A Hamiltonian Approach to Thermodynamics

XXVI International Fall Workshop on Geometry and Physics

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based on arXiv:1701.01119 and arXiv:1604.03117 and in collaboration with M.C. Baldiotti (Londrina State) and C.Molina (São Paulo U.))

Universidade Federal do ABC

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- On the other hand, consider the following Maxwell relations for a thermodynamic system described by entropy S, temperature T, volume V and pressure P: $\left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial P}{\partial T}\right|_V$ and $\left.\frac{\partial T}{\partial V}\right|_S = -\left.\frac{\partial P}{\partial S}\right|_V$

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- We see the strong resemblance between these sets of relations if we make the substitutions $q \to S$, $p \to T$, $t \to V$ and $H \to P$.

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- Because mixed partial derivatives commute, $\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S}$, we arrive at one of Maxwell's relations: $\frac{\partial T}{\partial V}\Big|_S = -\frac{\partial P}{\partial S}\Big|_V$

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- The other relation can be obtained from the integrability condition of the function $F = U - TS$. In fact, $dF = -SdT - PdV$ so $S = -\frac{\partial F}{\partial T}\big|_V$ and $P = -\frac{\partial F}{\partial V}\big|_T$. Then from Schwarz theorem, $\frac{\partial S}{\partial V}\big|_T = \frac{\partial P}{\partial T}\big|_V$.

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- The same effect can be achieved using Hamilton's principal function $S(q, t)$. We have $dS = pdq - Hdt$ for some functions p and H, so that $p = \frac{\partial S}{\partial q}\Big|_t$ and $H = -\frac{\partial S}{\partial t}\big|_p$

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- Finally, second derivatives of S give the Hamilton equation $\frac{\partial p}{\partial t}\Big|_q = -\frac{\partial H}{\partial q}\Big|_t$. The other relation can be obtained by considering the function $S - qp$.

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- On a more geometric standpoint [Herman 73], one assigns a contact structure to the thermodynamic phase space, such that the Legendre submanifolds describe equilibrium states. One then defines a Riemannian metric on the phase space which is compatible with the contact structure. The contact structure is responsible for encoding the first law, while the metric structure encodes the second law.

General Framework

- Consider the equations of state of a single thermodynamic system in the energy representation:

$$\begin{aligned} T &= T(S, V, N_1, ..., N_k) \\ P &= P(S, V, N_1, ..., N_k) \\ \mu_j &= \mu_j(S, V, N_1, ..., N_k) \end{aligned}$$

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- And a dictionary between thermodynamical variables and coordinates (q, p) in phase-space

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- One defines the tautological one-form $\theta = p_i dq^i$, the canonical symplectic form $\omega = d\theta$, and Poisson brackets:

$$\{f, g\} = \sum_{i=1}^{n} \frac{\partial f}{\partial q^i} \frac{\partial g}{\partial p_i} - \frac{\partial g}{\partial q^i} \frac{\partial f}{\partial p_i},$$

- The equations of state become primary constraints

$$p_i = \frac{\partial u}{\partial q^i}(q) \Leftrightarrow \phi_i(q,p) = p_i - \frac{\partial u}{\partial q^i}(q)\ ,\ i = 1, ..., n\,.$$

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- On the constraint surface $\phi_i = 0$, θ is the differential internal energy du:

$$\theta|_{\phi=0} = \sum_{i=1}^{n} p_i(q)\,dq^i = TdS - PdV + \sum_{i=1}^{k} \mu_i dN_i \equiv du\,.$$

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- Given two states in the thermodynamic configuration space any trajectory connecting them must be a valid thermodynamic path, there are no physical degrees of freedom in the corresponding mechanical analog.

Lagrange function and constraint structure

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- Let $\{\Phi_i\}_{i=1}^{k}$ be a set of irreducible primary time-independent first-class constraints, and $\{\chi_i\}_{i=1}^{p}$ a set of second-class constraints, such that $n = k + p/2$. Then the Lagrange function is a total derivative.

Legendre transformations

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- For instance, consider $\left(q^1, p_1\right) \mapsto (q', p') = \left(-p_1, q^1\right)$

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- The difference $\theta - \theta' = d\left(q^1 p_1\right)$ is a closed form.
- On the constraint surface $\theta'|_{\phi=0} = d\left(U - TS\right)$ is the Helmoltz potential $F\left(T, V, N_1, ..., N_k\right) = U - TS$.
- This is also expected: the thermodynamic description does not depend on the potential, so the mechanic description cannot either.

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The Ideal Gas

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$$\phi=p+Ae^{\frac{2}{3}\tau}q^{-\frac{5}{3}},\ H=\pi-Ae^{\frac{2}{3}\tau}q^{-\frac{2}{3}}.$$

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- The Hamiltonian is $H_c=\sigma H+\lambda\phi$ and conservation of the constraints in time provide the fundamental equation

$$u\left(s,v\right)=\frac{3}{2}\frac{A}{v^{2/3}}\exp\left(\frac{2}{3}s\right)\,.$$

- The Lagrange function for the ideal gas is

$$L\left(q,\dot{q},\tau\right)=Ae^{\frac{2}{3}\tau}q^{-\frac{5}{3}}\left(\dot{\tau}q-\dot{q}\right)\,.$$

- By means of the canonical transformation $\eta \mapsto \eta'$

$$q = q' - b\ ,\ \ p = p' - aq'^{-2}\ ,\ \ \pi = \pi'\ ,\ \ \tau = \tau',$$

- The primary constraints of the ideal gas become

$$H'\left(\eta'\right) = H\left(\eta\left(\eta'\right)\right) = \pi' - Ae^{\frac{2}{3}\tau'}(q' - b)^{-\frac{2}{3}}\ ,$$

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- Or, in thermodynamic variables,

$$T\left(u, v\right) = \frac{2}{3}\left(u + \frac{a}{v}\right) \ , \ P\left(T, v\right) = \frac{T}{v - b} - \frac{a}{v^2} \ .$$

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- And the fundamental equation follows from $du - du' = ad\left(q'^{-1}\right)$

$$u' = \frac{3}{2}\frac{Ae^{\frac{2}{3}\tau'}}{(q' - b)^{2/3}} - \frac{a}{q'} = \frac{3}{2}\frac{A}{(v - b)^{2/3}}\exp\left(\frac{2}{3}s\right) - \frac{a}{v}\ .$$

Clausius gas

- Consider the canonical transformation from the ideal gas

$$\tilde{\tau} = \tau + b\,,\ \tilde{\pi} = \pi - \frac{ap^{-1}}{(\tau + b - c)^2}\,,\ \tilde{q} = q + \frac{ap^{-2}}{\tau + b - c}\,,\ \tilde{p} = p\,.$$

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- The primary constraints are

$$\tilde{H} = \tilde{p} + (\tilde{\tau} - b)\left[\tilde{\pi} + \frac{a}{\tilde{p}\,(\tilde{\tau} - c)^2}\right]$$

$$\tilde{\phi} = \tilde{\pi} + \frac{a\tilde{p}^{-1}}{(\tilde{\tau} - c)^2} + \frac{A}{(\tilde{\tau} - b)^{\frac{5}{3}}} \exp\left[\frac{2}{3}\left(\tilde{q} - \frac{a\tilde{p}^{-2}}{\tilde{\tau} - c}\right)\right]$$

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$$\tilde{\phi}=\tilde{\pi}+\frac{a\tilde{p}^{-1}}{(\tilde{\tau}-c)^{2}}+\frac{A}{(\tilde{\tau}-b)^{\frac{5}{3}}}\exp\left[\frac{2}{3}\left(\tilde{q}-\frac{a\tilde{p}^{-2}}{\tilde{\tau}-c}\right)\right]$$

- Taking into account $d\tilde{u}=du'+d\left(\frac{1}{\tilde{p}}\frac{2a}{(\tilde{\tau}-c)}\right)$, we get the internal energy and Helmoltz free energy $f=\tilde{u}-Ts$

$$\tilde{u}=u+\frac{1}{\tilde{p}}\frac{2a}{(\tilde{\tau}-c)}=\frac{3}{2}T+\frac{1}{T}\frac{2a}{(v-c)}\ .$$
$$f=\frac{a}{T\,(v-c)}+\frac{3}{2}T\left[1-\ln\frac{T}{A}-\ln\left(v-b\right)^{\frac{2}{3}}\right]$$

Schwarzschild-anti-de Sitter back hole: minimal thermodynamics

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- The SAdS metric is the spherically symmetric solution of the Einstein equations in vacuum and asymptotically anti-de Sitter:

$$ds^2 = -(1 - \frac{2M}{r} - \frac{\Lambda}{3}r^2)dt^2 + (1 - \frac{2M}{r} - \frac{\Lambda}{3}r^2)^{-1}dr^2 + r^2 d\Omega^2.$$

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- Its thermodynamics can be minimally described by its mass M and surface gravity κ, with Killing horizon area $A = 4\pi r_+^2$

$$2M = r_+\left(1 - \frac{\Lambda}{3}r_+^2\right), \kappa = \frac{1}{2}\left(\frac{1}{r_+} - \Lambda r_+\right)$$

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$$\frac{3}{2}U - TS = \frac{1}{2\pi}(\pi S)^{\frac{1}{2}}\,, \; dM = \frac{\kappa}{8\pi}\,dA \Rightarrow dU = TdS\,.$$

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- However: no homogeneity! no Euler relation!

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- Consider Λ a thermodynamic variable [Teitelboim 85]
- 4-D Smarr formula $M = \frac{\kappa A}{4\pi} - \frac{\theta\Lambda}{4\pi}$, where $\theta = -\frac{4}{3}\pi r_+^3$.
- $\theta \sim$ *volume*, then $\Lambda \sim$ *pressure* and $M \sim$ *enthalpy* [Kastor 09]

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- $\theta \sim$ *volume*, then $\Lambda \sim$ *pressure* and $M \sim$ *enthalpy* [Kastor 09]
- In fact, $\left.\frac{\partial H}{\partial P}\right|_S = V$.
- However, from $U = H - PV$ one has

$$\frac{\kappa}{2\pi} = T \neq \frac{\partial U}{\partial S}$$

- So if one treats Λ as a thermodynamic variable, the physical interpretation of its conjugate is not clear.

- The one-dimensional thermodynamics has natural coordinates $q = S/\pi$ and $p = \pi T = \kappa/2$
- The equation of state gives the constraint $\phi = p - \frac{1}{4}q^{-\frac{1}{2}} - \frac{1}{4}\Lambda q^{\frac{1}{2}}$.

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SAdS black hole: some results

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- Thermodynamic instability for $a \in [1/2, a_{crit}]$, where $a_{crit} = \frac{D-1}{2}$.

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- We have not investigated a way to implement the second law from a geometric standpoint.
- The Dirac formalism for constrained systems is also the basis for canonical quantization, so one might think about possible quantizations and uncertainty relations [Wilk et al 2011].

obrigado!

Figure: UFABC Campus in Santo André, São Paulo

- Permanent positions open: 5 vacancies in Applied Math and 4 vacancies in Pure Math.
- Inscriptions up until 01/Nov/17. (http://www.ufabc.edu.br)