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Workshop 2: Answers

Some may spot that N_2 has more DoF than a point-like particle e.g. Argon.

Let us work with number density of N_2 molecules, and then each has $3 + 3$ (translate), 2 (stretch), and 2 (rotate), i.e. 10 DoF, at high temperature.

To estimate the heat capacity using Debye model, we need number density n and Debye temperature θ_D.

For n, we have $n = 4/a^3$ where a is the lattice constant (given) and 4 because FCC.

For θ_D:

Recall number of k states up to some maximum value of k is $n_k = k^3/6\pi^2$.

There are 3 phonon modes per k state, and there are $3n$ modes in total (n is the num density of atoms).

Hence, using the Debye model's maximum wavenumber, we have $3k_D^3/6\pi^2 = 3n \implies k_D = (6\pi^2 n)^{1/3}$.

i.e. $\omega_D = vk_D = v(6\pi^2 n)^{1/3}$ and $\theta_D = \hbar\omega_D/k_B$, or recall/lookup this formula.

We still need the speed of sound v.

The bulk modulus gives a good enough long-wavelength approximation:

$v = \sqrt{B/\rho}$ where $\rho = M$ where M is the mass of a nitrogen **molecule** i.e. $2 \times 14u$.

Plugging in numbers:

$n = 2.20 \times 10^{28}\,\mathrm{m}^{-3}$

$k_D = 1.09 \times 10^{10}\,\mathrm{m}^{-1}$

$v = 1200\,\mathrm{m/s}$

$\omega_D = 1.31 \times 10^{13}\,\mathrm{s}^{-1}$

$\theta_D = 99.7\,\mathrm{K}$

Hence, T/θ_D is between 0.4 and 0.6. Reading from the graph, we therefore expect a heat capacity of between 75% and nearly 90% of the classical limit.

$C_v = 10 \times (1/2)k_B n \times I(X) \approx 1.1 \ldots 1.4\,\mathrm{MJ/kg/K}$

or

$C_v = 10 \times (1/2)R \times I(X) \approx 31 \ldots 37\,\mathrm{J/mol/K}$

Experimental values (such as I could find) are around $35 \ldots 45\,\mathrm{J/mol/K}$.

The complexity of N_2 molecules, and their increased ability to store heat, as compared with frozen nobel gases for which this model has previously been so successful, gave me pause. Mostly, it is unclear whether the molecular bonds between N atoms will participate in heat storage at this low temperature. There is a well-known curve from introductory thermodynamics which shows the increasing heat capacity of a diatomic gas as thermal energy becomes sufficiently high to populate these modes. However, the high temperature limit is still well defined, and the model appears to work reasonably well.