Geometric thermodynamics

Algebraic and Geometric Methods in Engineering and Physics

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1 Introduction

In simple terms, the second law of thermodynamics states that the entropy of a closed system will tend to increase until an equilibrium is reached. Of course, this is merely a statistical law: there's always a non-zero probability that the entropy will spontaneously decrease.

The idea of geometric thermodynamics is to imagine a manifold where each point represents a state of a system, and the distance between them is associated to a probability such that, the farther away they are, the less likely it will be for the system to spontaneously "fluctuate" between these points. This manifold will be usually be a Riemmanian surface, since it's most common to work with two variables (like U and V).

For this, we simply define a metric, and everything else will follow from Riemmanian geometry in an elegant way. The most common one is the Ruppeiner metric[1], named after George Ruppeiner:

$$g_{ij} := -\partial_i \partial_j S \tag{1}$$

2 The Ruppeiner metric

To motivate Equation (1), we start with the statistical definition of entropy: $S = k_B \ln \Omega$. It's reasonable to assume that the probability of being in a given macrostate should be proportional to the amount of compatible microstates, Ω:

$$P \propto e^{\frac{S}{k_B}} \tag{2}$$

If a system is in equilibrium with its environment, then the universe has reached an entropy maximum. By assuming the environment is much larger than the system and doing a Taylor expansion around this point of equilibrium, p (using $\partial_i S\big|_p = 0$):

$$S(x^1, x^2) \approx S_0 + \frac{1}{2} \partial_i \partial_j S\big|_p x^i x^j \tag{3}$$

A full deduction can be found in Wei et al.[2]. By combining (2) and (3), we get

$$P(\mathbf{v}) \propto e^{-\frac{1}{2k_B}\|\mathbf{v}\|^2} \tag{4}$$

$$\|\mathbf{v}\|^2 := -\partial_i \partial_j S\big|_p v^i v^j \tag{5}$$

So, if we accept g_{ij} from (1) as our Riemannian metric, the right-hand side of(5) becomes $g_{ij}\big|_p v^i v^j$; this is just $\langle \mathbf{v}, \mathbf{v} \rangle$: so indeed, $\|\mathbf{v}\|^2$. Thus, we get our desired result: a metric with a notion of length which is related to the probability of each state. We just have to check that g_{ij} is a valid metric: it's symmetric due to Schwarz's lemma, and positive because a Hessian evaluated at a maximum is negative.

3 Thermodynamic length

A lot of authors[3][2] define (5) as the **thermodynamic length** — how far a given state is from equilibrium — even though it's not actually measuring lengths in M, since the vectors $\mathbf{v}$ reside on T_pM. But because M is smooth, T_pM approximates M around p, so lengths in M can be approximated as lengths in the tangent space. That is, to measure the distance between $p_0, p_1 \in M$, we project p_1 on $T_{p_0}M$ and take the length of the corresponding vector, $\|\mathbf{v}\|$.

However, if we wish to consider large fluctuations from equilibrium (or to simply be more rigorous), this is no longer satisfactory. So we have to start with the definition of curve length:

$$l(\mathbf{c}) := \int_{t_0}^{t_1} \|\dot{c}(t)\| = \int_{t_0}^{t_1} \sqrt{g_{ij}\big|_{\mathbf{c}(t)} \frac{\mathrm{d}c^i}{\mathrm{d}t} \frac{\mathrm{d}c^j}{\mathrm{d}t}} dt, \tag{6}$$

for a curve $\mathbf{c} : [t_0, t_1] \to M$. Then, to calculate the distance between two arbitrary points, we choose the curve which minimizes this length: a **geodesic**. In Euclidean space, this is just (a parametrization of) a straight line; in general, we can find geodesics by solving the following system of differential equations:

$$\frac{\mathrm{d}^2 c^k}{\mathrm{d}t^2} + \Gamma^k_{ij} \frac{\mathrm{d}c^i}{\mathrm{d}t} \frac{\mathrm{d}c^j}{\mathrm{d}t} = 0, \tag{7}$$

where Γ^k_{ij} are the **Christoffel symbols** (which are fully determined by the metric)[4].

It's important to note that this not a trivial endeavor at all; in practice, a closed-form expression for the distance function can only be obtained for very specific metrics.

4 Gauss curvature

Gauss's Theorema Egregium states that the Gauss curvature of a surface depends only on its metric. For a metric $ds^2 := g_{ij} dx^i dx^j = (\theta^1)^2 + (\theta^2)^2$, there's a connection form ω^1_2, defined such that $d\theta^1 = \theta^2 \wedge \omega^1_2$ and $d\theta^2 = -\theta^1 \wedge \omega^1_2$. Then, the **Gauss curvature** is K such that $d\omega^1_2 = K\theta^1 \wedge \theta^2$. This is, surprisingly, an intrinsic property of a given surface; it doesn't depend on the chosen metric/coordinate system[4].

This turns out to be one of the most useful and profound quantities in geometric thermodynamics, though its implications are still not fully understood. It's been particularly useful for probing the structure of black holes[3 5]. According to Ruppeiner[1], K seems to reflect the microscopic interactions of a system in the following ways:

- For mostly attractive interactions, $K < 0$;
- If there are no significant interactions, $K \approx 0$;
- For mostly repulsive interactions, $K > 0$;
- In critical points, K diverges.

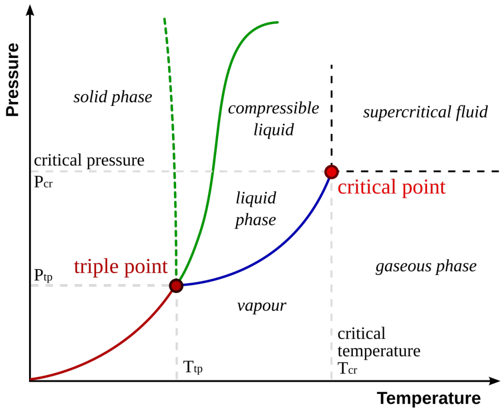

Figure 1: Phase diagram showing the critical point[6].

5 Examples

5.1 Ideal gas

An ideal gas is the simplest model of a gas, defined by the equation of state $PV = Nk_BT$. By writing the entropy as $S(U,V) = NC_V \ln U + Nk_B \ln V$, we get a Ruppeiner metric of:

$$ds^2 = \frac{NC_V}{U^2}dU^2 + \frac{Nk_B}{V^2}dV^2 \tag{8}$$

For this metric, the Christoffel symbols boil down to $\Gamma^k_{ij} = -\frac{1}{x^k}\delta_{ij}\delta_{jk}$. Plugging this into (7), we get $U\ddot{U} = \dot{U}^2$ (and similarly for V); therefore, all possible geodesics are of the form $(U,V) = (Ae^{Bt}, Ce^{Dt})$. So, for a curve between (U_0, V_0) and (U_1, V_1), we can use $\mathbf{c}(t) = \left(U_0 e^{\ln\left(\frac{U_1}{U_0}\right)t}, V_0 e^{\ln\left(\frac{V_1}{V_0}\right)t}\right)$, $t \in [0,1]$. Finally, the thermodynamic distance (6) is:

$$d(p_0,p_1) = \sqrt{NC_V \ln^2\left(\frac{U_1}{U_0}\right) + Nk_B \ln^2\left(\frac{V_1}{V_0}\right)} \tag{9}$$

It has units of $J^{\frac{1}{2}}K^{-\frac{1}{2}}$.

As for the Gauss curvature, it's easy to see that it's zero by noting that $\omega^1_2 = 0$. This corroborates the idea that no interactions implies $K \approx 0$, since the particles in an ideal gas are non-interacting by definition.

5.2 Van der Waals gas

The Van der Waals gas aims to improve the free gas model by introducing two parameters: **a**, which accounts for the electrostatic attraction between particles; and **b**, which accounts for the volume of the particles. The new equation of state becomes (using molar volume):

$$(P + \frac{a}{V^2})(V - b) = RT \tag{10}$$

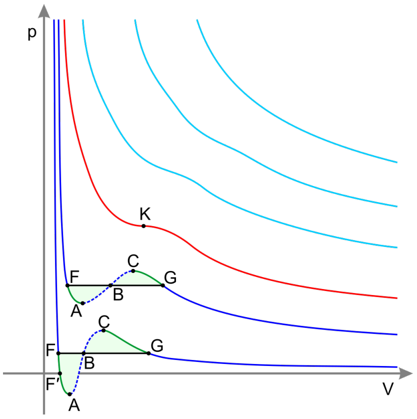

Figure 2: Various isothermal curves for the Van der Waals gas, from Equation 10. Below a critical temperature, a phase change region appears (F-G); K is the critical point[7].

Writing the entropy as $S = S(T,V)$[2], the metric is now:

$$ds^2 = \frac{C_V}{T^2}dT^2 + \frac{TV^3 - 2a(V-nb)^2}{TV^3(V-nb)^2}dV^2 \tag{11}$$

The thermodynamic length is a very unwieldy expression[8]. The Gauss curvature, on the other hand, becomes quite simple when using (P,V) coordinates (this calculation by Santoro and Preston uses the Weinhold metric[9]):

$$K(P,V) = \frac{aRV^3}{2C_V(PV^3 - aV + 2ab)^2} \tag{12}$$

By setting $a = 0$ — thus disabling the interactions — the original $R = 0$ result from the ideal gas is recovered. The same effect can be achieved by doing $V \to \infty$.

When looking for asymptotes, one can be found at $(P,V) = (\frac{a}{27b^2}, 3b)$; this suggests we've discovered a critical point in the system. To check, by looking at Figure 2, it's clear that it will be an inflection point on the (P,V) diagram. So we get the following conditions: $\partial_V P = \partial^2_V P = 0$. By applying them to 10, we find the point to be $(P,V,T) = (\frac{a}{27b^2}, 3b, \frac{8a}{27bR})$ — just as predicted!

References

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