Reading assignment

Schroeder, section 2.1.

Recap of lecture 3

- Work done by compression: $W = -\int_{V_i}^{V_f} P(V)\, dV\,.$
- Jargon:
  - Isothermal: At constant temperature.
  - Isotherm: A curve with constant temperature.
  - Adiabatic: Allowing no heat flow.
  - Adiabat: A curve with no heat flow.
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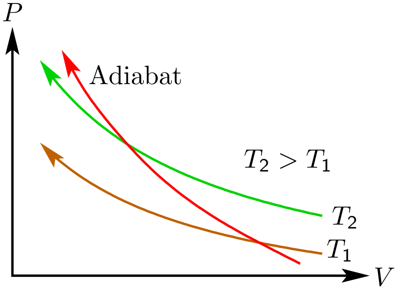


Homework

HW Problem

Schroeder problem 1.39, p. 27.

Heat capacity

This is just the amount of heat needed to raise the temperature by one degree (usually Celsius or Kelvin):

$$C = \frac{Q}{\Delta T} = \frac{\Delta U - W}{\Delta T} \, .$$

The tricky part is what to use for W. There are two common conventions, corresponding to two common approaches to determining the heat capacity.

If the volume is kept fixed, then no mechanical work is done, and in the absence of any other kinds of work, the heat capacity is just the *heat capacity at constant volume*:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \, .$$

Heat capacity

The simplicity of this derivative makes this heat capacity convenient in theoretical calculations, where one would rather not have to evaluate the contribution from the mechanical work.

On the other hand, in most cases it's really difficult (and/or dangerous!) to carry out experiments at constant volume. Most are done while the system is exposed to atmospheric pressure, which is unaffected by the experiment itself.

The relevant heat capacity in that case is the *heat capacity at constant pressure*:

$$C_P = \left(\frac{dU - (-P\,dV)}{dT}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P .$$

Relating C_P *and* C_V

The good news is that it's possible to relate these two quantities through two measured properties of materials:

$$C_P - C_V = TV\frac{\beta^2}{\kappa_T},$$

where

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

is the constant-pressure *thermal-expansion coefficient*, and

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

is the *isothermal compressibility*.

Relating C_P and C_V in an ideal gas

To see the difference for the ideal gas, write its volume as

$$V = \frac{NkT}{P}$$

and take the derivatives:

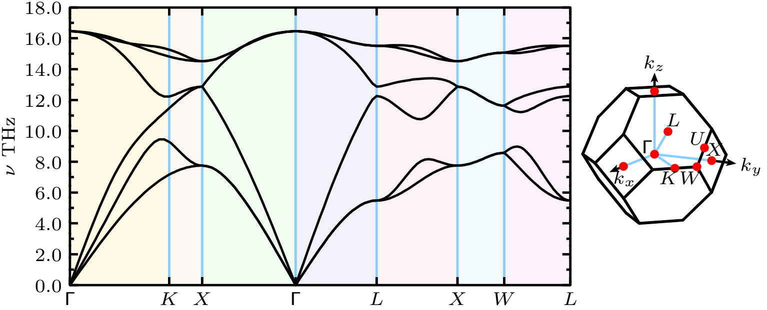
$$\beta = \frac{1}{V}\,\frac{Nk}{P} = \frac{Nk}{PV} \quad \text{and} \quad \kappa_T = -\frac{1}{V}\left(-\frac{NkT}{P^2}\right) = \frac{NkT}{P^2V}\,.$$

Combining the results, we get

$$C_P - C_V = TV\,\frac{N^2k^2}{P^2V^2}\,\frac{P^2V}{NkT} = Nk \quad \text{(ideal gas)}\,.$$

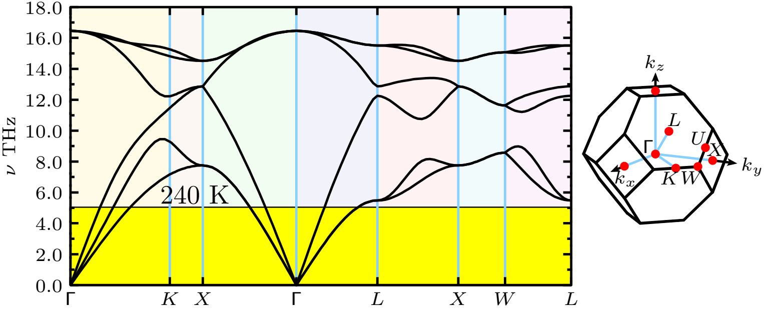
Lattice vibrations in a crystal

In a crystalline solid, all the atoms are locked in the crystal lattice, so there are no translational or rotational degrees of freedom, only vibrational degrees of freedom. The vibrations of a lattice can be expressed in terms of the collective wavelike normal modes, each of which behaves like a quantum oscillator. The frequencies of these normal modes exhibit quite interesting structure as a function of wavevector, shown here for Si:



Low-T freeze-out of lattice vibrational modes

At low temperatures, most of the vibrational modes are frozen out:



Thus, as $T \to 0$, the heat capacity due to lattice vibrations (the only significant contribution in an insulator) vanishes completely.

Vibrational heat capacity in the high-T limit

At the opposite extreme, the frequencies are bounded from above, so at sufficiently high temperature all modes participate in energy exchanges with each other and the environment, and the equipartion theorem applies for the energy

$$U = \frac{6N}{2} kT \,.$$

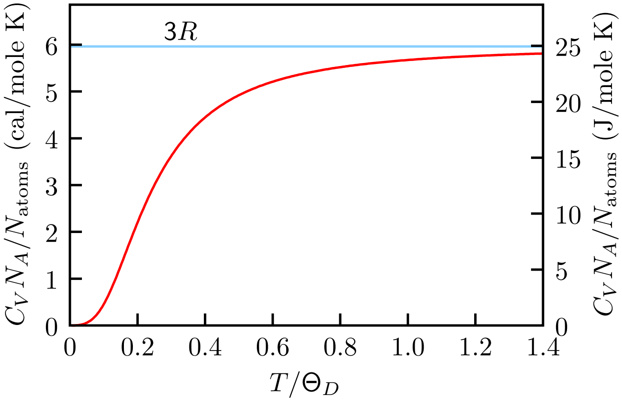
Thus, the heat capacity approaches

$$C = \frac{dU}{dT} = 3Nk$$

at high temperature.

Vibrational heat capacity vs T

The general behavior changes with T between these. At intermediate temperatures, the heat capacity increases from 0 to $3Nk$ like this graph *vs* normalized temperature:



Homework

HW Problem

Schroeder problem 1.45, p. 31.

HW Problem

Schroeder problem 1.46, p. 32.

Enthalpy

To build a system from scratch under constant (e.g., atmospheric) pressure, one must supply not just the energy needed to create the system in vacuum, but also the mechanical work needed to push out the surrounding material (e.g., air). That is just

$$\int_0^V P\,dV = PV\,.$$

Instead of keeping track of that as a separate term added on to the energy, it is convenient to define a new thermodynamic potential, called *enthalpy*, that has it built in:

$$H \equiv U + PV\,.$$

Enthalpy

The change in enthalpy is then, to first order,

$$dH = dU + P\,dV + V\,dP\,,$$

in which the final term vanishes if the pressure is constant.

From that, we find:

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P\,,$$

which just happens to be the constant-pressure heat capacity.

Thus:

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

is a simpler, more natural way to express C_P.

Homework

HW Problem

Schroeder problem 1.50, pp. 35–36.