NEW + OLD SURPRISES IN THERMODYNAMICS FAR FROM EQUILIBRIUM

- On the history of glass thermodynamics
- On my history of glass thermodynamics
- On toy models: p-spin and simpler
- Two-temperature thermodynamics
- Systems coupled to two heat baths
- Particle in quantum bath
- Black holes

On the history of glass thermodynamics

- Vogel, Fulcher, Tammann-Hesse 1921-26:

viscosity $\eta \sim \exp \frac{A}{T-T_0}$

- Prigogine-Defay 1944-46

specific heat $C_p = \partial_T U$
compressibility $\kappa = -\partial_p \ln V$
expansivity $\alpha = \partial_T \ln V$

Ehrenfest I: $\Delta\alpha = \Delta\kappa \frac{dp_g}{dT}$ glass at $p = p_g(T)$
Ehrenfest II: $\frac{\Delta C_p}{TV} = \Delta\alpha \frac{dp_g}{dT}$
PdF-ratio: $\Pi = \frac{\Delta C_p \Delta\kappa}{TV(\Delta\alpha)^2} = 1$

- Tool 1946: fictive (effective) temperature

useful to describe glass transition
$U(t) = U(T_e(t)) \to C = \frac{\dot{U}}{\dot{T}} = \frac{\partial U}{\partial T_e} \frac{\dot{T}_e}{\dot{T}} \sim \frac{\partial T_e}{\partial T}$

- Kauzmann 1948: “Entropy crisis”:

$S_{\text{configuration}} = 0$ at $T = T_K$ $T_K = T_0$

- Davies-Jones 1953: At glass transition an unspecified number of order parameters undergoes a thermodynamic phase transition.
$\Pi \geq 1$ in theory and experiment

- Gibbs-DiMarzio 1958: lattice model for polymer glasses. Equilibrium theory.

- Adam-Gibbs 1965: $\tau \sim \eta \sim \exp \frac{A}{TS_{conf}}$

- Goldstein 1977-Jäckle 1989: κ has configurational part (due to pressure of formation)

- Rehage-Oels 1977: careful experiments on polystyrene. $\Pi \approx 1$

Then confusion hath found its masterpiece...

“The most fundamental problem is to understand Ehrenfest I”

1981 DiMarzio: “An equilibrium theory of glasses is absolutely necessary”

“Thermodynamics does not work for glasses, since there is no equilibrium” $\leftrightarrow$ Thermostatics

BUT

McKenna ’89; N’97: Ehrenfest I is tautology.
Also κ must be measured on long timescale.
(in spin glasses: $\chi_{ZFC} < \chi_{FC}$;
for 1-step Replica Symmetry Breaking:
χ_{ZFC} is discontinuous)

On my history of glass thermodynamics

• Sompolinski '81 + (.., Horner, Cugliandolo-Kurchan): Violation of FDT

• 1988 Kirkpatrick-Thirumalai: dynamical results described by replica's with marginality

• 1992 Crisanti-Sommers: statics p-spin model

$$\mathcal{H} = -\sum_{i_1<i_2..<i_p} J_{i_1 i_2..i_p} S_{i_1} S_{i_2}..S_{i_p} - H\sum_i S_i$$

• $\begin{matrix} \text{'93 Crisanti−Horner−Sommers} \\ \text{1993 Cugliandolo−Kurchan} \end{matrix}$ p-spin dynamics

q=self-overlap=plateau correlation function

x=breakpoint=fluctuation-dissipation ratio

→ dynamics "talks" to marginal replica's.

• N '95: has marginal replica free energy a physical meaning?

Our friend: the p-spin model

TAP-states a : $m_i{}^a = \langle S_i \rangle_a$ minima of
$F_{TAP}(m_i, T) = \mathcal{H}(m_i) - T S_{\text{ep}}(m_i, T)$

Crisanti-Sommers '95: config. entropy
$\mathcal{I} = \log \#$ TAP-states

Simple check: $F \neq U - TS = F_{dyn} = F_{exp}$
$F_{\text{marginal replicas}} = U - T S_{\text{equilibrium processes}} - \frac{T\mathcal{I}}{x}$

Question: Is this a physical quantity ?

N' 95 (cond-mat): TAP at two temperatures:
$Z_{TAP} = \sum_a \exp[-\beta u F_{TAP}(m_i{}^a)]$.

TAP-replicas with 1RSB parameter x_1:
$F = -\frac{1}{n\beta u} \ln[(Z_{TAP})^n]_{\text{disorder}} = U - T S_{\text{ep}} - \frac{T\mathcal{I}}{u\, x_1}$

marginality $\rightarrow$ $x_1 = \frac{x}{u}$ QED Ackn. J.M. Luck

Cugliandolo-Kurchan-Peliti '97: effective temperatures: zeroth law, thermometer,..

N PRL '97, JPA '98: Two-temperature thermodynamical relations:

$$F = U - TS_{\mathrm{ep}} - T_e\mathcal{I} = U - T_1S_1 - T_2S_2$$

$T_e = \frac{T}{x}$ is Tool's effective temperature

$$đQ = T\mathrm{d}S_{\mathrm{ep}} + T_e\mathrm{d}\mathcal{I} = T_1\mathrm{d}S_1 + T_2\mathrm{d}S_2$$

$$\mathrm{d}F = -S_{\mathrm{ep}}\mathrm{d}T - \mathcal{I}\mathrm{d}T_e - M\mathrm{d}H$$

Modified Maxwell relation since $T_e = T_e(T, p)$

$$\frac{\partial U}{\partial p}|_T + p\frac{\partial V}{\partial p}|_T + T\frac{\partial V}{\partial T}|_p = T\frac{\partial \mathcal{I}}{\partial T}|_p\,\frac{\partial T_e}{\partial p}|_T + (T_e - T\frac{\partial T_e}{\partial T}|_p)\frac{\partial \mathcal{I}}{\partial p}|_T$$

Modified Ehrenfest II

$$\frac{\Delta C_p}{TV} = \Delta\alpha\frac{\mathrm{d}p_g}{\mathrm{d}T} + \frac{1}{V}\left(1 - \frac{\partial T_e}{\partial T}|_p\right)\left(\frac{\partial \mathcal{I}}{\partial T}|_p + \frac{\mathrm{d}p_g}{\mathrm{d}T}\,\frac{\partial \mathcal{I}}{\partial p}|_T\right)$$

Modified PdF: $\Pi = 1 + \frac{1}{V\Delta\alpha}\left(1 - \frac{\partial T_e}{\partial T}|_p\right)\frac{\mathrm{d}\mathcal{I}}{\mathrm{d}p}$

- Re-evaluation polystyrene data: $\Pi = 0.77$

Contadicts all previous theories; supports present

- Franz-Virasoro:

$$F = U - TS_{\mathrm{ep}} - T_e\mathcal{I} = F_{TAP} - T_e\mathcal{I}$$

T, H constant: $\mathrm{d}F = -\mathcal{I}\mathrm{d}T_e \to \frac{\mathrm{d}\mathcal{I}}{\mathrm{d}F_{TAP}} = \frac{1}{T_e}$

Other friends: exactly solvable models with slow Monte Carlo dynamics

- Bonilla, Padilla, Ritort '97: $\mathcal{H} = \frac{K}{2}\sum x_i^2$

N harmonic oscillators statically uncoupled;
dynamically coupled (parallel Monte Carlo)

Arrhenius law $\to$ at $T = 0$ and $T \ll K$ logarithmic time-dependence.
Interpretation with $T_e \sim \frac{1}{\ln t}$ works

- N '98,'00: $\mathcal{H} = -\sum_i (H + \Gamma_i) S_i$

Free spherical spins in random field.
Allow check of Modified Ehrenfest II relation.
Both $\Pi > 1$ and $\Pi < 1$ possible

- N '99 (cond-mat); Poster L. Leuzzi

$$\mathcal{H} = \sum_i \left[\frac{K}{2} x_i^2 - H x_i - J x_i S_i - L S_i\right]$$

- fast spins S; slow oscillators x
- Constraint $\frac{1}{N}\sum x_i^2 - \frac{1}{N^2}(\sum x_i)^2 \geq m_0$

$\to$ Kauzmann transition

N '98, '00: Study of correlations and responses yields thermodynamic picture for (class of) glassy systems

Well separated timescale → self-generated $T_e(t)$

T_e occurs in

- thermodynamic: $đQ = T\,\mathrm{d}S_{\mathrm{ep}} + T_e\,\mathrm{d}\mathcal{I}$

- fluctuations: $\chi^{\mathrm{fluct}} = \frac{\langle \delta M^2 \rangle_{\mathrm{fast}}}{T} + \frac{\langle \delta M^2 \rangle_{\mathrm{slow}}}{T_e{}^{\mathrm{fluct}}}$

$$\chi = \frac{\partial M}{\partial H}\Big|_T = \chi^{\mathrm{fluct}} + \underbrace{\chi^{\mathrm{conf}}}_{\mathrm{Goldstein-Jackle}} + \underbrace{\chi^{\mathrm{loss}}}_{\mathrm{aging}}$$

- fluctuation-dissipation: $T_e{}^{FD}(t,t') = \frac{\partial_{t'} C(t,t')}{G(t,t')}$

To leading order in $1/\ln t$: universal T_e:

$$T_e(t) = T_e{}^{\mathrm{fluct}}(t) = T_e{}^{FD}(t'',t)$$

Systems coupled to two heat baths

Coolen, Penney, Sherrington 1990;

$\mathcal{H}_{\text{couplings}} \sim \sum_{i_1<i_2..<i_p} J^2_{i_1 i_2..i_p}$

Couplings at temperature T_J.

Three temperatures:

$T_1 = T$: bath
$T_2 = \frac{T}{x(T)}$: self-generated effective temp.
$T_3 = T_J$: couplings

Uncorrelated disorder $\leftrightarrow$ $T_3 = \infty$

Crisanti, Hertz, N, Sherrington, in prep.
Poster van Mourik &Coolen:

$\tau_1 \ll \tau_2 \ll \tau_3 \to$ General arguments: Parisi-structure

$$\mathcal{Z} = \int \mathrm{d}x_3 \left(\int \mathrm{d}x_2 \left(\int \mathrm{d}x_1 \, e^{-\mathcal{H}/T_1} \right)^{T_1/T_2} \right)^{T_2/T_3}$$

$x_1 = S$: within TAP-state
$x_2 = m_i^a$: TAP states
x_3: couplings

$n = \frac{T_2}{T_3} = \frac{T}{x(T)T_3} \neq 0$ if T_3 finite

$$\chi_{\mathrm{fluct}} = \chi^{(1)}_{\mathrm{fluct}} + \chi^{(2)}_{\mathrm{fluct}} + \chi^{(3)}_{\mathrm{fluct}} = \sum_{i=1}^{3} \frac{\langle \delta_i M^2 \rangle}{T_i}$$

Hertz, N, Sherrington '00:
p-spin with ferromagnetic coupling J_0

- $\chi^{(1)}_{\mathrm{fluct}} = \frac{M}{(p-1)H+(p-2)J_0 M} \to \frac{1}{(p-2)J_0}$
- eq. for χ_{fluct} verified

Breakdown of thermodynamics for quantum brownian motion Allahverdyan+N 1-4-00

$$\mathcal{H} = \frac{p^2}{2m} + V(x) + \sum_i \left[\frac{p_i^2}{2m_i} + \frac{m_i\omega_i^2}{2}(x_i - \frac{c_i\, x}{m_i\omega_i^2})^2\right]$$

particle+oscillator bath+interaction $x_i x + x^2$

"Caldeira-Leggett" model; Hamiltonian; bath 1981/83/85
→ P. Ullersma (Utrecht), 4 papers in Physica 1966

- Drude-Ullersma coupling $J(\omega) = \frac{\Gamma^2}{\Gamma^2+\omega^2}\gamma\omega$

γ: strength of interaction (damping constant)
Γ: Debye frequency: cut-off of interaction with bath

Equivalent Langevin equation (operator-valued)

$$\underbrace{\dot{p}}_{\text{acceleration}} = \underbrace{-V'(x)}_{\text{force}} \underbrace{- \frac{\gamma\Gamma}{m}\int_0^t \mathrm{d}t' e^{-\Gamma(t-t')} p(t')}_{\text{friction}} + \underbrace{\eta(t)}_{\text{noise}}$$

- timescale of friction $1/\Gamma$; of noise: $\max(\hbar/T, 1/\Gamma)$

→ non-Gibbsian behavior for $T < \hbar\Gamma$

• At $t = 0$: coupling γ switched on rapidly

• Density matrices of particle and bath factorize

• Work $\sim \gamma$ has to be done for the switching
(The large energy of bath + particle is increased by this)

• Von Neumann entropy $\mathrm{tr}(-\rho_0 \ln \rho_0)$ conserved

$\to$ system goes to non-Gibbsian equilibrium

Results:
• Harmonic potential, adiabatic change of m
$\mathrm{d}Q(T = 0) = \frac{\hbar\gamma}{2\pi m^2}\mathrm{d}m$ violates Clausius $\mathrm{d}Q \leq T\mathrm{d}S = 0$

• By periodic change of system parameter work can be extracted from bath

Reason:
Bath does not thermalize $\to$ it is mechanical part of system. Thermodynamics need not (and does not) apply.

Surprise:
The same occurs at large T, but then the Gibbs distribution enforces thermodynamics

Thermodynamics of black holes

BH has: mass M, charge Q, ang. momentum J.

Bekenstein 1973: BH entropy $S_{BH} = \frac{A}{4L_P^2}$
A= area; L_P = Planck length=$\sqrt{\hbar G/c^3} = 10^{-34}$ cm

Hawking 1975: Black holes have temperature
$T_H = \frac{\hbar G}{2\pi c^3}\kappa$ (κ=surface tension) $T_H \sim \frac{1}{M}$
Solar mass BH: $T_H = 10^{-8}\,K$.

The four laws of black hole dynamics
(Bardeen, Carter, Hawking, 1975)

0: T_H is constant at the horizon

1: $\mathrm{d}U = \frac{\kappa}{8\pi}\mathrm{d}A + đW = T_H \mathrm{d}S_{BH} + đW$ $\quad đW \sim \mathrm{d}Q + \mathrm{d}J$

2: Total entropy $S = S_{BH} + S_m$ cannot decrease

3: Extremal (maximally charged/rotating) black holes, with $T_H = 0$, unattainable

Are these the laws of black hole thermodynamics?

• Thermal bath = cosmic microwave background
$T_H = 3$ K $\to$ mass BH = 1 mountain

First law:System=black hole +Gedanken sphere
.... slow fast

Try: $đQ = T_H \, \mathrm{d}S_{BH} + T_{cmb} \, \underbrace{\mathrm{d}S_m^{\text{Gedanken sphere}}}_{=0}$

$\mathrm{d}U = đQ + đW = T_H \, \mathrm{d}S_{BH} + đW$ QED

Second law Clausius: $đQ \leq T_{cmb}\mathrm{d}S \quad S = S_{BH} + S_m^{\text{Gedanken sphere}}$

Yes, because there is also absorption of CMB
small BH : $T_H > T_{cmb}$, more evaporation
large BH : $T_H < T_{cmb}$, more absorption

$\to$ heat goes from high T to low T QED
• entropy production

Third law: System= Universe with BH in it.

$\to S = 0$ if $T_{cmb} = 0$, not $T_H = 0$.

$T_{cmb} < t^{-1/3} \to$ all BH's finally evaporate
$\to S = 0$ at $T_{cmb} = 0$ QED

(deviates from third law of BH dynamics)

CONCLUSION + OUTLOOK

"Thermodynamics does not work for glasses, since there is no equilibrium"

becomes

"Thermodynamics does work for glasses.
Since there is no equilibrium at least one effective temperature and/or pressure (field) must introduced."

Systems coupled to two heat baths + 2 timescales
- violation of Onsager relations for heat flow

- p-spin model + heat bath for couplings:
fluctuations = inside TAP + between TAP + sample-to-sample

Thermodynamics does not apply to quantum baths

It does apply to Black holes, star clusters,...

But: Godrèche & Luck:
$x < 1$ at T_c, but no effective temperatures