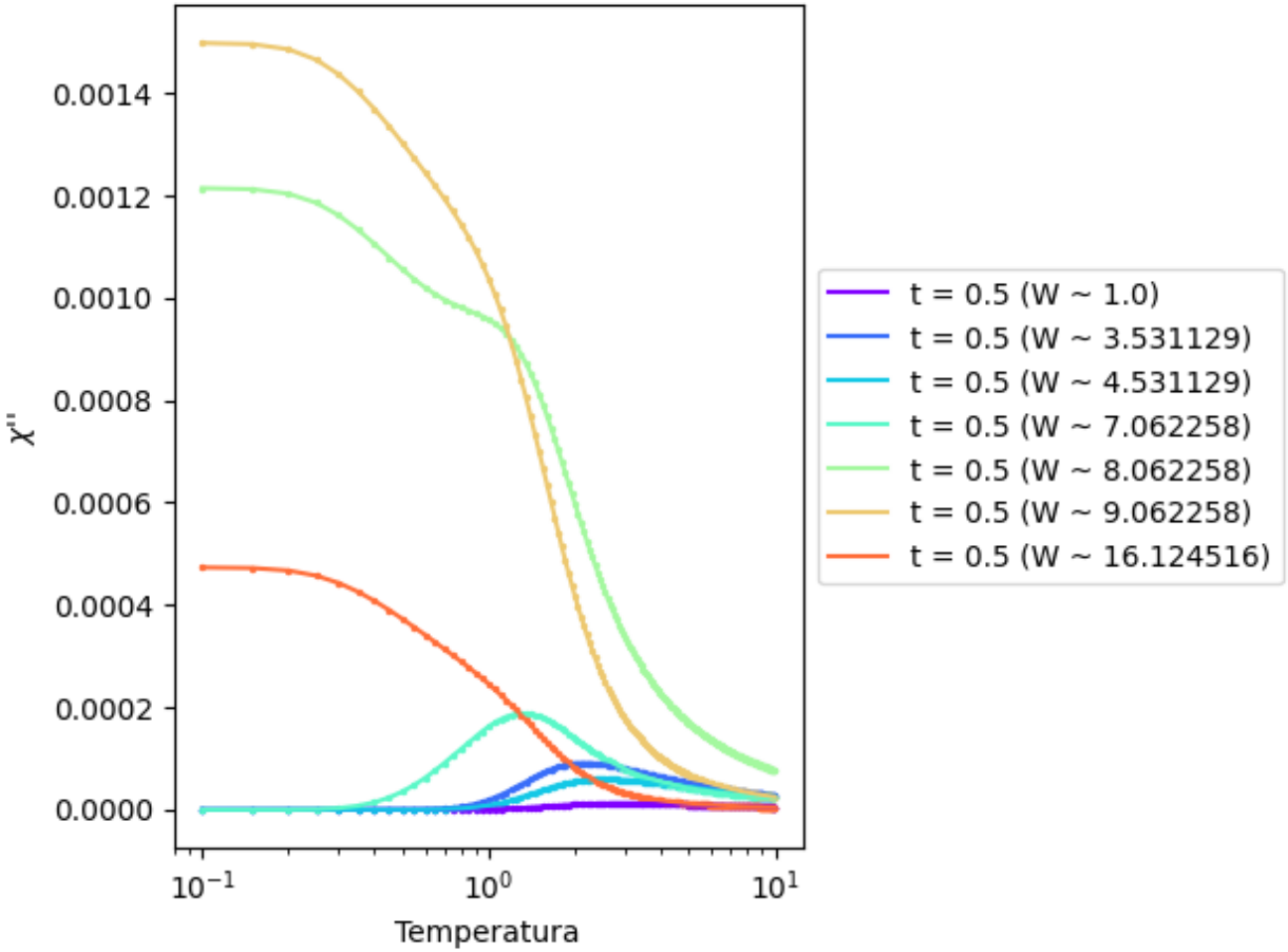

t = 0
Número de hoppings
Frequência
0
1
2
3
4
5
0
25
50
75
100
125

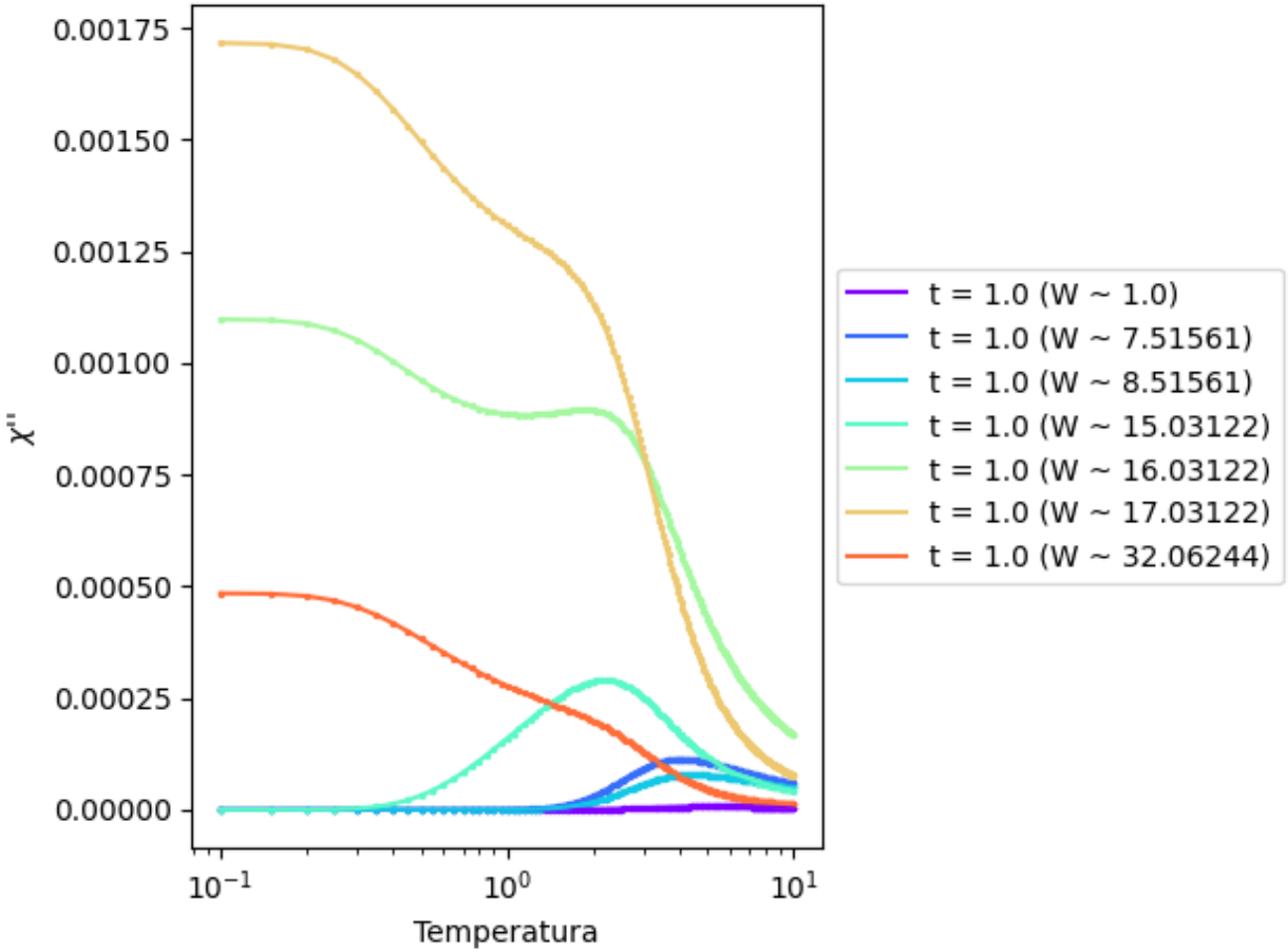

t = 1.0
Número de hoppings
Frequência
0
1
2
3
4
5
0
5
10
15
20
25
30

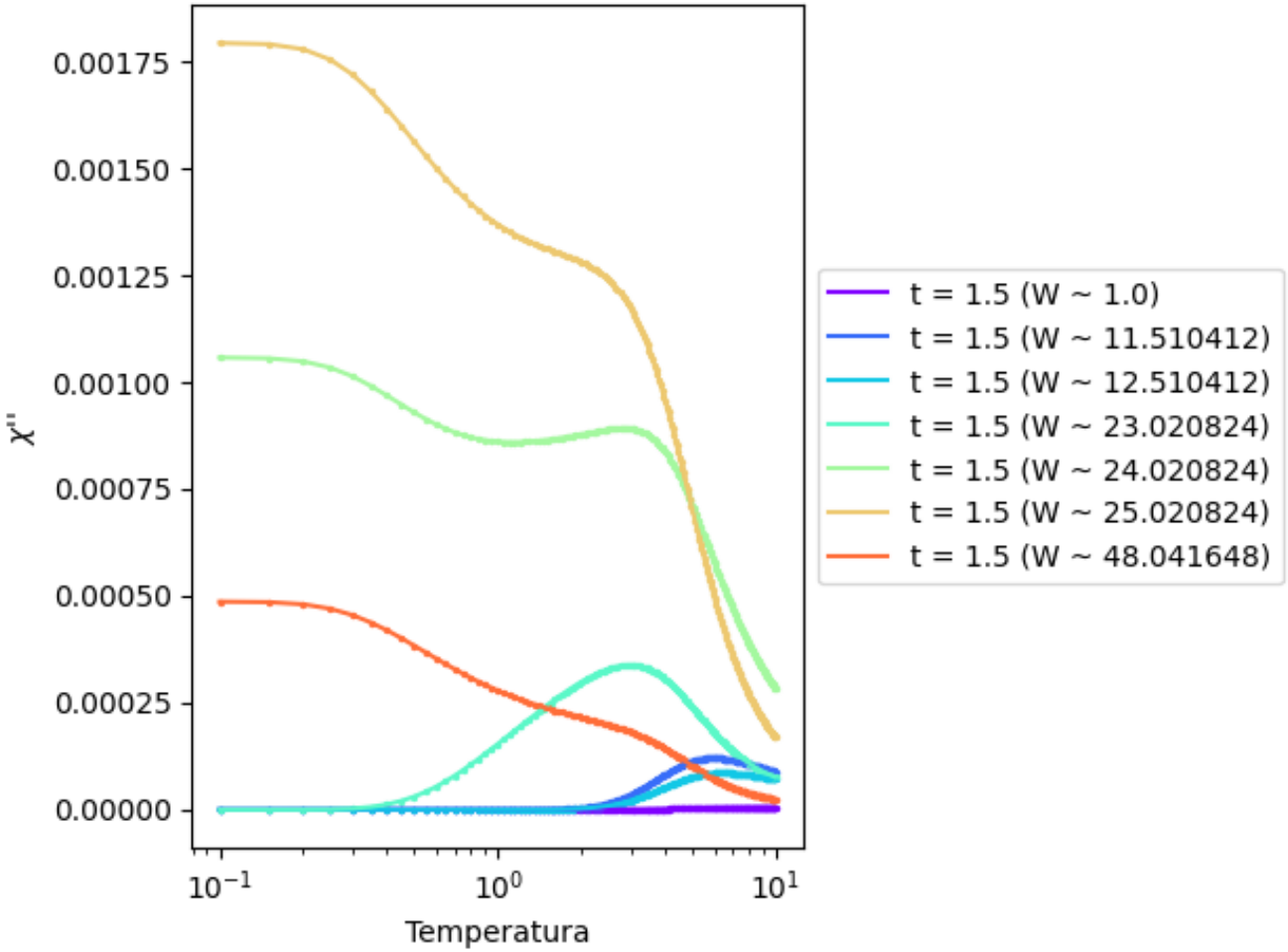
Resultados Numéricos de Sistema Bidimensional com 4 oxigênios

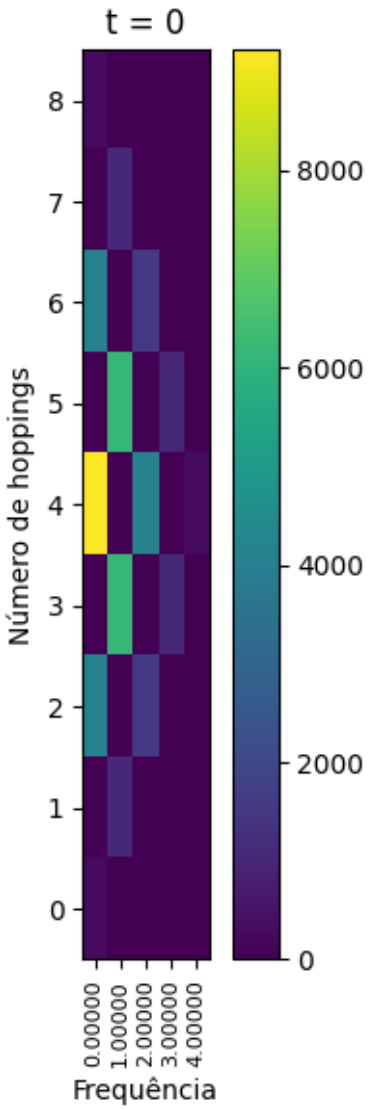

c
d
a
a
b
b
c
d
oxigênio
hidrogênio
sítio desocupado

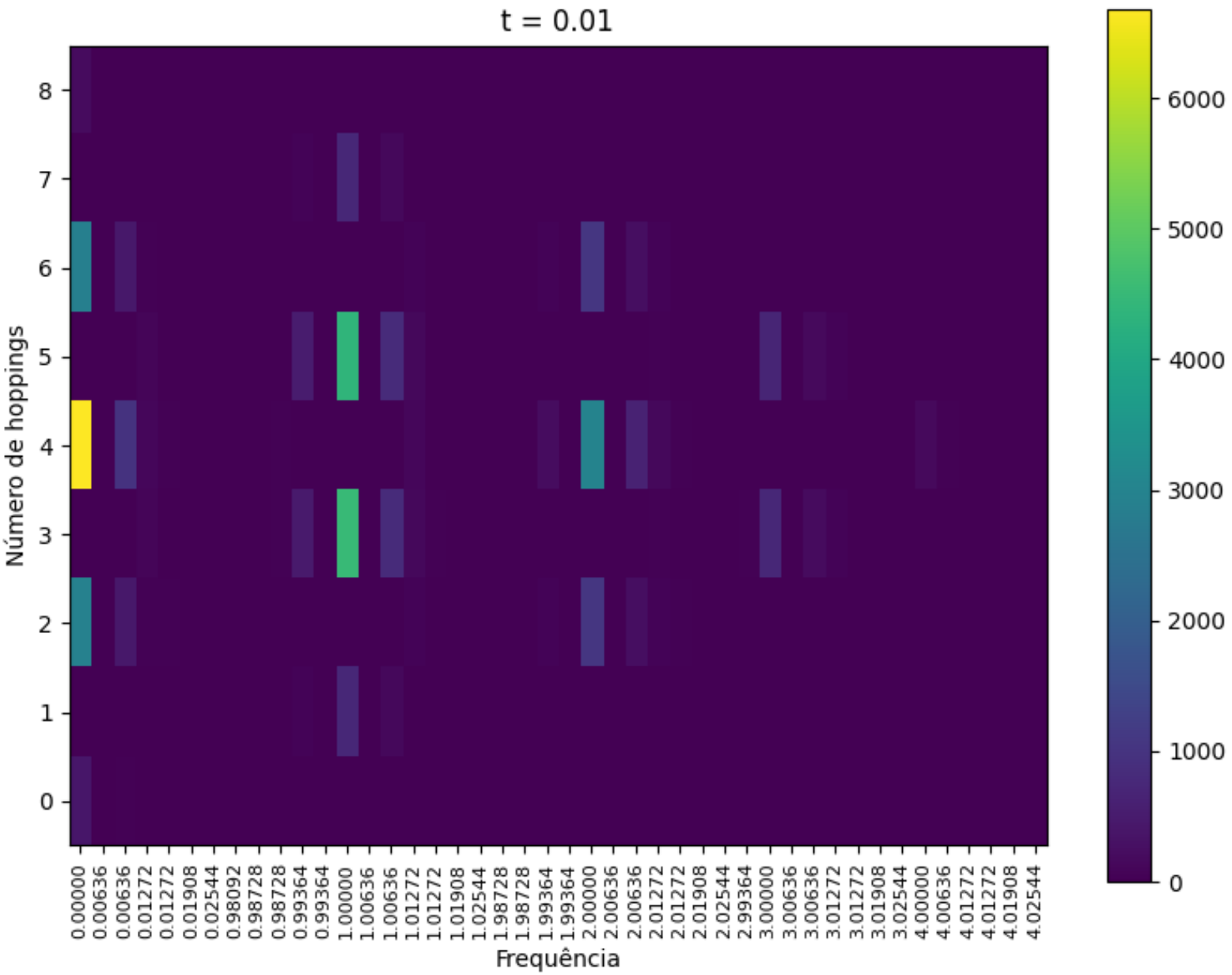

4 oxigênios
0.04
0.02
0.00
−0.02
−0.04
χ''
−4
−3
−2
−1
0
1
2
3
4
Frequência (w_{nm})
T=0.1
T=0.25
T=0.5
T=1
T=2
T=5
T=7
T=8
T=10
T=15
T=20

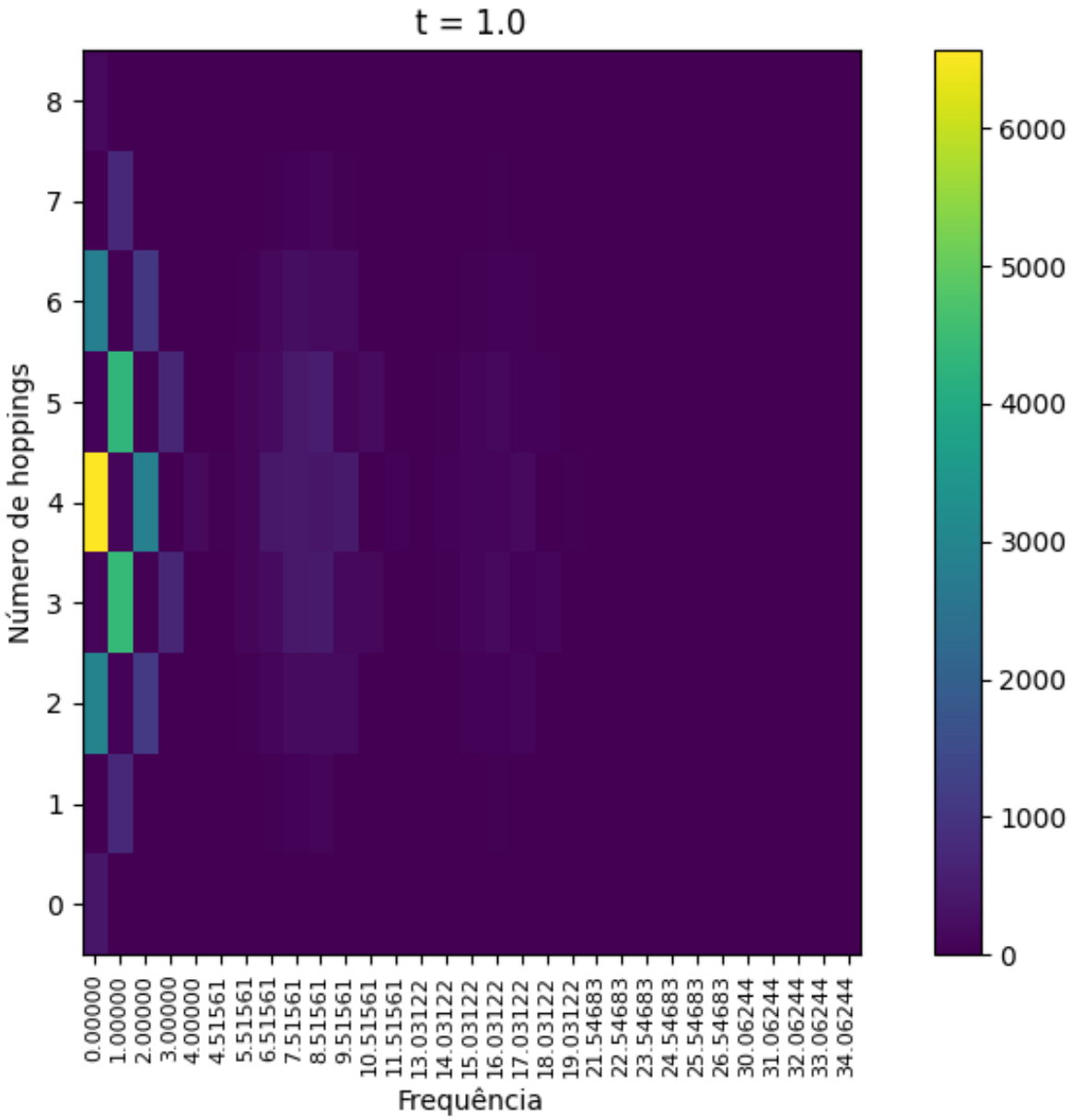

0.0014
0.0012
0.0010
0.0008
0.0006
0.0004
0.0002
0.0000
χ''
10^{-1}
10^{0}
10^{1}
Temperatura
t = 0.5 (W ~ 1.0)
t = 0.5 (W ~ 3.531129)
t = 0.5 (W ~ 4.531129)
t = 0.5 (W ~ 7.062258)
t = 0.5 (W ~ 8.062258)
t = 0.5 (W ~ 9.062258)
t = 0.5 (W ~ 16.124516)

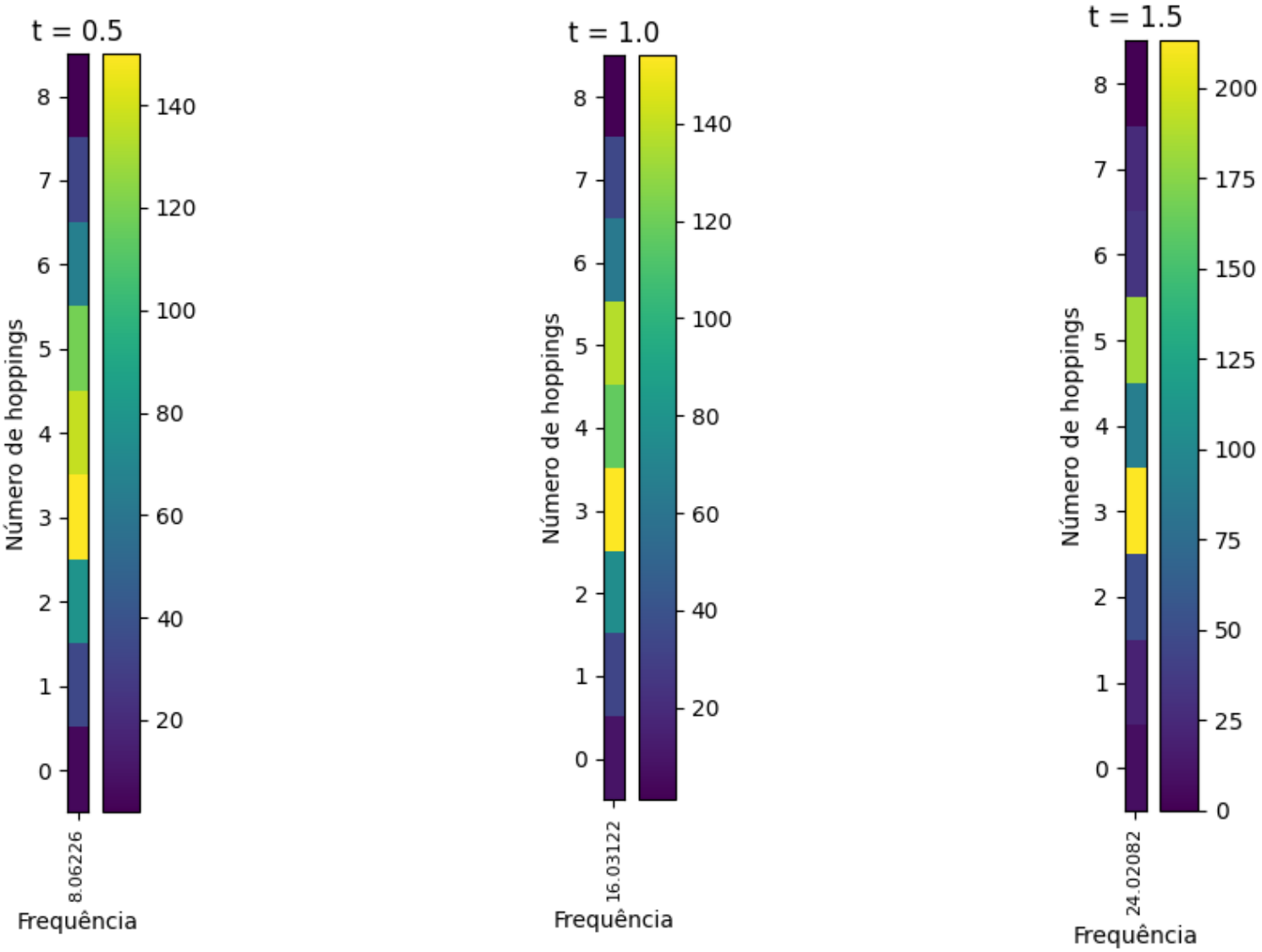

0.00175
0.00150
0.00125
0.00100
0.00075
0.00050
0.00025
0.00000
χ''
10^{-1}
10^{0}
10^{1}
Temperatura
t = 1.0 (W ~ 1.0)
t = 1.0 (W ~ 7.51561)
t = 1.0 (W ~ 8.51561)
t = 1.0 (W ~ 15.03122)
t = 1.0 (W ~ 16.03122)
t = 1.0 (W ~ 17.03122)
t = 1.0 (W ~ 32.06244)


0.00175
0.00150
0.00125
0.00100
0.00075
0.00050
0.00025
0.00000
χ''
10^{-1}
10^{0}
10^{1}
Temperatura
t = 1.5 (W ~ 1.0)
t = 1.5 (W ~ 11.510412)
t = 1.5 (W ~ 12.510412)
t = 1.5 (W ~ 23.020824)
t = 1.5 (W ~ 24.020824)
t = 1.5 (W ~ 25.020824)
t = 1.5 (W ~ 48.041648)

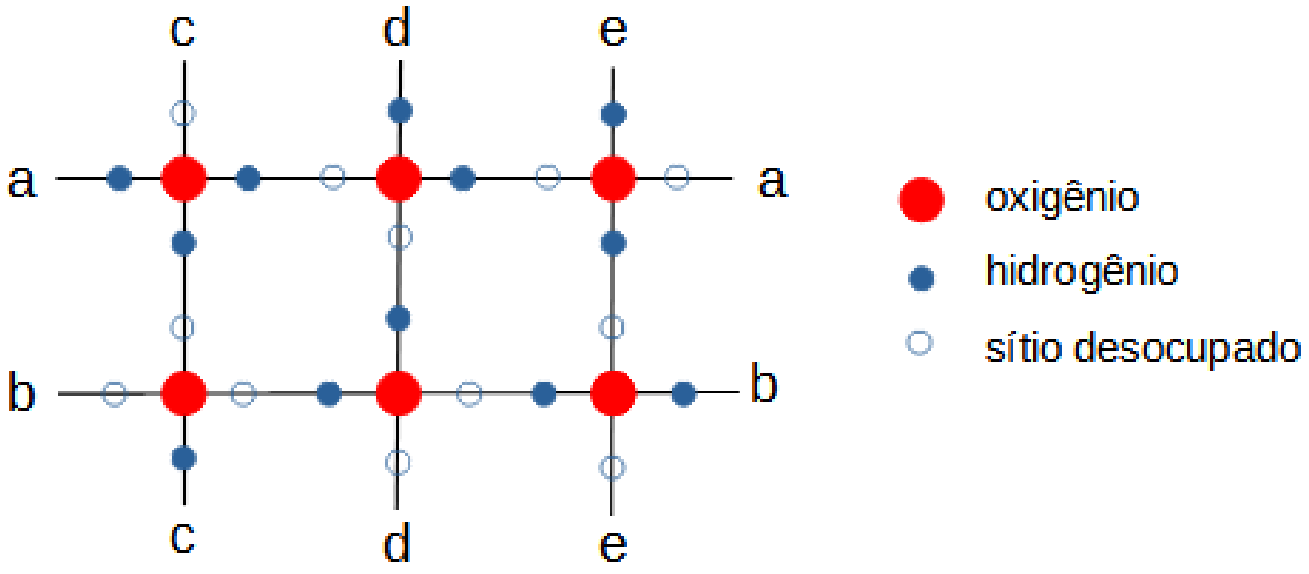

t = 0
Número de hoppings
0
1
2
3
4
5
6
7
8
0.00000
1.00000
2.00000
3.00000
4.00000
Frequência
0
2000
4000
6000
8000

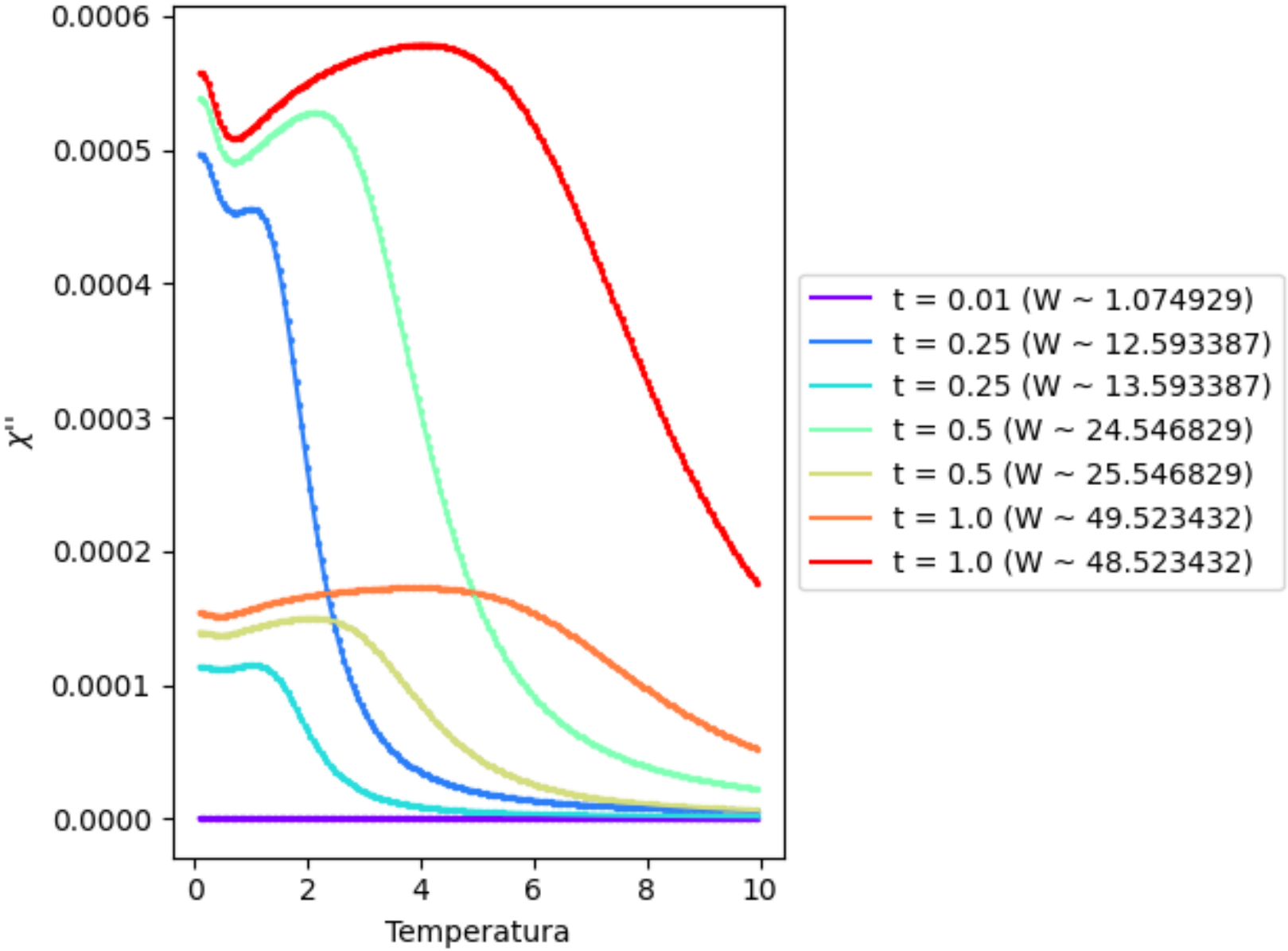

t = 0.01
Número de hoppings
Frequência
0
1
2
3
4
5
6
7
8
0.00000
0.00636
0.00636
0.01272
0.01272
0.01908
0.02544
0.98092
0.98728
0.98728
0.99364
0.99364
1.00000
1.00636
1.00636
1.01272
1.01272
1.01908
1.02544
1.98728
1.98728
1.99364
1.99364
2.00000
2.00636
2.00636
2.01272
2.01272
2.01908
2.02544
2.99364
3.00000
3.00636
3.00636
3.01272
3.01272
3.01908
3.02544
4.00000
4.00636
4.01272
4.01272
4.01908
4.02544
0
1000
2000
3000
4000
5000
6000

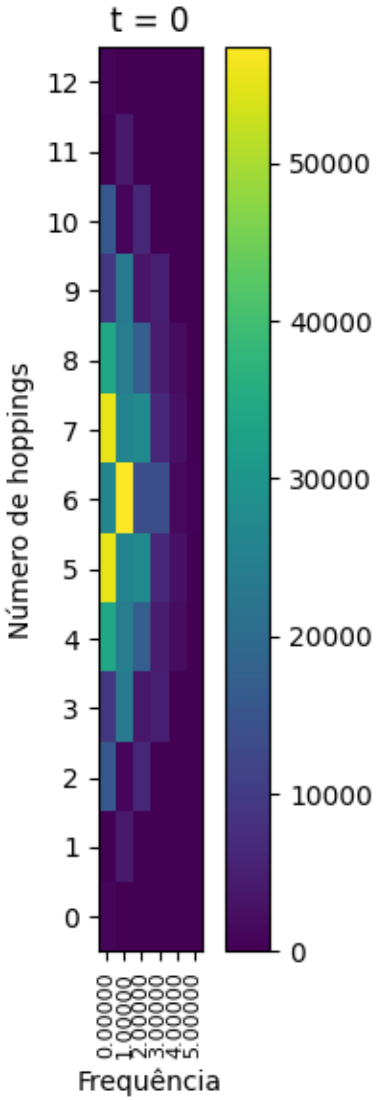

t = 1.0
Número de hoppings
0
1
2
3
4
5
6
7
8
Frequência
0.00000
1.00000
2.00000
3.00000
4.00000
4.51561
5.51561
6.51561
7.51561
8.51561
9.51561
10.51561
11.51561
13.03122
14.03122
15.03122
16.03122
17.03122
18.03122
19.03122
21.54683
22.54683
23.54683
24.54683
25.54683
26.54683
30.06244
31.06244
32.06244
33.06244
34.06244
0
1000
2000
3000
4000
5000
6000

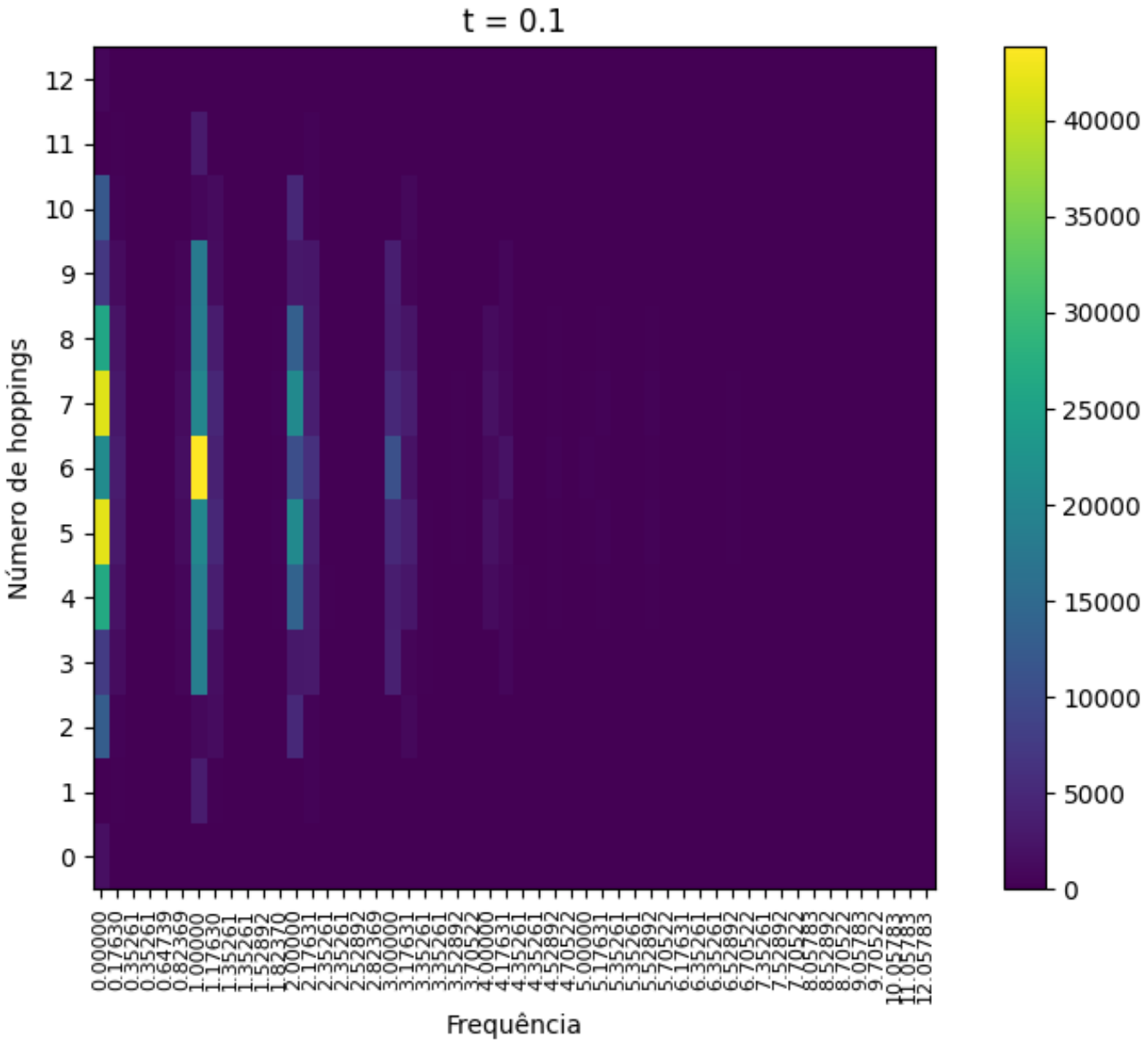

t = 0.5
Número de hoppings
Frequência
8.06226
t = 1.0
Número de hoppings
Frequência
16.03122
t = 1.5
Número de hoppings
Frequência
24.02082

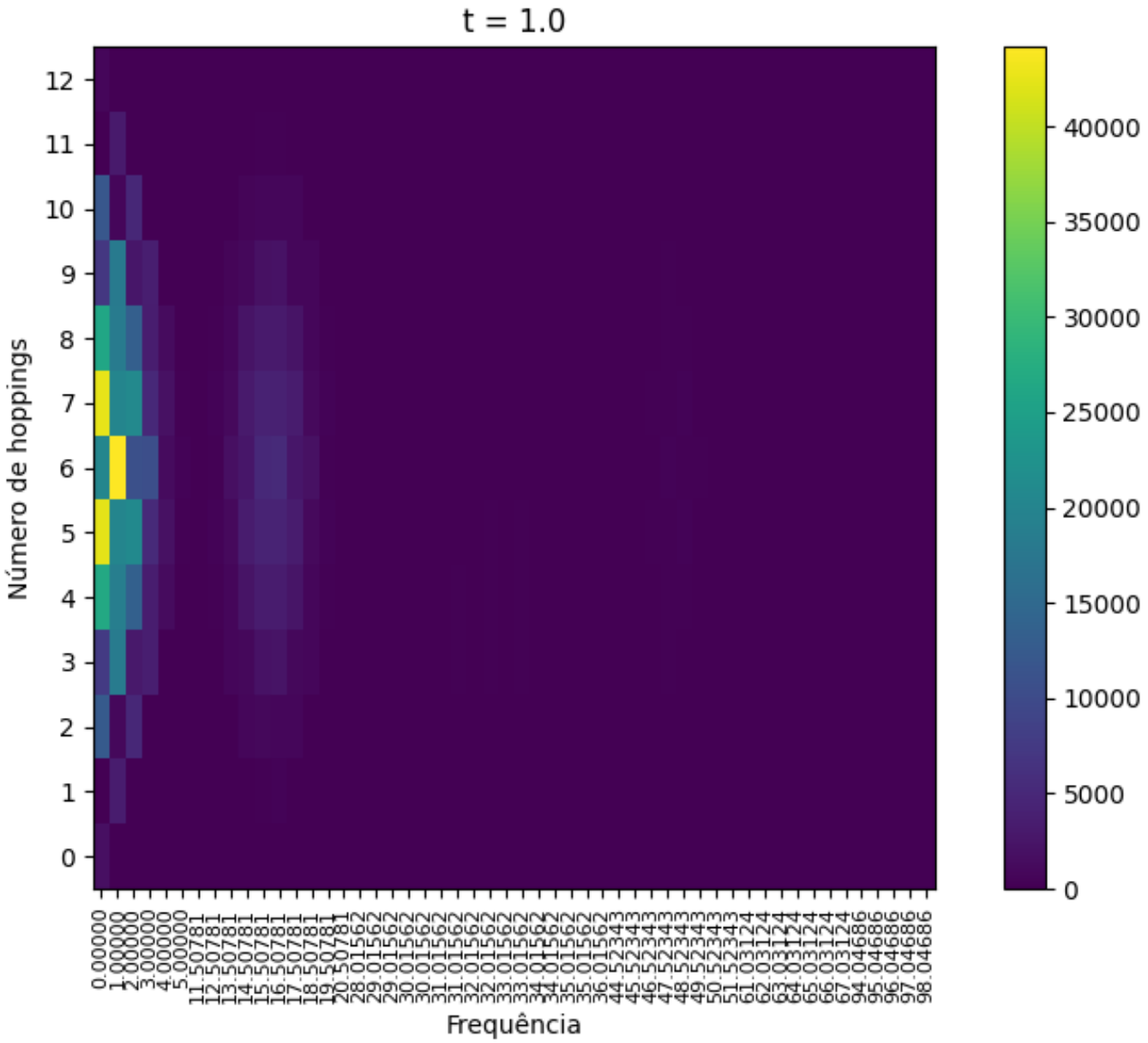
Resultados Numéricos de Sistema Bidimensional com 6 oxigênios


c
d
e
a
a
b
b
c
d
e
oxigênio
hidrogênio
sítio desocupado


0.0006
0.0005
0.0004
0.0003
0.0002
0.0001
0.0000
χ''
0
2
4
6
8
10
Temperatura
t = 0.01 (W ~ 1.074929)
t = 0.25 (W ~ 12.593387)
t = 0.25 (W ~ 13.593387)
t = 0.5 (W ~ 24.546829)
t = 0.5 (W ~ 25.546829)
t = 1.0 (W ~ 49.523432)
t = 1.0 (W ~ 48.523432)


t = 0
Número de hoppings
Frequência
0
1
2
3
4
5
6
7
8
9
10
11
12
0.00000
1.00000
2.00000
3.00000
4.00000
5.00000
0
10000
20000
30000
40000
50000


t = 0.1
Número de hoppings
Frequência
0
1
2
3
4
5
6
7
8
9
10
11
12
0
5000
10000
15000
20000
25000
30000
35000
40000


t = 1.0
Número de hoppings
Frequência
0
1
2
3
4
5
6
7
8
9
10
11
12
0
5000
10000
15000
20000
25000
30000
35000
40000

1 Introdução

2 Objetivos

3 Referencial Teórico

4 Modelo

5 Metodologia

6 Resultados

7 Conclusões

8 Referências

Conclusões

Sistema Unidimensional:

- Não existe anomalia para sistemas unidimensionais periódicos;
- Facilitar o hopping aumenta a susceptibilidade imaginária e as frequências dos picos;
- Temperatura somente altera a intensidade de χ'', mas não altera as frequências que ocorrem;
- Susceptibilidade imaginária é nula para sistemas sem hopping;

Conclusões

Sistema Bidimensional:

- É possível obter a anomalia para uma rede quadrada periódica;
- Susceptibilidade imaginária é nula para sistemas sem hopping;
- Existe tunelamento coletivo para frequências sem anomalia;

Conclusões

Sistema Bidimensional:

- É possível obter a anomalia para uma rede quadrada periódica;
- Susceptibilidade imaginária é nula para sistemas sem hopping;
- Existe tunelamento coletivo para frequências sem anomalia;

Não foi possível concluir que a coletividade dos tunelamentos é o mecanismo da anomalia da constante dielétrica

1 Introdução

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8 Referências

CHAPLIN, M. *Water Structure and Science*. ⟨https://water.lsbu.ac.uk/water/water_structure_science.html⟩.
ELLISON, W. J.; LAMKAOUCHI, K.; MOREAU, J. M. Water: a dielectric reference. *Journal of Molecular Liquids*, v. 68, p. 171–279, 1996.
FUENTES-LANDETE, V. et al. Crystalline and amorphous ices. *IOS Press*, 2015.
YEN, F.; GAO, T. Dielectric anomaly in ice near 20 k: Evidence of macroscopic quantum phenomena. *The Journal of Physical Chemical Letters*, v. 6, n. 14, p. 2822–2825, 2015.

Obrigada!

Susceptibilidade complexa

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}' \tag{10}$$

Susceptibilidade complexa

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}' \tag{10}$$

$$\hat{\mathcal{H}}' = -f(t)\hat{A} \tag{11}$$

$$\rho_{eq} = \frac{\exp(-\beta\hat{\mathcal{H}}_0)}{Tr\exp(-\beta\hat{\mathcal{H}}_0)} \tag{12}$$

Susceptibilidade complexa

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}' \tag{10}$$

$$\hat{\mathcal{H}}' = -f(t)\hat{A} \tag{11}$$

$$\rho_{eq} = \frac{\exp(-\beta\hat{\mathcal{H}}_0)}{Tr\exp(-\beta\hat{\mathcal{H}}_0)} \tag{12}$$

$$\langle \delta B(t) \rangle_{\rho_{eq}} = \langle B \rangle_{\delta\rho(t)} \tag{13}$$

$$\hat{\rho}(t) = \rho_{eq} + \delta\rho(t) \tag{14}$$

Pela representação de Heinsenberg:

$$-\frac{[\hat{\rho}, \hat{\mathcal{H}}]}{i\hbar} = \frac{d\hat{\rho}}{dt} = -i\mathcal{L}\hat{\rho} \tag{15}$$

$$\mathcal{L} = \mathcal{L}_0 + \delta\mathcal{L}(t) \tag{16}$$

Assim,

$$\frac{d\hat{\rho}}{dt} = \frac{d\delta\rho}{dt} = -i\delta\mathcal{L}(t)\rho_{eq} - i\mathcal{L}_0\delta\rho(t) \tag{17}$$

$$\frac{d\hat{\rho}}{dt} = \frac{d\delta\rho}{dt} = -i\delta\mathcal{L}(t)\rho_{eq} - i\mathcal{L}_0\delta\rho(t) \tag{18}$$

A solução dessa equação diferencial não-homogênea é:

$$\delta\rho(t) = -\frac{i}{\hbar}\int_{-\infty}^{t} dt' f(t')[\rho_{eq}, \hat{A}(t'-t)] \tag{19}$$

$$\langle \hat{B} \rangle_{\delta\rho(t)} = \int_{-\infty}^{t} dt' f(t') \frac{Tr\left([\rho_{eq}, \hat{A}(t'-t)]\hat{B}(0)\right)}{i\hbar} = \\ = \int_{-\infty}^{t} dt' \Phi_{AB}(t-t') f(t') \tag{20}$$

Sendo $t - t' = \tau$

$$\Phi_{AB}(\tau) = \frac{1}{i\hbar\mathcal{Z}} Tr\left([\rho_{eq}, \hat{A}(\tau)]\hat{B}(0)\right) = \\ = \frac{1}{i\hbar} \langle [\hat{A}(0), \hat{B}(\tau)] \rangle_{\rho_{eq}} \tag{21}$$

$$
\begin{aligned}
\Phi_{AB}(\tau) &= \frac{1}{i\hbar} \left\langle [\hat{A}(0), \hat{B}(\tau)] \right\rangle_{\rho_{eq}} = \\
&= \frac{1}{i\hbar \mathcal{Z}} \sum_{n,m} \langle n| A |m\rangle \langle m| B |n\rangle e^{-i\omega_{nm}\tau} \left(e^{-\beta E_n} - e^{-\beta E_m} \right)
\end{aligned}
\tag{22}
$$

$$\Phi_{AB}(\tau) = \frac{1}{i\hbar} \left\langle [\hat{A}(0), \hat{B}(\tau)] \right\rangle_{\rho_{eq}} = \\ = \frac{1}{i\hbar\mathcal{Z}} \sum_{n,m} \langle n| A |m\rangle \langle m| B |n\rangle e^{-i\omega_{nm}\tau} \left(e^{-\beta E_n} - e^{-\beta E_m}\right) \tag{22}$$

Com a transformada de Fourier:

$$\tilde{\chi}_{AB}(\tau) = \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \Phi_{AB}(\tau) H(\tau) = \\ = \lim_{\xi \to 0} \frac{1}{\hbar\mathcal{Z}} \sum_{n,m} \frac{\langle n| A |m\rangle \langle m| B |n\rangle \left(e^{-\beta E_n} - e^{-\beta E_m}\right)}{w_{nm} - w + i\xi} \tag{23}$$

$$\tilde{\chi}_{AB}(\tau) = \lim_{\xi \to 0} \frac{1}{\hbar \mathcal{Z}} \sum_{n,m} \langle n| A |m\rangle \langle m| B |n\rangle \left(e^{-\beta E_n} - e^{-\beta E_m} \right) \frac{w_{nm} - w - i\xi}{(w_{nm} - w)^2 + \xi^2} \quad (24)$$

$$\lim_{\xi \to 0} \frac{\xi}{(w_{nm} - w)^2 + \xi^2} = \pi \delta(w_{nm} - w), \quad (25)$$

$$Im(\tilde{\chi}) = -\frac{\pi}{\hbar \mathcal{Z}} \sum_{n,m} \langle n| A |m\rangle \langle m| B |n\rangle \left(e^{-\beta E_n} - e^{-\beta E_m}\right) \delta(w_{nm} - w) \tag{26}$$

$$Im(\tilde{\chi}) = -\frac{\pi}{\hbar \mathcal{Z}} \sum_{n,m} |\langle n| P |m\rangle|^2 \left(e^{-\beta E_n} - e^{-\beta E_m}\right) \delta(w_{nm} - w) \tag{27}$$

$$Im(\tilde{\chi}) = -\frac{\pi}{\hbar \mathcal{Z}} \sum_{n,m} \langle n| A |m\rangle \langle m| B |n\rangle \left(e^{-\beta E_n} - e^{-\beta E_m}\right) \delta(w_{nm} - w) \tag{26}$$

$$Im(\tilde{\chi}) = -\frac{\pi}{\hbar \mathcal{Z}} \sum_{n,m} |\langle n| P |m\rangle|^2 \left(e^{-\beta E_n} - e^{-\beta E_m}\right) \delta(w_{nm} - w) \tag{27}$$

$$\epsilon = \chi + 1 \tag{28}$$