Interesting Results from Statistical Mechanics

- Reality of $\frac{1}{2}$ in $\epsilon_n = (n + \frac{1}{2})\hbar\omega$
- Fluctuations in the *thermodynamic* variables
- Counter intuitive thermodynamic results

Reality of $\frac{1}{2}$ in $\epsilon_n = (n + \frac{1}{2})\hbar\omega$

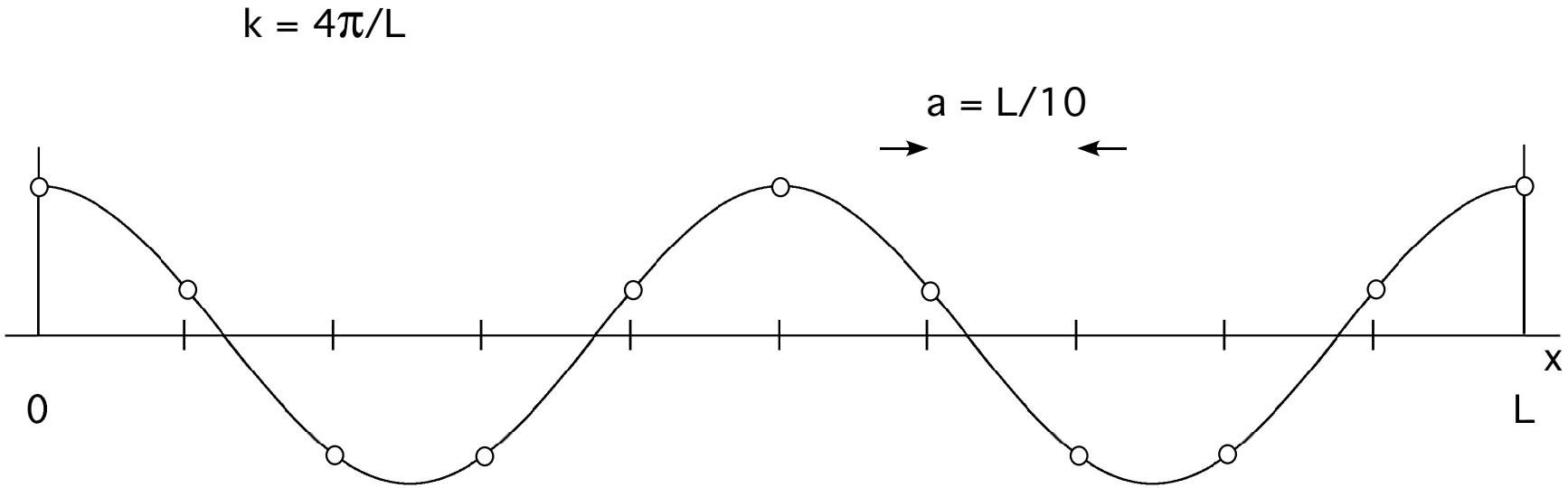
Difference in the zero temperature lattice spacing of ^{6}Li and ^{7}Li

Begin with a review of phonons as elementary excitations in solids

When dealing with motion on a lattice with spacing a, only a finite set of wavevectors is necessary, those that fall in the interval

$$-\frac{\pi}{a} < k_x \leq \frac{\pi}{a}$$

Those outside this region give no new states.



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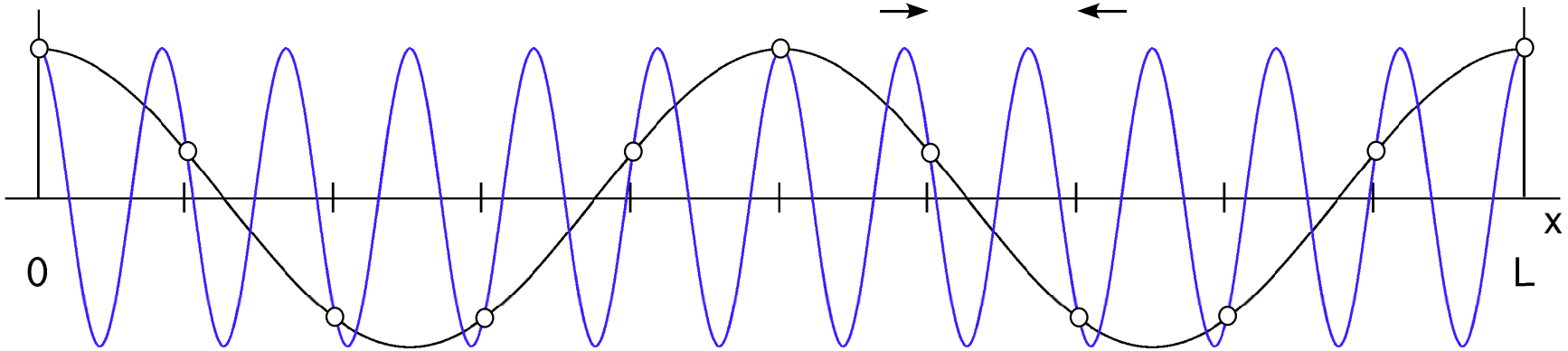
$k = 4\pi/L$

$k' = 4\pi/L + (1)(2\pi/a) = 24\pi/L$

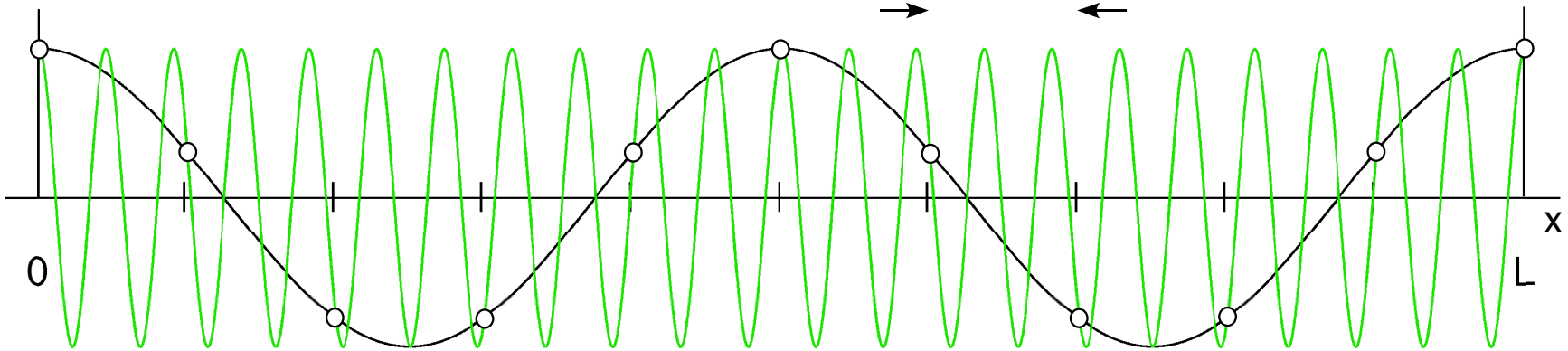
$a = L/10$



$k = 4\pi/L$

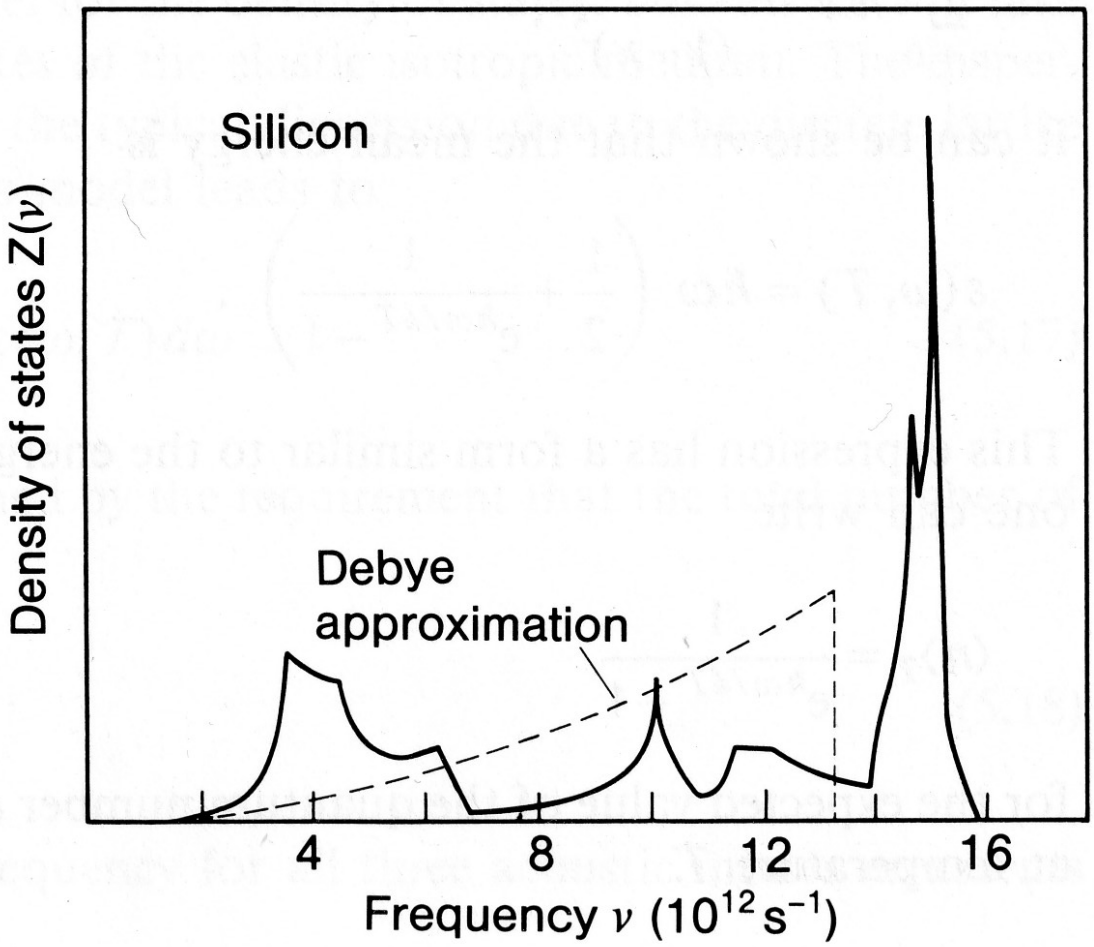
$k'' = 4\pi/L + (2)(2\pi/a) = 44\pi/L$

$a = L/10$



The total number of distinct wavevectors is exactly equal to the number of lattice points, whether one is in one, two or three dimensions. In a solid the number of lattice points is equal to the number of unit cells

There are 3J phonon frequencies for each allowed wavevector where J is the number of atoms in the primitive unit cell.



The density of states is high where $d\omega/dk = 0$

Our system, the phonons, consists of $3JN$ harmonic oscillators with a variety of different frequencies.

$$\omega_{\vec{k},j} \qquad j = 1, 2 \cdots J$$

It has been observed that all the frequencies respond in the same way to a change in volume of the crystal.

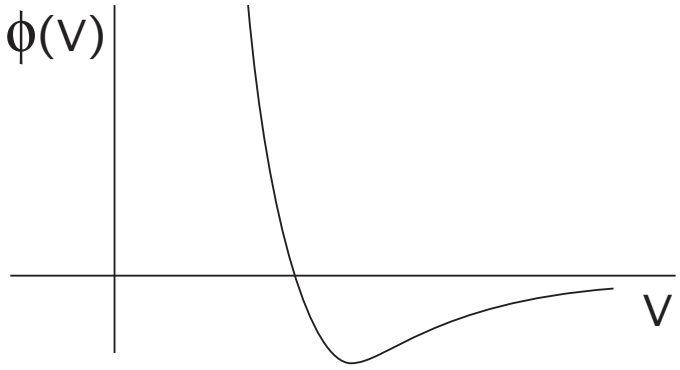
$$\frac{d\omega}{\omega} = -\gamma \frac{dV}{V}$$

Second Law: $dS \geq dQ/T \rightarrow dQ \leq TdS$

$$
\begin{aligned}
F &= U - TS \\
dF &= dU - TdS - SdT \\
dF &= dQ - PdV - TdS - SdT \\
dF &\leq TdS - PdV - TdS - SdT \\
dF &\leq -SdT - PdV
\end{aligned}
$$

Spontaneous process at constant T and V

minimize F.



$$F = \phi(V) + F_{\text{phonons}}(T,V) = \phi(V) + \sum_{\vec{k},j} F_{\vec{k},j}$$

$$F_{\vec{k},j} = -k_B T \ln Z_{\vec{k},j}$$

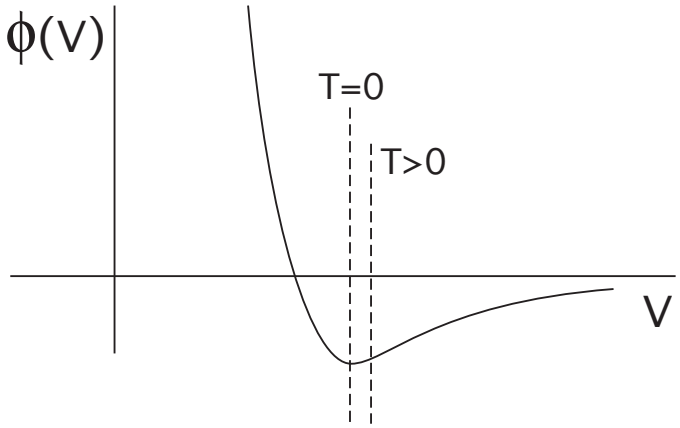
$$\left(\frac{\partial \phi}{\partial V}\right)_T = k_B T \sum_{\vec{k},j} \frac{1}{Z_{\vec{k},j}} \left(\frac{\partial Z_{\vec{k},j}}{\partial V}\right)_T$$

$$Z_1 = \sum_n \exp[-(n+\tfrac{1}{2})\hbar\omega\beta]$$

$$\left(\frac{\partial Z_1}{\partial V}\right)_T = \sum_n -(n+\tfrac{1}{2})\hbar\beta \exp[-(n+\tfrac{1}{2})\hbar\omega\beta] \underbrace{\frac{d\omega}{dV}}_{-\gamma\omega/V}$$

$$= \frac{\gamma\beta}{V} \underbrace{\sum_n (n+\tfrac{1}{2})\hbar\omega \exp[-(n+\tfrac{1}{2})\hbar\omega\beta]}_{<\epsilon> Z_1}$$

$$\frac{1}{Z_1}\left(\frac{\partial Z_1}{\partial V}\right)_T = \frac{\gamma}{V}\frac{1}{k_B T} < \epsilon >$$



$$\left(\frac{\partial \phi}{\partial V}\right)_T = k_B T \sum_{\vec{k},j} \frac{1}{Z_{\vec{k},j}} \left(\frac{\partial Z_{\vec{k},j}}{\partial V}\right)_T = \frac{\gamma}{V} \sum_{\vec{k},j} < \epsilon_{\vec{k},j} >$$

$$= \gamma \frac{U_{\text{phonons}}}{V}$$

You showed in PS9 that for low temperatures

$$U_{\text{phonons}} = U_{z.p.} + aT^4$$
$$U_{z.p.} = N \times \tfrac{1}{2}\hbar < \omega >$$

Just as in a mechanical H.O.

$$\omega_{\vec{k},j} \propto 1/\sqrt{m_{\text{atoms}}} \quad \text{for all modes}$$

Therefore

$$U_{z.p.}(^6\text{Li})/U_{z.p.}(^7\text{Li}) = \sqrt{7/6} = 1.08$$

At $T = 0$ the lattice spacing of ^{6}Li is observed to be about 0.07% larger than that for ^{7}Li .

Fluctuations in the *thermodynamic* variables

We have often argued that the fluctuations in the thermodynamic variables are very small. That is generally true, but we will see that in rare instances they can become so large that they dominate the behavior of the system.

We will study the fluctuations in the number density, N/V.

$$\left(\frac{\partial \mathcal{Z}}{\partial \mu}\right)_{T,V} = \sum_{N=1}^{\infty} \beta N \int \exp[\beta(\mu N - \mathcal{H})]\{dp, dq\}$$

$$\frac{1}{\beta \mathcal{Z}}\left(\frac{\partial \mathcal{Z}}{\partial \mu}\right)_{T,V} = \sum_{N=1}^{\infty} N \int \left(\frac{\exp[\beta(\mu N - \mathcal{H})]}{\mathcal{Z}}\right)\{dp, dq\}$$

$$\frac{1}{\beta \mathcal{Z}}\left(\frac{\partial \mathcal{Z}}{\partial \mu}\right)_{T,V} = \sum_{N=1}^{\infty} N \int p(\{p, q\}, N)\{dp, dq\}$$

$$\frac{1}{\beta}\left(\frac{\partial \ln \mathcal{Z}}{\partial \mu}\right)_{T,V} = < N >$$

$$\left(\frac{\partial \mathcal{Z}}{\partial \mu}\right)_{T,V} = \sum_{N=1}^{\infty} \beta N \int \exp[\beta(\mu N - \mathcal{H})]\{dp, dq\}$$

$$\left(\frac{\partial^2 \mathcal{Z}}{\partial \mu^2}\right)_{T,V} = \sum_{N=1}^{\infty} \beta^2 N^2 \int \exp[\beta(\mu N - \mathcal{H})]\{dp, dq\}$$

$$\frac{1}{\beta^2 \mathcal{Z}} \left(\frac{\partial^2 \mathcal{Z}}{\partial \mu^2}\right)_{T,V} = \sum_{N=1}^{\infty} N^2 \int \left(\frac{\exp[\beta(\mu N - \mathcal{H})]}{\mathcal{Z}}\right) \{dp, dq\}$$

$$\frac{1}{\beta^2 \mathcal{Z}} \left(\frac{\partial^2 \mathcal{Z}}{\partial \mu^2}\right)_{T,V} = \sum_{N=1}^{\infty} N^2 \int p(\{p, q\}, N)\{dp, dq\}$$

$$\frac{1}{\beta^2 \mathcal{Z}} \left(\frac{\partial^2 \mathcal{Z}}{\partial \mu^2}\right)_{T,V} = < N^2 >$$

$$\left(\frac{\partial^2 \ln \mathcal{Z}}{\partial \mu^2}\right) = \frac{\partial}{\partial \mu}\left(\frac{\partial \ln \mathcal{Z}}{\partial \mu}\right) = \frac{\partial}{\partial \mu}\left(\frac{1}{\mathcal{Z}}\frac{\partial \mathcal{Z}}{\partial \mu}\right)$$

$$= -\frac{1}{\mathcal{Z}^2}\frac{\partial \mathcal{Z}}{\partial \mu}\frac{\partial \mathcal{Z}}{\partial \mu} + \frac{1}{\mathcal{Z}}\frac{\partial^2 \mathcal{Z}}{\partial \mu^2}$$

$$= -\left(\frac{\partial \ln \mathcal{Z}}{\partial \mu}\right)^2 + \frac{1}{\mathcal{Z}}\frac{\partial^2 \mathcal{Z}}{\partial \mu^2}$$

$$= -\beta^2 < N >^2 + \beta^2 < N^2 >$$

$$< N^2 > - < N >^2 = k_B T \left(\frac{\partial^2 (k_B T \ln \mathcal{Z})}{\partial \mu^2}\right)$$

Recall that the grand potential $\Phi = -k_B T \ln \mathcal{Z}$, so

$$< N^2 > - < N >^2 = -k_B T \left(\frac{\partial^2 \Phi}{\partial \mu^2} \right)_{T,V}$$

It can be shown that for hydrostatic systems

$$\left(\frac{\partial^2 \Phi}{\partial \mu^2} \right)_{T,V} = - \frac{< N >^2}{V} \kappa_T$$

So

$$\frac{< N^2 > - < N >^2}{< N >^2} = \frac{< n^2 > - < n >^2}{< n >^2} = \frac{k_B T}{V} \kappa_T$$

$$\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{V}{\left(\frac{\partial P}{\partial V}\right)_T}$$

Watch the video 4C50.10 Critical Opalescence
Watch the video Critical point and critical opalescence

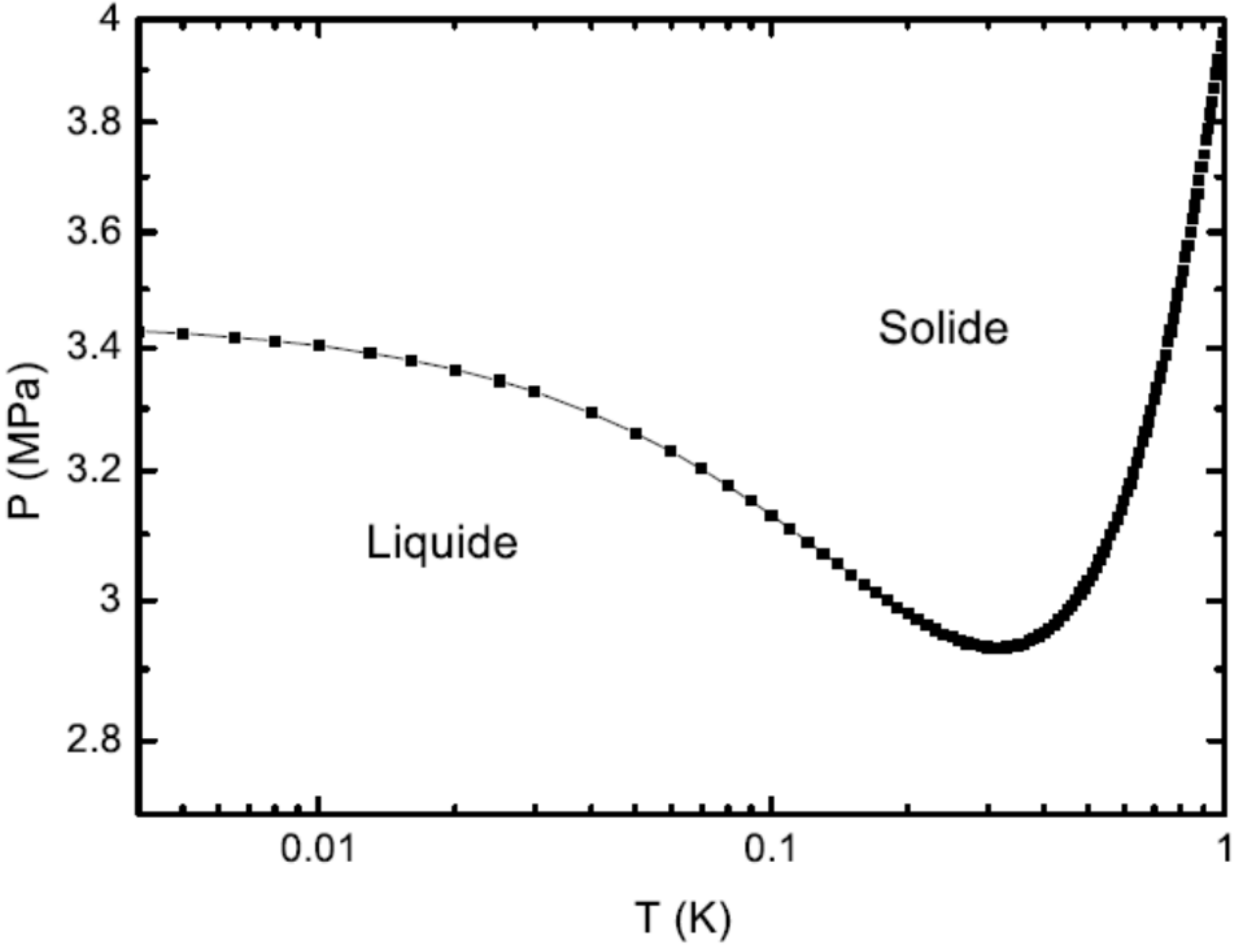
Counter intuitive thermodynamic results

Increasing the force/pressure causes the length/volume to decrease?

Raising the temperature causes the length or volume to increase?

When liquids freeze their volume decreases?

A solid melts when heated and a liquid solidifies when cooled?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3.8
3.6
3.4
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P (MPa)
Solide
Liquide
0.01
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1
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8.044 Statistical Physics I

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