ENTROPY AND "THERMODYNAMIC" RELATIONS FOR NONEQUILIBRIUM STEADY STATES

HAL TASAKI WITH T.S.KOMATSU, N.NAKAGAWA, S.SASA PRL 100, 230602 (2008), arXiv:0711.0246 J. STAT. PHYS. 159, 1237 (2015), arXiv:1405.0697

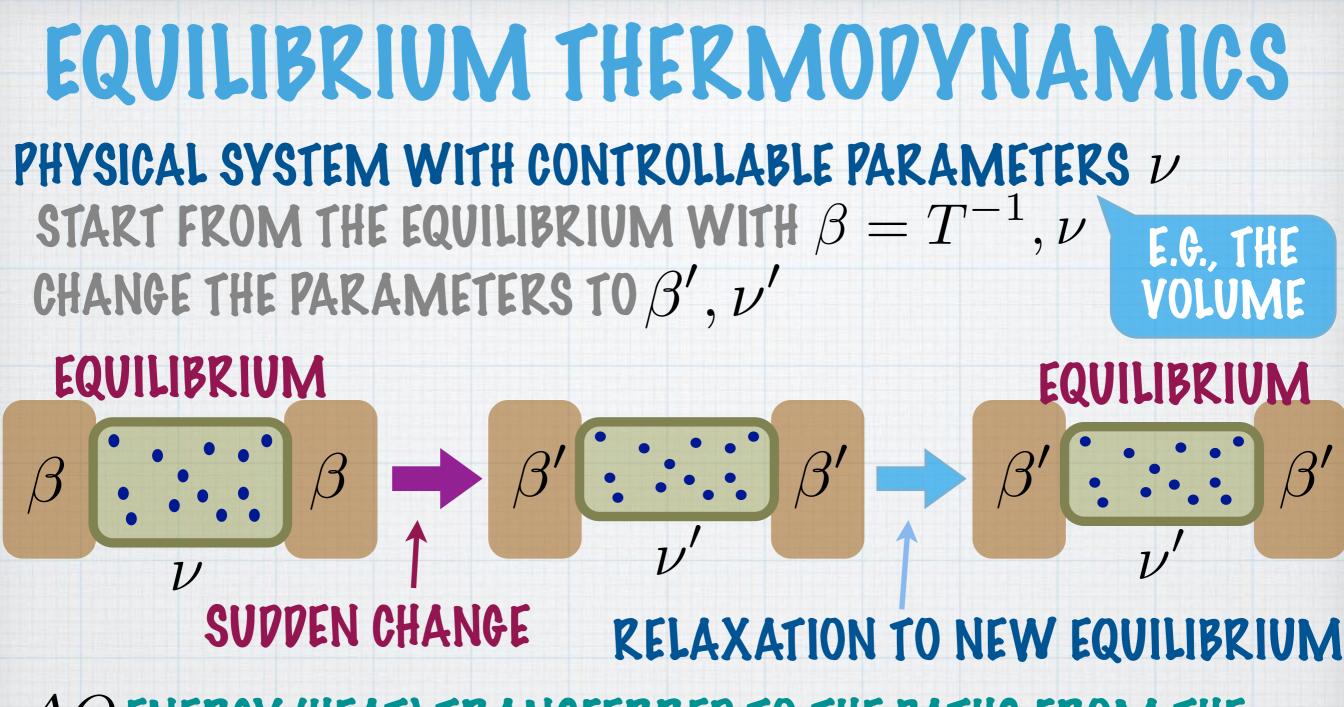
webinar, November 2020

TWO "TWISTS" IN STEADY STATE THERMODYNAMICS

HAL TASAKI WITH T.S.KOMATSU, N.NAKAGAWA, S.SASA PRL 100, 230602 (2008), arXiv:0711.0246 J. STAT. PHYS. 159, 1237 (2015), arXiv:1405.0697

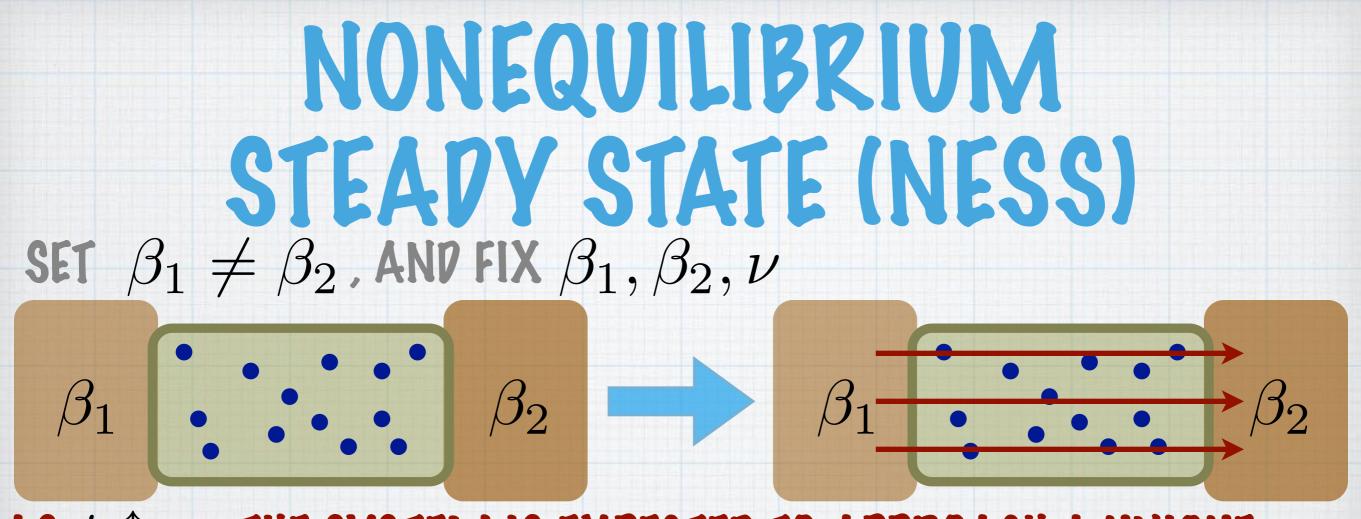
webinar, November 2020





 ΔQ ENERGY (HEAT) TRANSFERRED TO THE BATHS FROM THE SYSTEM DURING THE RELAXATION PROCESS CLAUSIUS RELATION

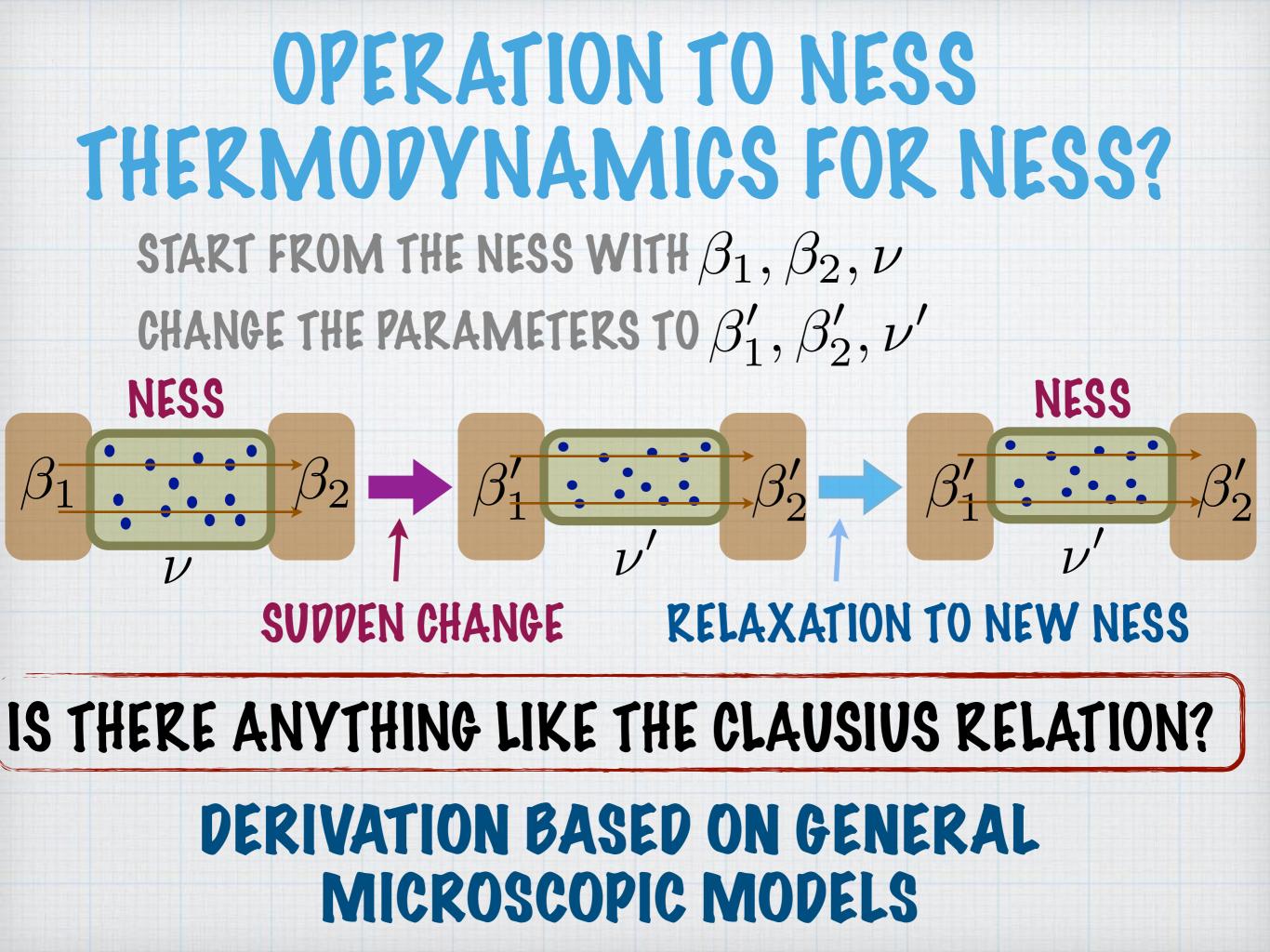
 $\frac{S(\beta',\nu') - S(\beta,\nu) = -\beta \Delta Q + O((\Delta Q)^2))}{\text{STARTING POINT OF EQUILIBRIUM THERMODYNAMICS}}$



AS $t \uparrow \infty$ the system is expected to approach a unique stationary state = nonequilibrium steady state (ness) (provided that the "degree of nonequilibrium" is small)

EQUILIBRIUM STATE: INO MACROSCOPIC CHANGES INO MACROSCOPIC FLOWS

> NESS: INO MACROSCOPIC CHANGES INONVANISHING MACROSCOPIC FLOW OF ENERGY OR MATTER



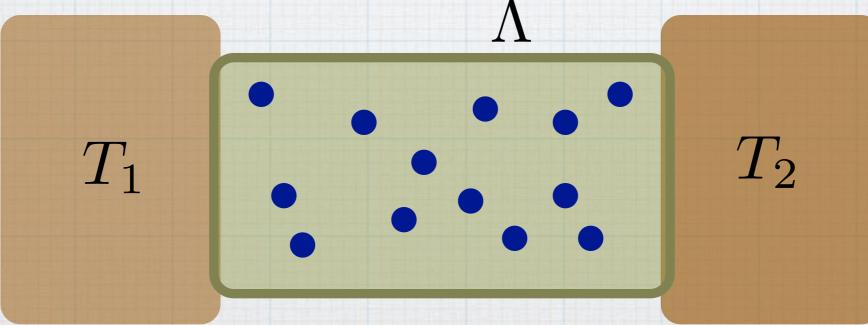


SYSTEM OF PARTICLES

CLASSICAL MECHANICAL SYSTEM WITH N particles in a finite box Λ

 $m{r}_i \in \Lambda \subset \mathbb{R}^3$ position $p_i \in \mathbb{R}^3$ momentum of the i-th particle $p_i = m m{v}_i$

$$\boldsymbol{r} = (\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N; \boldsymbol{p}_1, \ldots, \boldsymbol{p}_N)$$



THE SYSTEM IS ATTACHED TO TWO HEAT BATHS

TIME EVOLUTION

USUAL NEWTON EQUATION

 $m\frac{d^2\boldsymbol{r}_i(t)}{dt^2} = -\operatorname{grad}_i V(\boldsymbol{r}_1(t),\ldots,\boldsymbol{r}_N(t))$

 $V(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N) = \sum V_{\text{ext}}^{(\nu)}(\boldsymbol{r}_i) + \sum v(\boldsymbol{r}_i-\boldsymbol{r}_j)$ i < j

ν (controllable) parameter (E.G., the volume)

MARKOVIAN TIME EVOLUTION AT THE WALLS

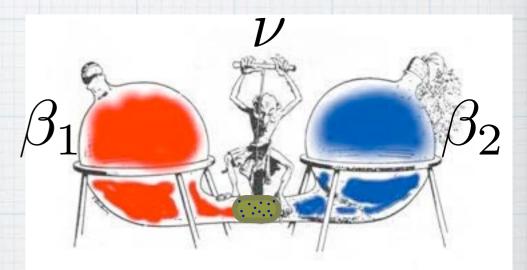
THERMAL WALL, LANGEVIN DYNAMICS (ONLY NEAR THE WALLS), T₂ ETC.

WE NEED LOCAL DETAILED BALANCE CONDITION

THERMAL WALL A PARTICLE WITH ANY INCIDENT VELOCITY $v^{
m in}$ is bounced back WITH A RANDOM VELOCITY $v^{
m out}$ with the probability density $p_T(\boldsymbol{v}^{\text{out}}) = A v_x^{\text{out}} \exp\left[-\frac{m |\boldsymbol{v}^{\text{out}}|^2}{2kT}\right] \qquad A = \frac{1}{2\pi} \left(\frac{m}{kT}\right)^2$ $\boldsymbol{v}^{\text{out}} = (v_{\text{x}}^{\text{out}}, v_{\text{y}}^{\text{out}}, v_{\text{z}}^{\text{out}}) \quad v_{\text{x}}^{\text{out}} > 0 \quad v_{\text{y}}^{\text{out}}, v_{\text{z}}^{\text{out}} \in \mathbb{R}$ vⁱⁿ k boltzmann constant T temperature of T TEMPERATURE OF THE WALL v^{out} ENERGY (HEAT) TRANSFERED FROM THE TSYSTEM TO THE BATH $q = rac{m}{2} |v^{ ext{in}}|^2 - rac{m}{2} |v^{ ext{out}}|^2$ X



BASIC INGREDIENTS CONTROLLABLE PARAMETERS $\alpha = (\beta_1, \beta_2, \nu)$ β_1 μ β_2 (INVERSE) TEMPERATURES OF THE BATHS



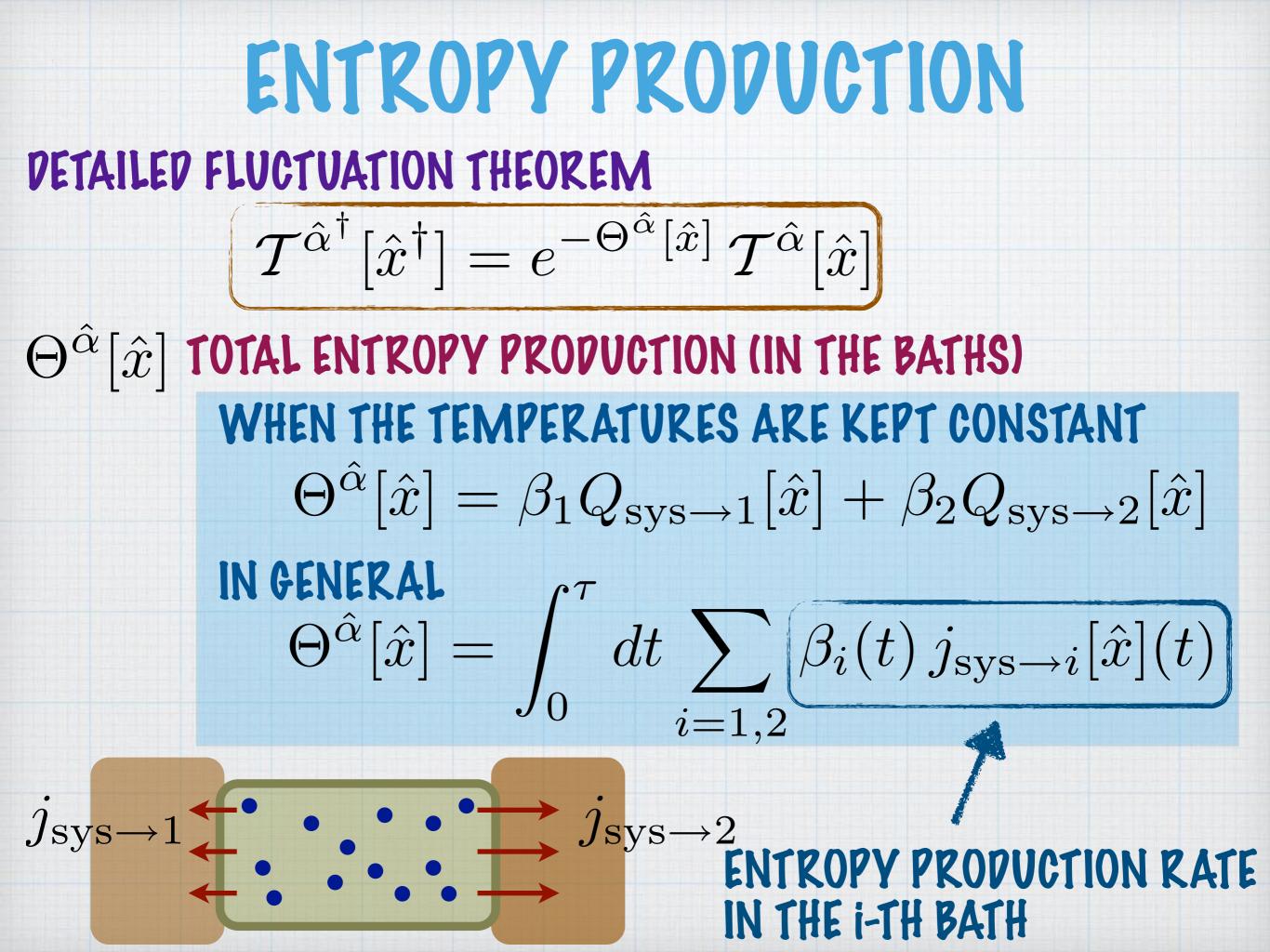
x state of the system

$$x \leftrightarrow (\boldsymbol{r}_1, \dots, \boldsymbol{r}_N; \boldsymbol{p}_1, \dots, \boldsymbol{p}_N)$$

 $x^* \leftrightarrow (\boldsymbol{r}_1, \dots, \boldsymbol{r}_N; -\boldsymbol{p}_1, \dots, -\boldsymbol{p}_N)$

ENERGY $H_x^{\nu} = H_{x^*}^{\nu}$

TIME EVOLUTION TIME INTERVAL $t \in [0, \tau]$ **OPERATION BY OUTSIDE AGENT** FIXED PROTOCOL (OR FUNCTION) $\hat{\alpha} = (\alpha(t))_{t \in [0,\tau]}$ $\alpha(t) = (\beta_1(t), \beta_2(t), \nu(t))$ **PATH** $\hat{x} = (x(t))_{t \in [0,\tau]}$ MARKOV PYNAMICS WITH PATH PROBABILITY DENSITY $\mathcal{T}^{\hat{lpha}}[\hat{x}]$ $\int_{x(0)=x_{\text{init}}} D\hat{x} \, \mathcal{T}^{\hat{\alpha}}[\hat{x}] = 1$ **DETAILED FLUCTUATION THEOREM** $\mathcal{T}^{\hat{\alpha}^{\dagger}}[\hat{x}^{\dagger}] = e^{-\Theta^{\hat{\alpha}}[\hat{x}]} \mathcal{T}^{\hat{\alpha}}[\hat{x}]$ TIME REVERSEP PROTOCOL $\hat{\alpha}^{\dagger} = (\alpha(\tau - t))_{t \in [0, \tau]}$ $\hat{x}^{\dagger} = (x^*(\tau - t))_{t \in [0,\tau]}$ TIME REVERSED PATH



NESS AND THE AVERAGE

WHEN THE PARAMETERS ARE KEPT CONSTANT THE SYSTEM EVENTUALLY CONVERGES TO A UNIQUE NONEQUILIBRIUM STEADY STATE (NESS)

 ρ_x^α probability distribution of ness with α

PATH AVERAGE OF ANY FUNCTION $F[\hat{x}]$

$$\langle F \rangle^{\hat{\alpha}} := \int \mathcal{D}\hat{x} \, \rho_{x(0)}^{\alpha(0)} \, \mathcal{T}^{\hat{\alpha}}[\hat{x}] \, F[\hat{x}]$$

START FROM THE NESS FOR THE INITIAL PARAMETERS AND CHANGE THE PARAMETER ACCORDING TO $\hat{\alpha}$

CLAUSIUS RELATION AND EXTENDED CLAUSIUS RELATION

EQUILIBRIUM CASE **OPERATION BETWEEN TWO EQUILIBRIUM STATES** $\alpha(t) = \begin{cases} (\beta, \beta, \nu), & t \in [0, \tau/2] \\ (\beta', \beta', \nu'), & t \in (\tau/2, \tau] \end{cases}$ AMOUNT OF CHANGE $\delta = \max\{|\beta' - \beta|, |\nu' - \nu|\}$ EQUILIBRIUM EQUILIBRIUM $\beta \longleftrightarrow \beta \Rightarrow \beta' \longleftrightarrow \beta' \Rightarrow \beta' \longleftrightarrow \beta'$ STANDARD CLAUSIUS RELATION (FOR LARGE τ) $S(\beta',\beta',\nu') - S(\beta,\beta,\nu) = -\langle \Theta^{\hat{\alpha}} \rangle^{\hat{\alpha}} + O(\delta^2)$ THERMOPYNAMIC ENTROPY = SHANNON ENTROPY OF ρ^{α} $S(\alpha) = -\int dx \rho_x^{\alpha} \log \rho_x^{\alpha}$

THE MEANING OF THE CLAUSIUS RELATION

STANDARD CLAUSIUS RELATION

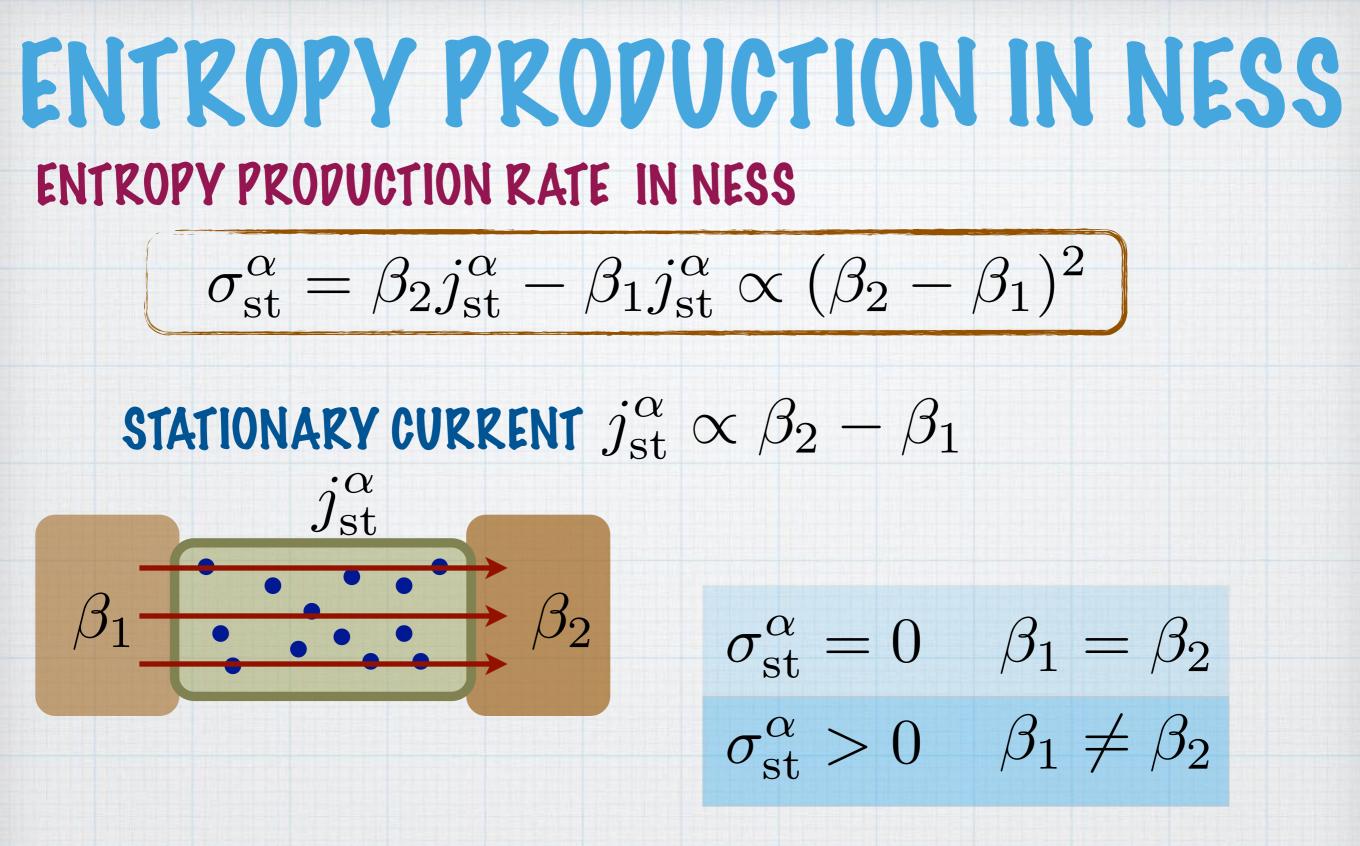
$$S(\beta',\beta',\nu') - S(\beta,\beta,\nu) = -\langle \Theta^{\hat{\alpha}} \rangle^{\hat{\alpha}} + O(\delta^2)$$

 $S(\beta, \beta, \nu) + S_{\text{baths}}^{\text{init}} = S(\beta', \beta', \nu') + S_{\text{baths}}^{\text{fin}} + O(\delta^2)$ The total entropy of (the system + the baths) is constant

THIS IS NO LONGER TRUE IN NESS! -

THERE IS A CONSTANT ENTROPY PRODUCTION

 $S_{\text{baths}}^{\text{fin}} - S_{\text{baths}}^{\text{init}}$



NESS IS ACCOMPANIED BY A CONSTANT NONVANISHING ENTROPY PRODUCTION IN THE BATHS

CLAUSIUS RELATION FOR NESS? OPERATION BETWEEN TWO NESS $\alpha(t) = \begin{cases} (\beta_1, \beta_2, \nu), & t \in [0, \tau/2] \\ (\beta'_1, \beta'_2, \nu'), & t \in (\tau/2, \tau] \end{cases}$ NESS NESS $\beta_2 \rightarrow \beta'_1 \qquad \beta'_2 \rightarrow \beta'_1 \qquad \beta'_2 \rightarrow \beta'_1 \qquad \beta'_2 \qquad \beta'_1 \qquad \beta'_2 \qquad \beta'_1 \qquad \beta'_2 \qquad \beta'_1 \qquad \beta'_2 \qquad \beta'_2 \qquad \beta'_1 \qquad \beta'_2 \qquad \beta$ IS IT POSSIBLE THAT $S(\beta'_1, \beta'_2, \nu') - S(\beta_1, \beta_2, \nu) \simeq -\langle \Theta^{\hat{\alpha}} \rangle^{\hat{\alpha}}$? NO! BECAUSE $S(eta_1',eta_2', u')-S(eta_1,eta_2, u)$ is independent of au $\langle \Theta^{\hat{\alpha}} \rangle^{\hat{\alpha}} \sim \frac{7}{2} \sigma_{\rm st}^{\alpha} + \frac{7}{2} \sigma_{\rm st}^{\alpha'}$ piverges as $\tau \uparrow \infty$

ENTROPY PRODUCTION RATE $\sigma(t) = \beta_1 \, j_{\text{sys} \rightarrow 1}(t) + \beta_2 \, j_{\text{sys} \rightarrow 2}(t)$

 $\sigma(t)$

 $\sigma(t)$

 $\sigma_{
m st}^{lpha}$

 $\sigma^{lpha'}_{
m st}$

OPERATION IN EQUILIBRIUM

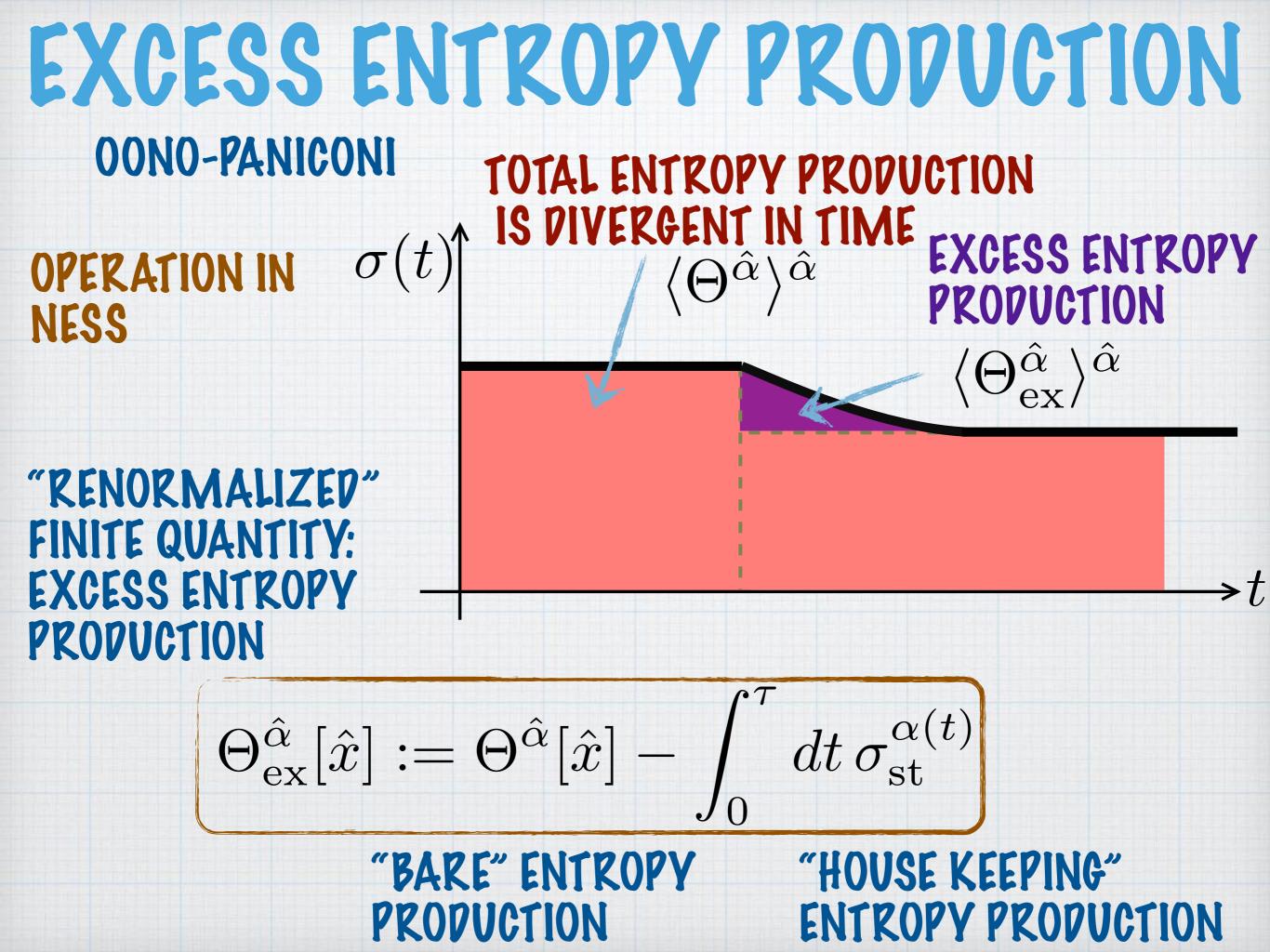
TOTAL ENTROPY PRODUCTION IS DIVERGENT IN TIME

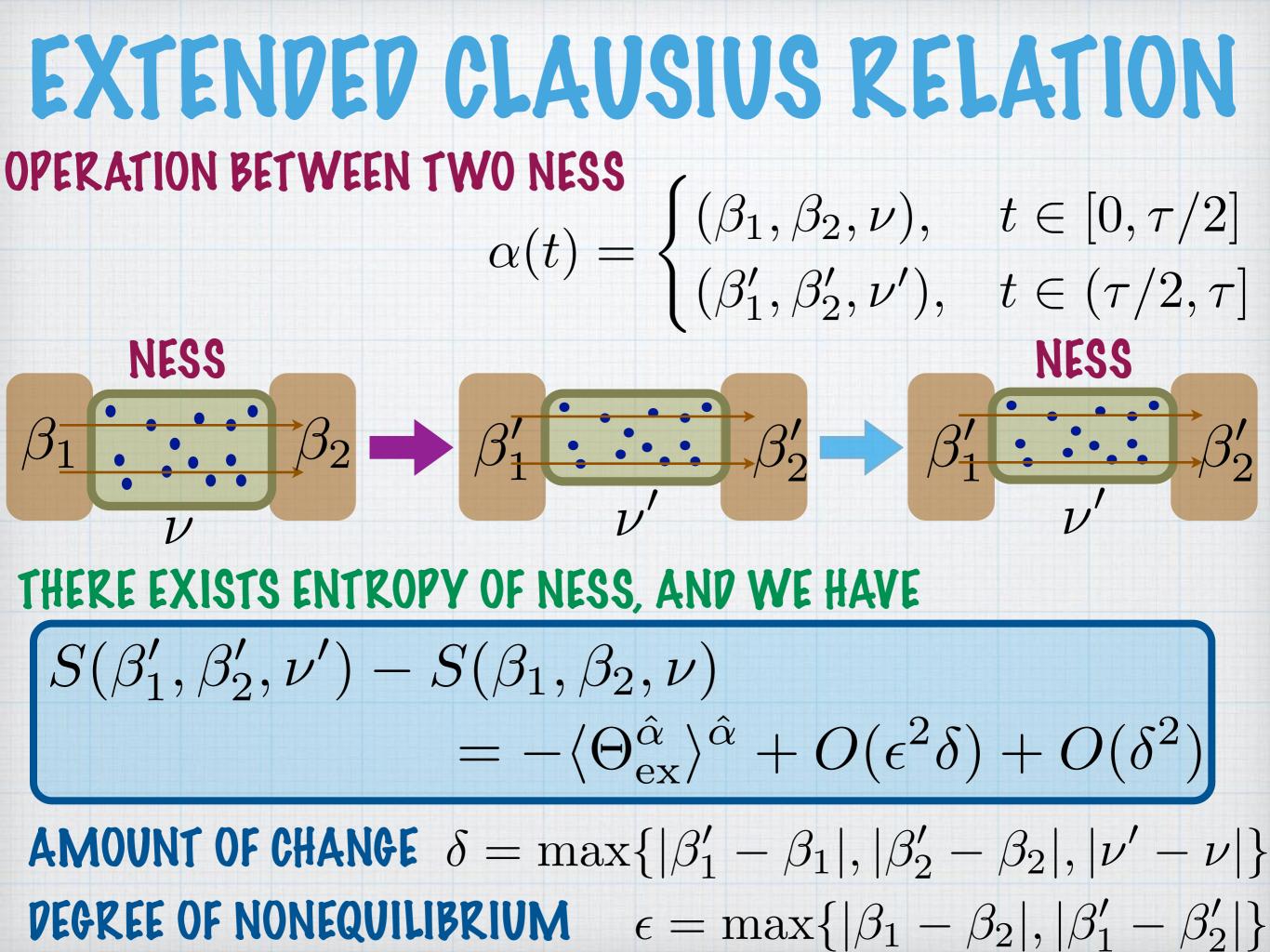
TOTAL ENTROPY PRODUCTION

 $\langle \Theta^{\hat{\alpha}} \rangle^{\hat{\alpha}} = \int_0^\tau dt \, \sigma(t)$

 $\langle \Theta^{\hat{\alpha}} \rangle^{\hat{\alpha}} = \int_0^\tau dt \, \sigma(t)$

OPERATION IN NESS





MICROSCOPIC EXPRESSION FOR THE ENTROPY

THE NONEQUILIBRIUM ENTROPY IS RELATED TO THE PROBABILITY DENSITY BY

$$S(\alpha) = S_{\text{sym}}[\rho^{\alpha}]$$

WITH THE "SYMMETRIZED SHANNON ENTROPY"

$$S_{\rm sym}[\rho] := -\int dx \,\rho_x \,\log \sqrt{\rho_x \,\rho_{x^*}}$$

STATE $x \leftrightarrow (r_1, \dots, r_N; p_1, \dots, p_N)$ TIME REVERSAL $x^* \leftrightarrow (r_1, \dots, r_N; -p_1, \dots, -p_N)$

THE FIRST "TWIST" IN SST

THE NONEQUILIBRIUM ENTROPY IS RELATED TO THE PROBABILITY DENSITY BY

$$S(\alpha) = S_{\rm sym}[\rho^{\alpha}]$$

WITH THE "SYMMETRIZED SHANNON ENTROPY"

$$S_{\rm sym}[\rho] := -\int dx \,\rho_x \,\log \sqrt{\rho_x \,\rho_{x^*}}$$

STATE $x \leftrightarrow (r_1, \dots, r_N; p_1, \dots, p_N)$ TIME REVERSAL $x^* \leftrightarrow (r_1, \dots, r_N; -p_1, \dots, -p_N)$

A "NATURAL" EXTENSION OF THE TRADITIONAL CLAUSIUS RELATION, IN WHICH (DIVERGENT) "BARE" ENTROPY PRODUCTION IS REPLACED BY ITS "RENORMALIZED" COUNTERPART MEANINGFUL WHEN THE DEGREE OF NONEQULIBRIUM IS SMALL

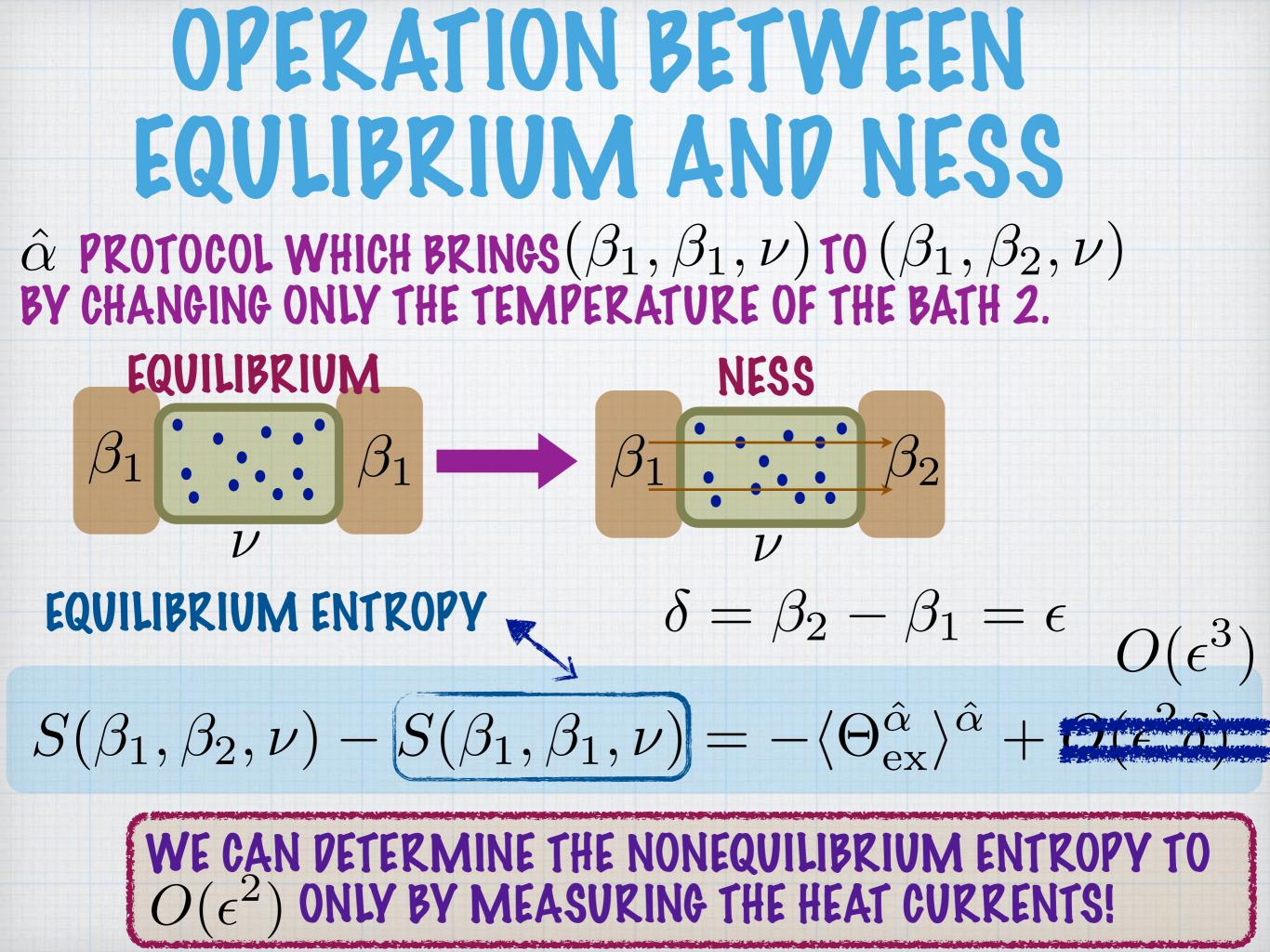
AMOUNT OF CHANGE $\delta = \max\{|\beta'_1 - \beta_1|, |\beta'_2 - \beta_2|, |\nu' - \nu|\}$ DEGREE OF NONEQUILIBRIUM $\epsilon = \max\{|\beta_1 - \beta_2|, |\beta'_1 - \beta'_2|\}$

$$S(\beta_1',\beta_2',\nu') - S(\beta_1,\beta_2,\nu) = -\langle \Theta_{\mathrm{ex}}^{\hat{\alpha}} \rangle^{\hat{\alpha}} + O(\epsilon^2 \delta)$$

FOR "SLOW AND GENTLE" PROTOCOL
$$\hat{\alpha} = (\alpha(t))_{t \in [0,\tau]}$$

WITH $\alpha(0) = (\beta_1, \beta_2, \nu)$ AND $\alpha(\tau) = (\beta'_1, \beta'_2, \nu')$

OPERATIONAL DETERMINATION OF ENTROPY



COMPARING ENTROPIES OF TWO NESS

1/

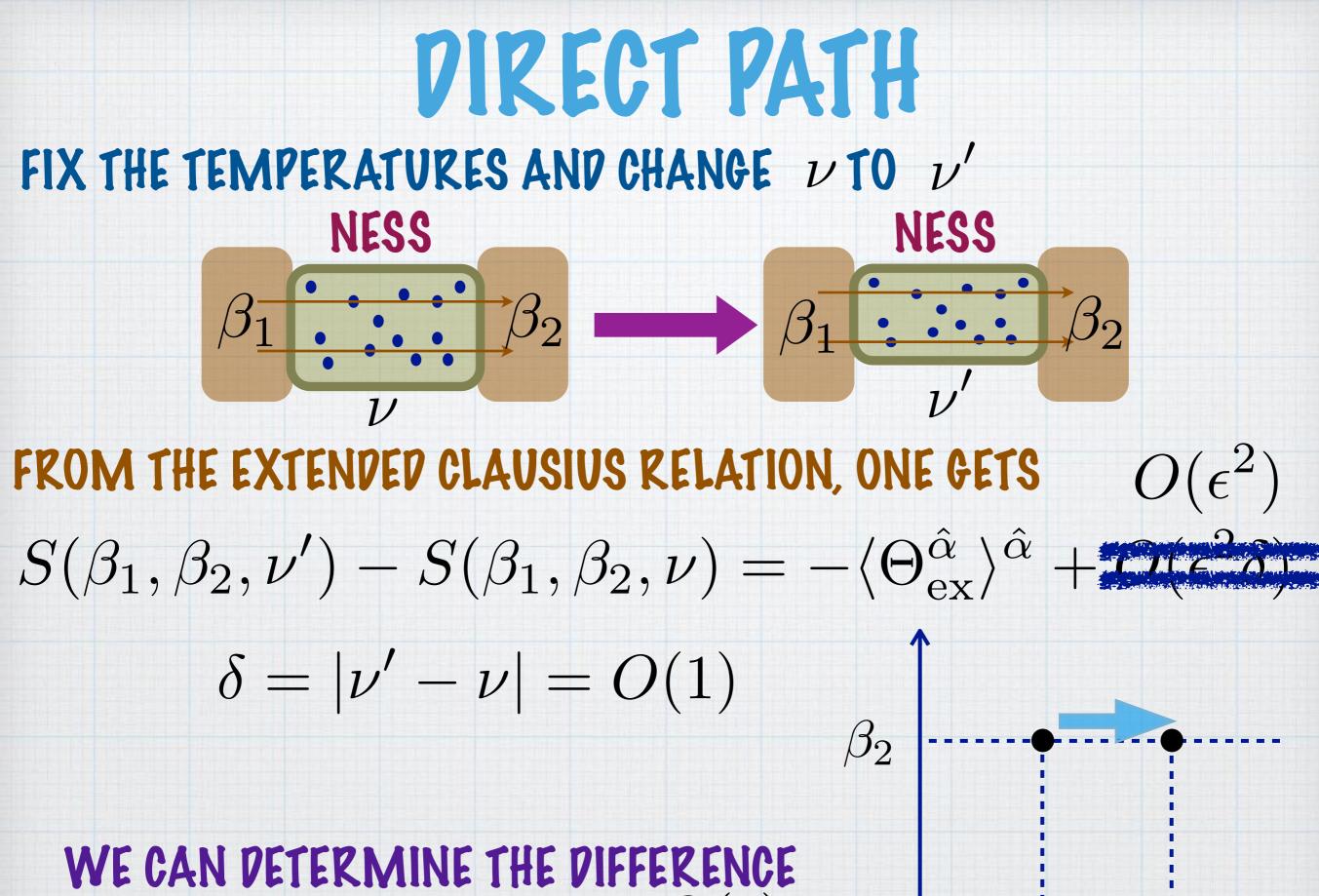
SUPPOSE THAT WE WANT TO DETERMINE THE DIFFERENCE $S(\beta_1,\beta_2,\nu')-S(\beta_1,\beta_2,\nu)$

TEMPERATURE OF THE RIGHT BATH

 β_2

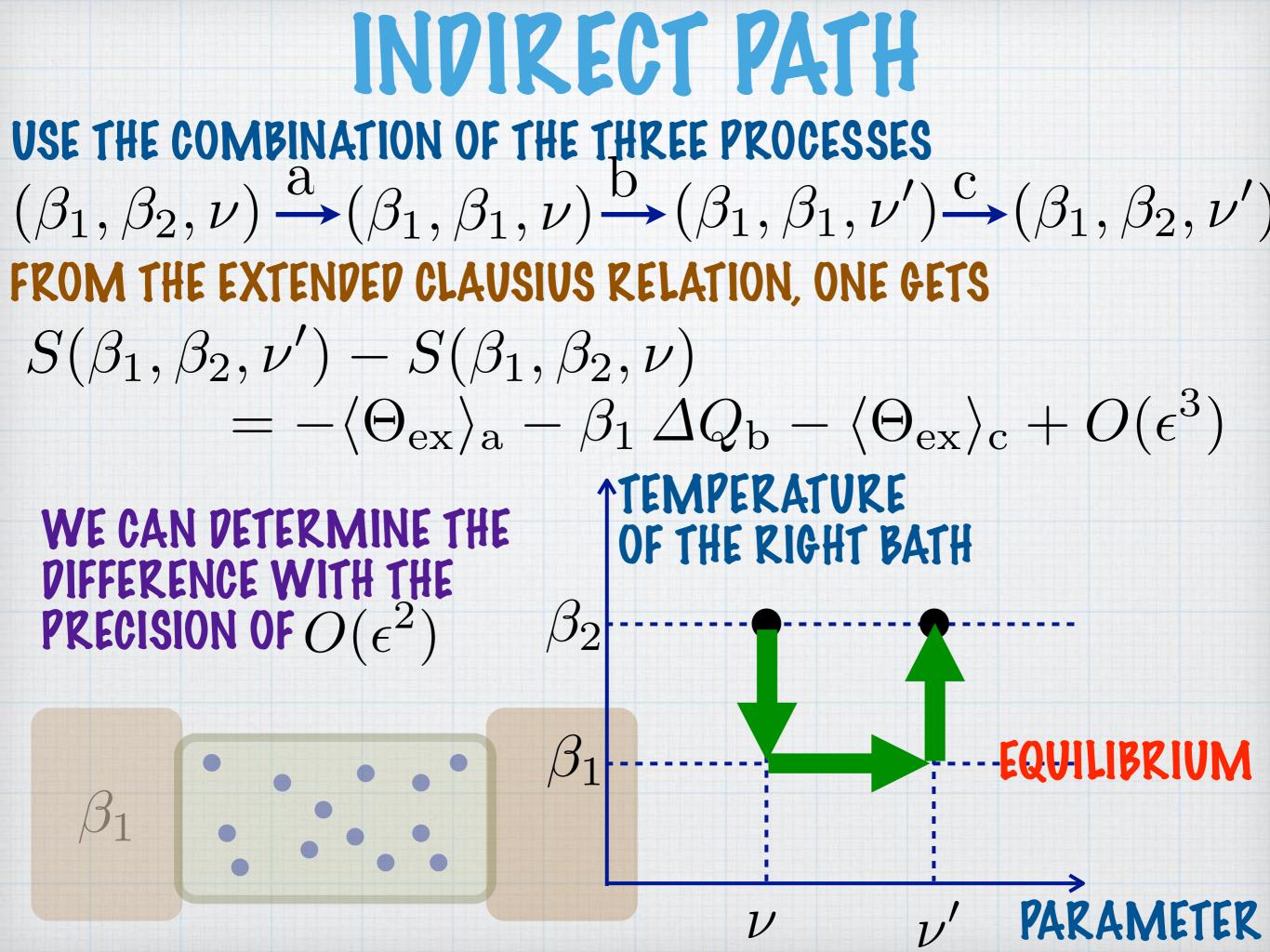
TEMPERATURES ARE THE SAME $|\nu' - \nu| = O(1)$



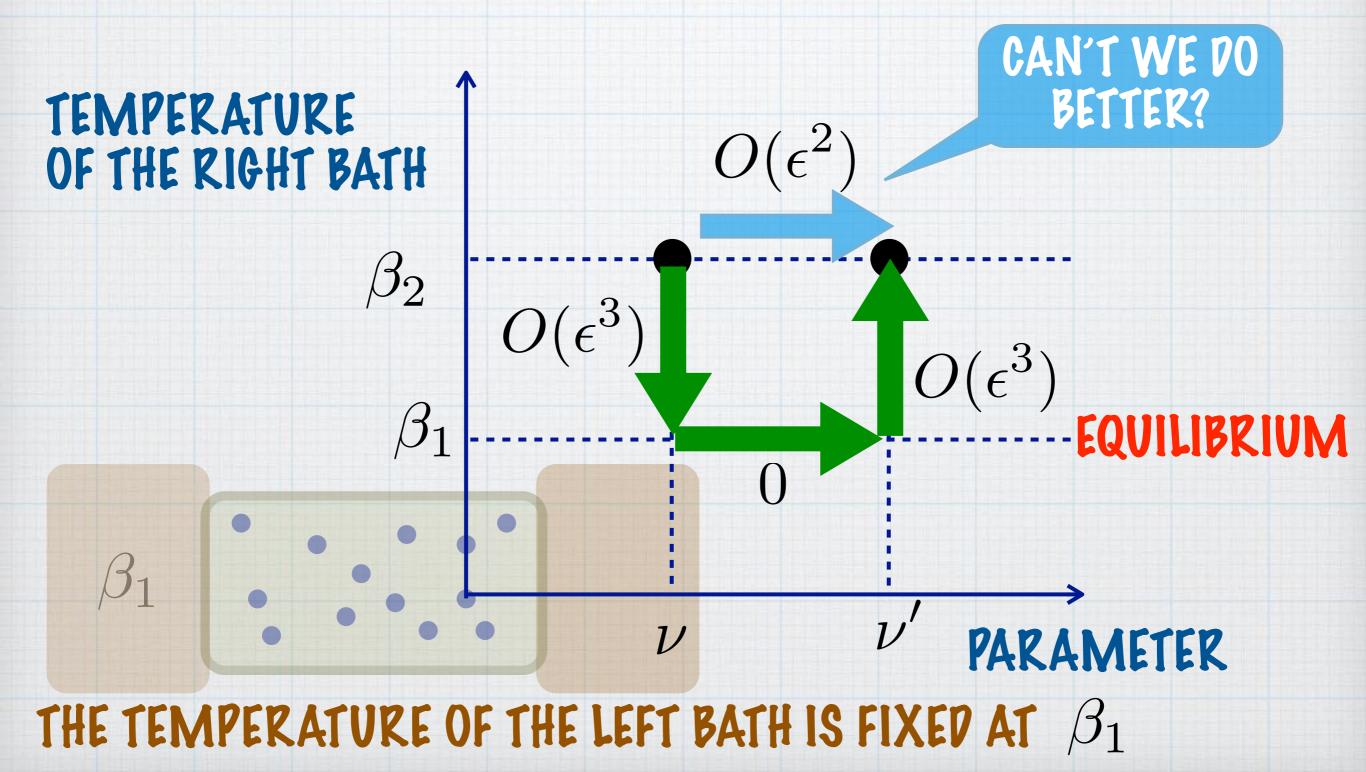


11

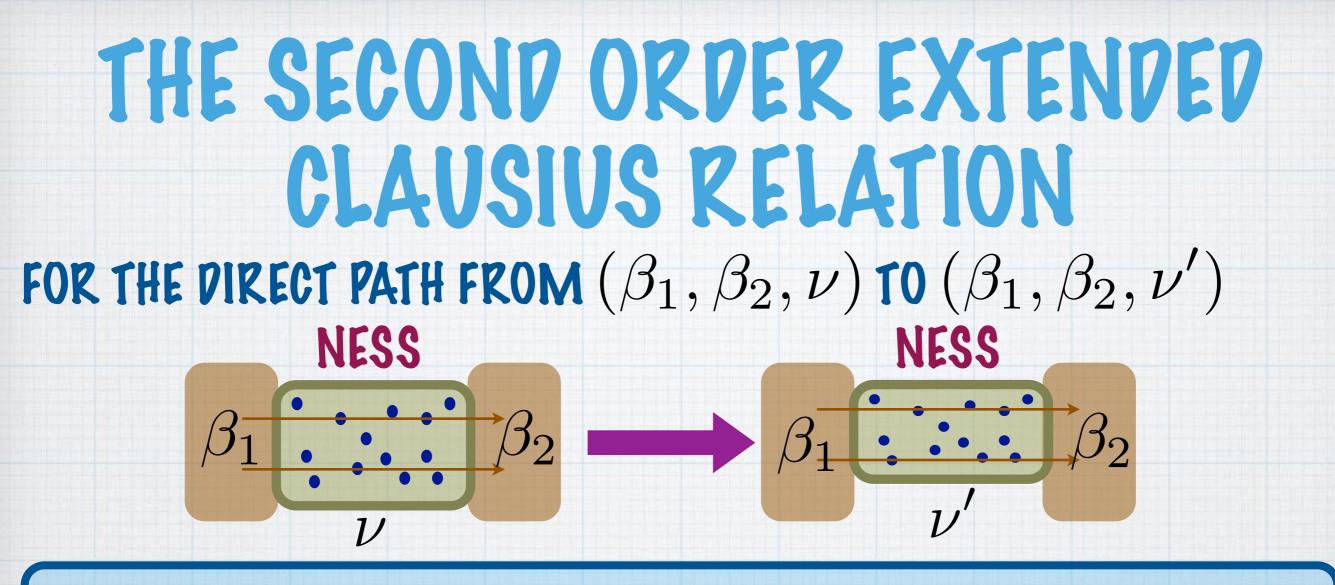
ONLY WITH THE PRECISION OF $O(\epsilon)$



POSSIBLE ERROR IN EACH PROCESS



NONLINEAR NONEQULIBRIUM RELATION



 $S(\beta_1, \beta_2, \nu') - S(\beta_1, \beta_2, \nu)$ $= -\langle \Theta_{\mathrm{ex}}^{\hat{\alpha}} \rangle^{\hat{\alpha}} + \frac{\beta_1 + \beta_2}{\Lambda} \langle W^{\hat{\alpha}}; \Theta^{\hat{\alpha}} \rangle^{\hat{\alpha}} + O(\epsilon^3 \delta)$

 $\begin{array}{l} W \text{ work pone to the system} \qquad \qquad \delta = |\nu' - \nu| \\ \langle W; \Theta \rangle := \langle W \Theta \rangle - \langle W \rangle \langle \Theta \rangle \end{array}$

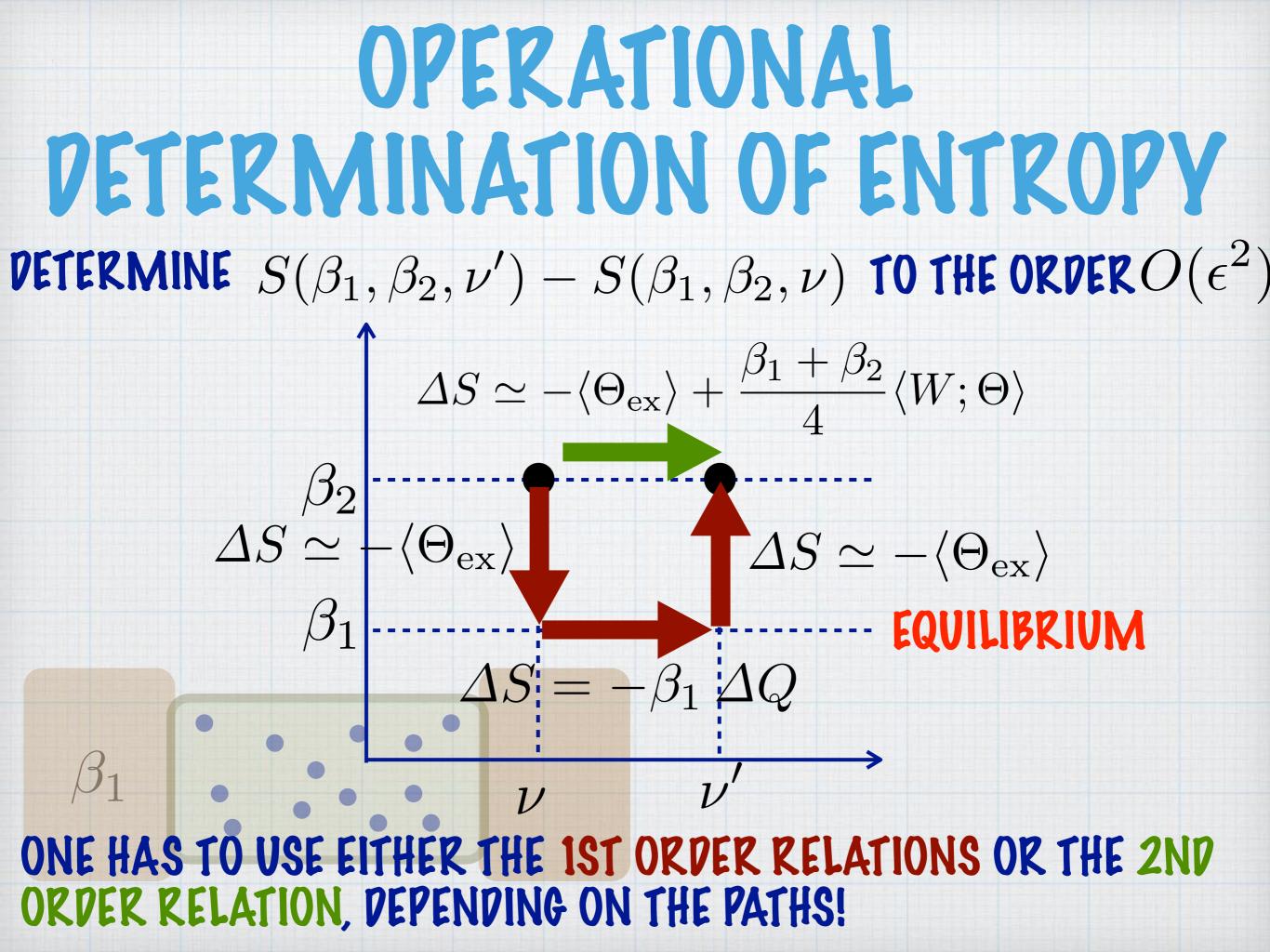
THE SECOND ORDER EXTENDED CLAUSIUS RELATION

 $S(\beta_1, \beta_2, \nu') - S(\beta_1, \beta_2, \nu)$ = $-\langle \Theta_{\text{ex}}^{\hat{\alpha}} \rangle^{\hat{\alpha}} + \frac{\beta_1 + \beta_2}{4} \langle W^{\hat{\alpha}}; \Theta^{\hat{\alpha}} \rangle^{\hat{\alpha}} + O(\epsilon^3 \delta)$

THE RELATION TAKES INTO ACCOUNT "NONLINEAR NONEQUILIBRIUM" CONTRIBUTIONS, AND HAS A DESIRED HIGHER PRECISION.

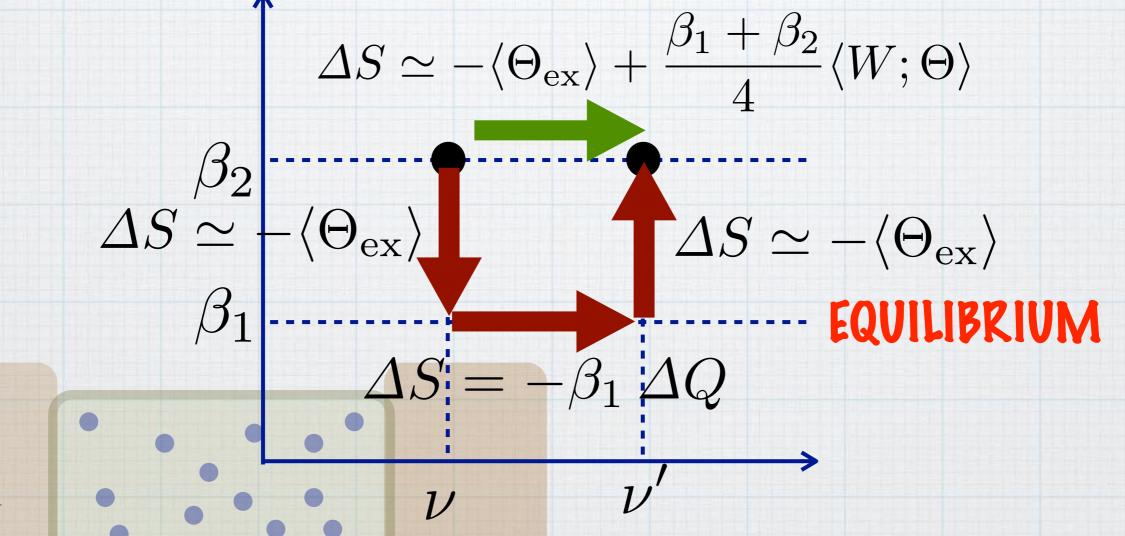
BUT IT CONTAINS A CORRELATION BETWEEN HEAT AND WORK.

IT IS A RELATION BETWEEN MACROSCOPIC QUANTITIES; BUT CAN WE CALL IT A THERMODYNAMIC RELATION?



THE SECOND "TWIST" IN SST

DETERMINE $S(eta_1,eta_2,
u')-S(eta_1,eta_2,
u)$ to the order $O(\epsilon^2)$



ONE HAS TO USE EITHER THE 1ST ORDER RELATIONS OR THE 2ND ORDER RELATION, DEPENDING ON THE PATHS!



■ OUR RESULTS ARE MATHEMATICALLY RIGOROUS FOR MARKOV JUMP PROCESSES, BUT NOT ENTIRELY RIGOROUS FOR OTHER MODELS

WE FOUND A NATURAL EXTENSION OF CLAUSIUS RELATION FOR OPERATIONS BETWEEEN NESS, WHICH ENABLES ONE TO OPERATIONALLY DETERMINE NONEQULIBRIUM ENTROPY TO THE SECOND ORDER IN $\epsilon = |\beta_1 - \beta_2|$

THE NONEQUILIBRIUM ENTROPY HAS AN EXPRESSION IN TERMS OF SYMMETRIZED SHANNON ENTROPY $S_{sym}[\rho] := -\int dx \, \rho_x \, \log \sqrt{\rho_x \, \rho_{x^*}}$ WHAT DOES IT MEAN??

✓IS THERE A MEANINGFUL THERMODYNAMICS FOR NESS WHICH YIELDS NONTRIVIAL EXPERIMENTAL PREDICTIONS?

THERE ARE MANY DIFFERENT ATTEMPTS, E.G., BY Netochny-Maes, Jona-Lasinio et al., Nakagawa-Sasa,