Thermodynamics

1. *Temperature scales:* Prove the equivalence of the ideal gas temperature scale Θ, and the thermodynamic scale T, by performing a Carnot cycle on an ideal gas. The ideal gas satisfies $PV = Nk_B\Theta$, and its internal energy E is a function of Θ only. However, *you may not assume that* $E \propto \Theta$. You may wish to proceed as follows:

(a) Calculate the heat exchanges Q_H and Q_C as a function of Θ_H, Θ_C, and the volume expansion factors.

(b) Calculate the volume expansion factor in an adiabatic process as a function of Θ.

(c) Show that $Q_H/Q_C = \Theta_H/\Theta_C$.

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2. *Equations of State:*

(a) Starting from $dE = TdS - PdV$, show that the equation of state $PV = Nk_BT$, in fact implies that E can only depend on T.

(b) What is the most general equation of state consistent with an internal energy that depends only on temperature?

(c) Show that for a van der Waals gas C_V is a function of temperature alone.

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3. *Clausius–Clapeyron equation* describes the variation of boiling point with pressure. Consider a Carnot engine using one mole of water. At the source (P, T) the latent heat L is supplied converting water to steam. There is a volume increase V associated with this process. The pressure is adiabatically decreased to $P - dP$. At the sink $(P - dP, T - dT)$ steam is condensed back to water.

(a) Show that the work output of the engine is $W = VdP + \mathcal{O}(dP^2)$. Hence obtain the Clausius–Clapeyron equation

$$\left.\frac{dP}{dT}\right|_{\text{boiling}} = \frac{L}{TV}. \tag{1}$$

(b) What is wrong with the following argument: "The heat Q_H supplied at the source to convert one mole of water to steam is $L(T)$. At the sink $L(T - dT)$ is supplied to condense one mole of steam to water. The difference $dTdL/dT$ must equal the work $W = VdP$, equal to LdT/T from eq.(1). Hence $dL/dT = L/T$ implying that L is proportional to T!"

(c) Assume that L is approximately temperature independent, and that the volume change is dominated by the volume of steam treated as an ideal gas, i.e. $V = Nk_BT/P$. Integrate equation (1) to obtain $P(T)$.

(d) A hurricane works somewhat like the engine described above. Water evaporates at the warm surface of the ocean, steam rises up in the atmosphere, and condenses to water at the higher and cooler altitudes. The Coriolis force converts the upwards suction of the air to spiral motion. (Using ice and boiling water, you can create a little storm in a tea cup.) Typical values of warm ocean surface and high altitude temperatures are 80^0F and -120^0F respectively. The warm water surface layer must be at least 200 feet thick to provide sufficient water vapor, as the hurricane needs to condense about 90 million tons of water vapor per hour to maintain itself. Estimate the maximum possible efficiency, and power output, of such a hurricane. (The latent heat of vaporization of water is about $2.3 \times 10^6 Jkg^{-1}$.)

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4. *Glass:* Liquid quartz, if cooled slowly, crystallizes at a temperature T_m, and releases latent heat L. Under more rapid cooling conditions, the liquid is supercooled and becomes glassy.

(a) As both phases of quartz are almost incompressible, there is no work input, and changes in internal energy satisfy $dE = TdS + \mu dN$. Use the extensivity condition to obtain the expression for μ in terms of E, T, S, and N.

The heat capacity of crystalline quartz is approximately $C_X = \alpha T^3$, while that of glassy quartz is roughly $C_G = \beta T$, where α and β are constants.

(b) Assuming that the third law of thermodynamics applies to both crystalline and glass phases, calculate the entropies of the two phases at temperatures $T \leq T_m$.

(c) At zero temperature the local bonding structure is similar in glass and crystalline quartz, so that they have approximately the same internal energy E_0. Calculate the internal energies of both phases at temperatures $T \leq T_m$.

(d) Use the condition of thermal equilibrium between two phases to compute the equilibrium melting temperature T_m in terms of α and β.

(e) Compute the latent heat L in terms of α and β.

(f) Is the result in part (e) correct? If not, which of the steps leading to it is most likely to be incorrect?

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Suggested Reading: Chapters 1 and 2 of Huang.