10/9 Lecture outline

• Write $U = U(T,V)$. Exact differential means

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV, \quad \text{with} \quad \left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right)_V.$$

Using first law,

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V, \qquad C_P = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] V\beta.$$

Note that c_P, c_V, and β are easily measured, as are P and V. So we can use the above to then determine $U(T,V)$.

• Physically clear that $C_P > C_V$: consider fixed $đQ$ heating two containers, one with V fixed and one with P fixed. Get $(đW)_V = 0$ and $(đW)_P > 0$. So $(dU)_V > (dU)_P$. Since T is a measure of U, get $(dT)_V > (dT)_P$; so $C_P > C_V$. Let's show it mathematically. Use above to write

$$C_P - C_V = \left(\frac{đQ}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = \frac{VT\beta^2}{\kappa_T}.$$

The last equality uses a Maxwell relation, $\left(\frac{\partial P}{\partial T}\right)_V = T^{-1}\left(\frac{đQ}{\partial V}\right)_T$, which is related to the fact that we'll see later that $đQ = TdS$ (explain it a bit, via $F = U - TS$). There is a stability condition, that systems find the state of lowest energy, which implies that $\kappa_T > 0$. The above relation then implies that $C_P > C_V$, as we expected. Define $\gamma \equiv C_P/C_V$.

• Plot of C_V and C_P over big temperature range. Interesting behavior at low T. Rather universal behavior at large T (ideal gas).

• Ideal gas has $U = U(T)$, so $đQ = C_V dT + pdV$. Using ideal gas law, get $đQ = (C_V + nR)dT - VdP$. Conclude $C_P = C_V + nR$ for ideal gas. Thus $C_V = nR/(\gamma - 1)$, $C_P = \gamma nR/(\gamma - 1)$.