Statistically Interacting Particles With Shapes

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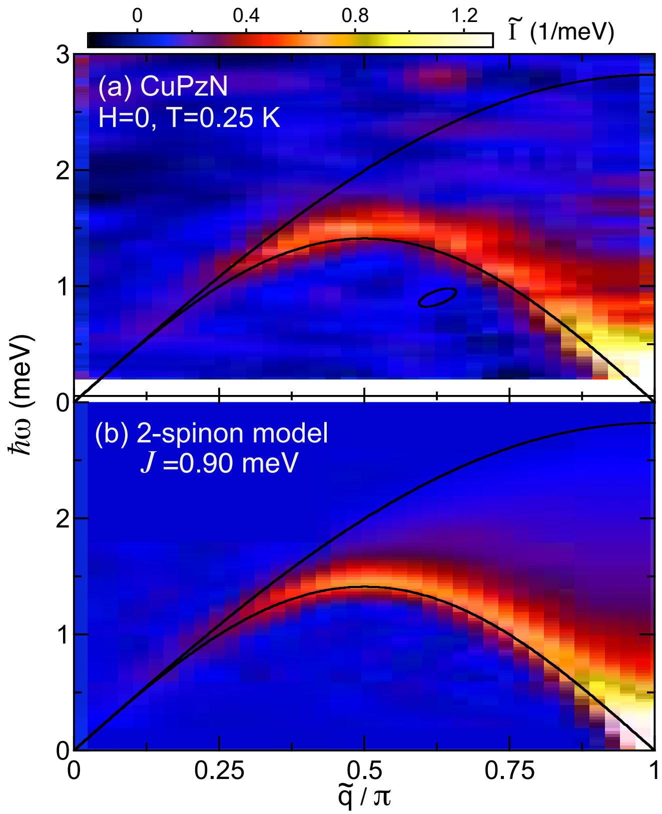
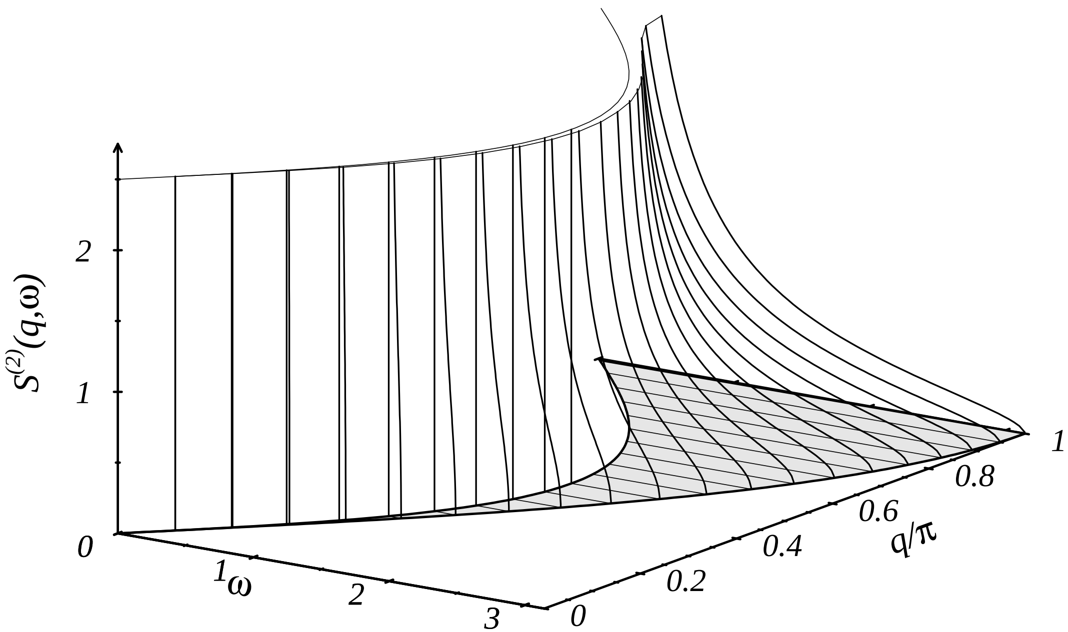
$Cu(C_4H_4N_2)(NO_3)_2$



Stone et al. (2003)

Dynamic structure factor



Karbach et al. (1997)

Ising Spin Chains

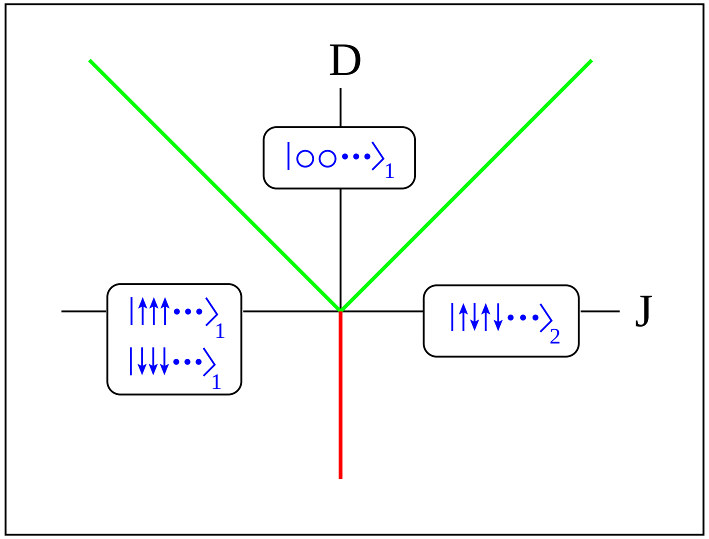
$$\mathcal{H} = \sum_{l=1}^{N} \left[J S_l^z S_{l+1}^z + L S_l^z S_{l+2}^z - h S_l^z + D(S_l^z)^2 + \cdots \right]$$

- P. Lu, J. Vanasse, C. Piecuch, M. Karbach, and G. Müller
  Statistically interacting quasiparticles in Ising chains
  J. Phys. A **41** (2008), 265003, pp. 1-18. [arXiv:0710.1687]

- D. Liu, P. Lu, G. Müller, and M. Karbach
  Taxonomy of particles in Ising spin chains
  Phys. Rev. E **84** (2011), 021136, pp. 1-11 [arXiv:1104.0693]

- P. Lu, D. Liu, G. Müller, and M. Karbach
  Interlinking motifs and entropy landscapes of statistically interacting particles
  Condensed Matter Physics **15** (2012), 13001, pp. 1-17 [arXiv:1108.2990]

- D. Liu, J. Vanasse, G. Müller, and M. Karbach
  Generalized Pauli principle for particles with distinguishable traits
  Phys. Rev. E **85** (2012), 011144, pp. 1-12 [arXiv:1112.3011]



$$\mathcal{H}_D^1 = \sum_{l=1}^{N} \left[J S_l^z S_{l+1}^z + D (S_l^z)^2 \right], \qquad s = 1$$

- $|\circ \cdots \circ\circ\circ \cdots \circ\rangle \xrightarrow{\circ\downarrow\circ} |\circ \cdots \circ \downarrow \circ \cdots \circ\rangle$
- $|\uparrow\downarrow \cdots \uparrow\downarrow\uparrow \cdots \uparrow\downarrow\rangle \xrightarrow{\uparrow\circ\uparrow} |\uparrow\downarrow \cdots \uparrow \circ \uparrow \cdots \uparrow\downarrow\rangle$

motif	m_A	ϵ_m	cat.
$\uparrow\uparrow$	1	$2J$	compact
$\downarrow\downarrow$	2	$2J$	compact
$\circ\circ$	3	$J-D$	tag
$\uparrow\circ\uparrow$	4	$2J-D$	host
$\downarrow\circ\downarrow$	5	$2J-D$	host
$\uparrow\circ\downarrow, \downarrow\circ\uparrow$	6	$2J-D$	host

motif	m_S	ϵ_m	cat.
$\circ\uparrow\circ$	1	D	host
$\circ\downarrow\circ$	2	D	host
$\circ\uparrow\downarrow\circ$	3	$2D-J$	host
$\circ\downarrow\uparrow\circ$	4	$2D-J$	host
$\uparrow\uparrow$	5	$D+J$	hybrid
$\downarrow\downarrow$	6	$D+J$	hybrid
$\uparrow\downarrow\uparrow, \downarrow\uparrow\downarrow$	7	$2D-2J$	hybrid

Generalized Pauli principle [Haldane 1991]

How is the number of states accessible to one particle of species m affected if particles (of any species m') are added?

$$\Delta d_m \doteq -\sum_{m'} g_{mm'} \Delta N_{m'} \qquad \Rightarrow \; d_m = A_m - \sum_{m'} g_{mm'}(N_{m'} - \delta_{mm'})$$

Energy and multiplicity of many-body states

$$E(\{N_m\}) = E_{pv} + \sum_{m=1}^{M} N_m \epsilon_m, \qquad W(\{N_m\}) = n_{pv} \prod_{m=1}^{M} \underbrace{\binom{d_m + N_m - 1}{N_m}}_{\frac{\Gamma(d_m + N_m)}{\Gamma(N_m+1)\Gamma(d_m)}}$$

Statistical interaction coefficients

- $g_{mm} > 0$ for compacts and hosts
- $g_{mm} = 0$ for tags and hybrids
- $g_{th} = -1$ and $g_{ht} > 0$ for hosts and tags
- $g_{cc'} < 0$ possible for compacts

Capacity constants

- $A_m \propto N$ for compacts and hosts
- $A_m = 0$ for tags and hybrids

Thermodynamics with Statistical Interaction

System specifications:

- particle energies ϵ_m
- statistical interaction coefficients $g_{mm'}$
- capacity constants A_m

Two tasks:

- combinatorial problem: $W(\{N_m\})$
- extremum problem: $\delta(U - TS - \mu\mathcal{N}) = 0$

Grand potential [Wu 1994]: $\Omega = -k_B T \ln Z, \quad Z = \prod_m \left(\frac{1+w_m}{w_m}\right)^{A_m}$

$$\frac{\epsilon_m}{k_B T} = \ln(1+w_m) - \sum_{m'} g_{m'm} \ln\left(\frac{1+w_{m'}}{w_{m'}}\right), \quad m = 1, \ldots M$$

Average number of particles: $w_m\langle N_m\rangle + \sum_{m'} g_{mm'}\langle N_{m'}\rangle = A_m, \quad m = 1, \ldots, M$

Configurational entropy [Isakov 1994]:

$$S(\{N_m\}) = k_B \sum_{m=1}^{M} \Big[\big(N_m + Y_m\big)\ln\big(N_m + Y_m\big) - N_m \ln N_m - Y_m \ln Y_m\Big]$$

$$Y_m \doteq A_m - \sum_{m'=1}^{M} g_{mm'} N_{m'}$$

Lattice Gas in One Dimension

Statistically interacting vacancy particles

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Lattice Gas In One Dimension

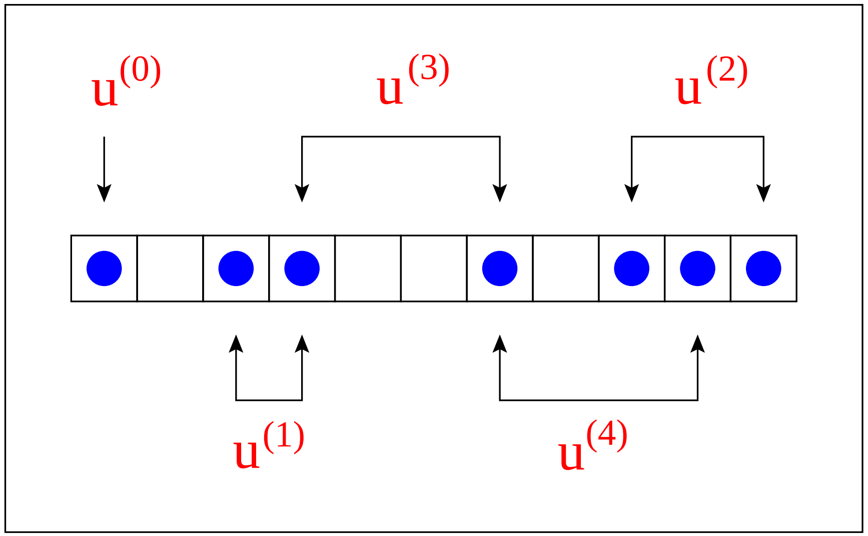
N cells, N_A atoms.

Two hierarchies of interactions:

- $u^{(0)}$: hardcore repulsion (no multiple occupancies)

- $u^{(1)}$: coupling between nn cells
- $u^{(2)}$: coupling between nnn cells

- $u^{(3)}$: coupling between nn atoms
- $u^{(4)}$: coupling between nnn atoms



Transfer Matrix (nn)

Cell variable: $\tau_l = \begin{cases} 0 & \text{vacant} \\ 1 & \text{occupied} \end{cases}$

Hamiltonian: $\mathcal{H} = -\sum_{l=1}^{N} u_1 \tau_l \tau_{l+1}$ (nn cell coupling only)

Partition function: $Z = \sum_{\{\tau_l\}} \exp\left(\beta \sum_{l=1}^{N} \left[u_1 \tau_l \tau_{l+1} + \frac{1}{2}\mu(\tau_l + \tau_{l+1})\right]\right) = \mathrm{Tr}\left[\mathbf{V}^N\right], \quad \beta \doteq \frac{1}{k_B T}$

Transfer matrix: $\mathbf{V} = \begin{pmatrix} e^{U_1+2M} & e^M \\ e^M & 1 \end{pmatrix} \qquad U_1 \doteq \frac{u_1}{k_B T}, \quad M \doteq \frac{\mu}{2k_B T}$

Eigenvalues: $\lambda_\pm = e^w \left[\cosh w \pm \sqrt{\sinh^2 w + e^{-U_1}}\right], \qquad w \doteq \frac{1}{2}(U_1 + 2M)$

Grand potential: $\Omega(T, V, \mu) = -k_B T \ln Z, \quad Z = \lambda_+^N \left[1 + \left(\frac{\lambda_-}{\lambda_+}\right)^N\right], \quad N = \frac{V}{V_c}$

Relation to Ising Spin Chain

Cell variable: $\tau_l = \begin{cases} 0 & \text{vacant} \\ 1 & \text{occupied} \end{cases}$ Ising spin: $\sigma_l = \begin{cases} +1 & \text{up} \\ -1 & \text{down} \end{cases}$ $\tau_l = \frac{1}{2}(1-\sigma_l)$

Hamiltonians: $\mathcal{H}_{LG} = -\sum_{l=1}^{N} u_1 \tau_l \tau_{l+1}, \qquad \mathcal{H}_I = -\sum_{l=1}^{N} \left[J\sigma_l\sigma_{l+1} + H\sigma_l \right]$

Partition functions:

$$Z_{LG}^{(gc)} = \sum_{\{\tau_l\}} \exp\left(\beta \sum_{l=1}^{N} \left[u_1 \tau_l \tau_{l+1} + \frac{1}{2}\mu(\tau_l + \tau_{l+1}) \right] \right)$$

$$Z_I^{(c)} = \sum_{\{\sigma_l\}} \exp\left(\beta \sum_{l=1}^{N} \left[J\sigma_l\sigma_{l+1} + \frac{1}{2}H(\sigma_l + \sigma_{l+1}) \right] \right)$$

Relation: $Z_{LG}^{(gc)} = Z_I^{(c)} e^{-\beta N(J+H)}, \qquad u_1 = 4J, \quad \mu = -2H - 4J$

Thermodynamic potentials: $\Omega(T,V,\mu) = -k_B T \ln Z_{LG}^{(gc)}, \qquad G(T,H,N) = -k_B T \ln Z_I^{(c)}$

Ideal Lattice Gas $(u = 0)$

Grand potential: $\Omega(T, V, \mu) = -\frac{V}{V_c} k_B T \ln\left(1 + e^{\beta\mu}\right), \quad N \doteq \frac{V}{V_c}$

Pressure: $p = -\left(\frac{\partial\Omega}{\partial V}\right)_{T,\mu} = \frac{k_B T}{V_c} \ln\left(1 + e^{\beta\mu}\right)$

Number of atoms: $N_A = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V} = \frac{N}{1 + e^{-\beta\mu}}$

Entropy: $S = -\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu} = N k_B \left[\ln\left(1 + e^{\beta\mu}\right) - \frac{\beta\mu}{1 + e^{-\beta\mu}}\right]$

Internal energy: $U = TS - pV + \mu N_A \equiv 0$

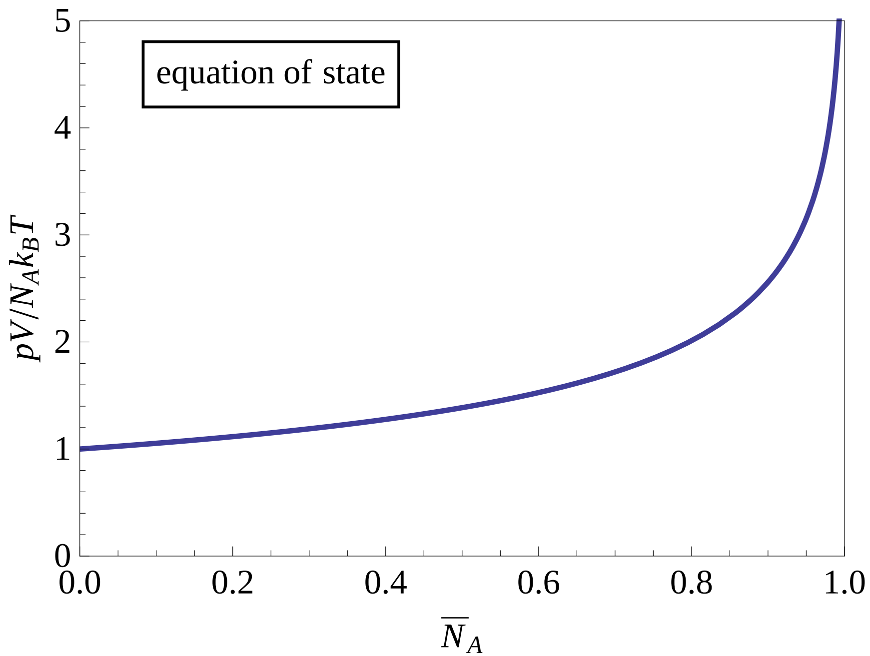
Heat capacity: $C_V \equiv 0$

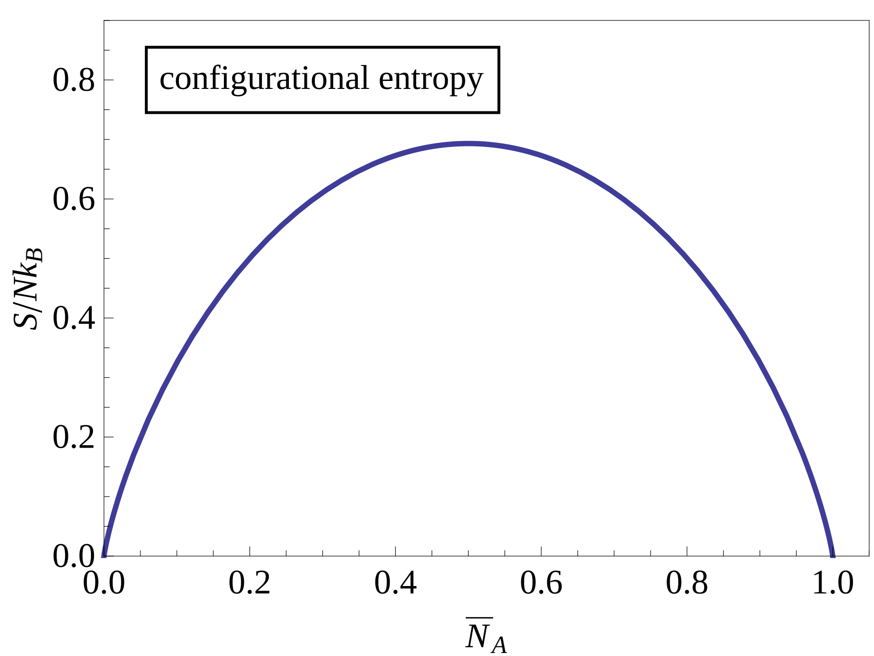
Equation of State and Configurational Entropy

$\bar{N}_A \doteq \dfrac{N_A}{N}$ (density of occupied cells)

$$\frac{pV}{N_A k_B T} = -\frac{1}{\bar{N}_A} \ln\left(1 - \bar{N}_A\right) = 1 + \frac{1}{2}\bar{N}_A + \ldots$$ (relative to classical ideal gas)

$$\frac{S}{N k_B} = -\bar{N}_A \ln \bar{N}_A - (1 - \bar{N}_A)\ln(1 - \bar{N}_A)$$ (fermionic)





Isothermal Process

Exclusion volume: $V_{ex} = N_A V_c$

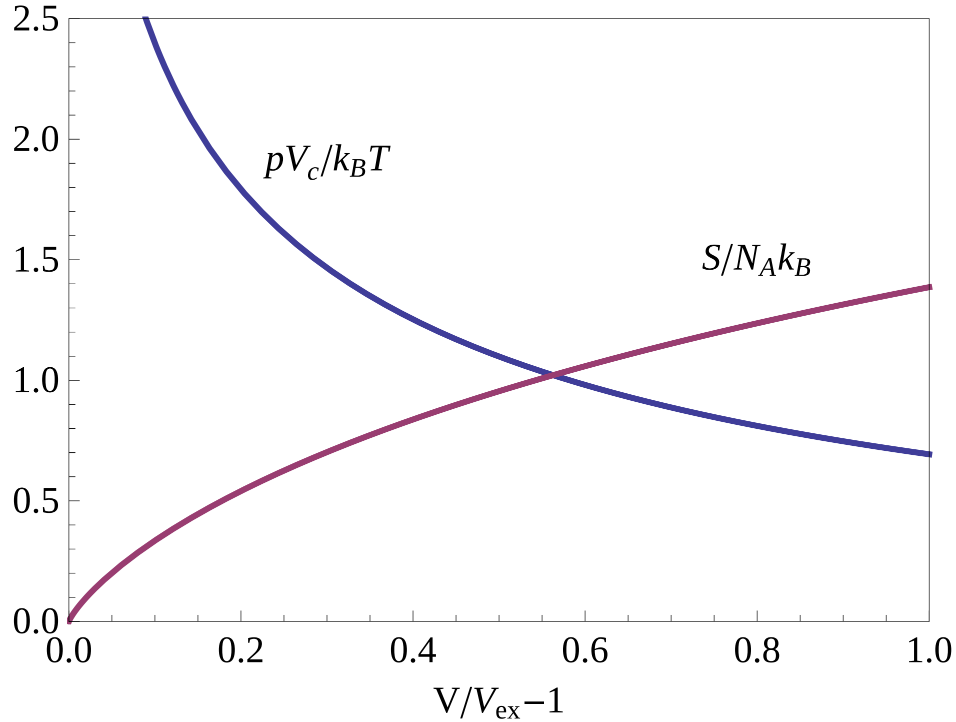
Pressure: $\frac{pV_c}{k_B T} = -\ln\left(1 - \frac{V_{ex}}{V}\right)$

Entropy: $\frac{S}{N_A k_B} = \left(1 - \frac{V}{V_{ex}}\right)\ln\left(1 - \frac{V_{ex}}{V}\right) - \ln\frac{V_{ex}}{V}$

Relation: $p = T\left(\frac{\partial S}{\partial V}\right)_{U,N_A}$

Expansion: add vacant cells

Compression: remove vacant cells



Entropic Pressure

Isothermal compression: $V_{ini} > V > V_{fin}$

Thermodynamic identity: $p = T\left(\frac{\partial S}{\partial V}\right)_U$

Energy transfer: $\Delta U = \Delta Q + \Delta W = 0$

Heat expulsion: $\Delta Q = T\Delta S = T(S_{fin} - S_{ini}) < 0$

Work performance: $\Delta W = -\int_{V_{ini}}^{V_{fin}} pdV = -T\int_{V_{ini}}^{V_{fin}}\left(\frac{\partial S}{\partial V}\right)_U dV = -T\Delta S > 0$

Distinguish

- kinetic pressure
- interaction pressure
- entropic pressure

Change of Perspective

method of analysis	transfer matrix	statistical interaction
fundamental degrees of freedom	individual cells (vacant or occupied)	vacant cells (individual or clusters)
interactions	between cells (nn, nnn, etc.)	between atoms (nn, nnn, etc.)
number of cells	fixed	fluctuating
number of atoms	fluctuating	fixed
ensemble	grandcanonical	grandcanonical
boundary conditions	periodic	open

Vacancy Particles

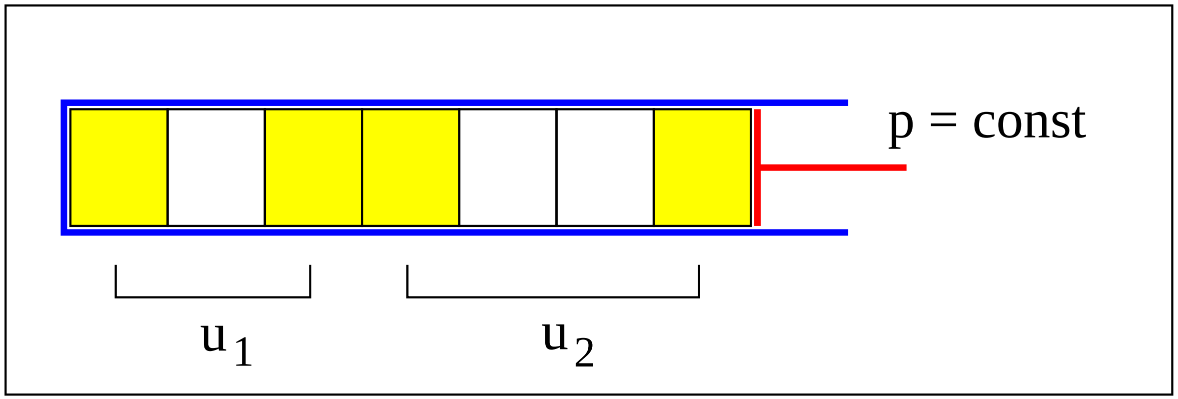
Ground state: ■■ $\cdots$ ■ (N_A occupied cells)

nn coupling between occupied cells:

motif	category	ϵ_m
■□■	host	$pV_c + u_1$
□□	tag	pV_c

nn coupling between atoms:

motif	category	ϵ_m
■□■	compact	$pV_c + u_1$
■□□■	compact	$2pV_c + u_2$
⋮	⋮	⋮



Combinatorics of Vacancy Particles

Hosts and tags

motif	category	m	ϵ_m	A_m
■□■	host	h	$pV_c + u_1$	$N-1$
□□	tag	t	pV_c	0

$g_{mm'}$	h	t
h	1	0
t	-1	0

Compacts

motif	category	m	ϵ_m	A_m
■□■	compact	1	$pV_c + u_1$	$N-1$
■□□■	compact	2	$2pV_c + u_2$	$N-1$
■□□□■	compact	3	$3pV_c + u_3$	$N-1$
$\vdots$	$\vdots$	$\vdots$		

$g_{mm'}$	1	2	1	$\cdots$
1	1	1	1	$\cdots$
2	0	1	1	$\cdots$
3	0	0	1	$\cdots$
$\vdots$	$\vdots$	$\vdots$	$\vdots$	

Statistical Mechanics of Hosts and Tags

Gibbs free energy: $\bar{G}(T,p) = -k_BT\ln\left(1+\frac{e^{-K_u}}{e^{K_p}-1}\right), \qquad K_p \doteq \frac{pV_c}{k_BT}, \quad K_u \doteq \frac{u_1}{k_BT}$

Population densities: $\langle\bar{N}_h\rangle = \frac{1}{1+e^{K_u}(e^{K_p}+1)}, \quad \langle\bar{N}_t\rangle = \frac{1}{(e^{K_p}-1)[1+e^{K_u}(e^{K_p}+1)]}$

Volume: $\frac{V}{V_{ex}} - 1 = \langle\bar{N}_h\rangle + \langle\bar{N}_t\rangle = \frac{e^{K_p}}{(e^{K_p}-1)[1+e^{K_u}(e^{K_p}+1)]}$

Entropy: $\frac{\bar{S}}{k_B} = \ln\left(1+\frac{1}{e^{K_u}(e^{K_p}+1)}\right) + \frac{e^{K_p}(K_p+K_u)-K_u}{(e^{K_p}-1)[1+e^{K_u}(e^{K_p}+1)]}$

Limiting cases:

- $u_1 \to +\infty$: $\frac{\bar{S}}{k_B} \to 0, \quad \frac{V}{V_{ex}} - 1 \to 0$
- $u_1 \to 0$: $\frac{\bar{S}}{k_B} \to \frac{K_p}{e^{K_p}-1} - \ln\left(1-e^{-K_p}\right), \quad \frac{V}{V_{ex}} - 1 \to \frac{1}{e^{K_p}-1}$
- $u_1 \to -\infty$: $\frac{\bar{S}}{k_B} \to \frac{K_p}{e^{K_p}-1} - \ln\left(1-e^{-K_p}\right), \quad \frac{V}{V_{ex}} - 1 \to \frac{1}{1-e^{-K_p}}$

Statistical Mechanics of Compacts

Gibbs free energy: $\bar{G}(T,p) = -k_B T \ln\left(1 + \sum_{m=1}^{\infty} e^{-K_m}\right), \quad K_m = \frac{mpV_c + u_m}{k_B T}$

Population densities: $\langle \bar{N}_m \rangle = \frac{e^{-K_m}}{1 + \sum_{m'=1}^{\infty} e^{-K_{m'}}}$

Limit of zero inter-atomic coupling $(u_m = 0)$:

$$\bar{G}(T,p) = -k_B T \ln\left(\sum_{m=0}^{\infty} e^{-mK_p}\right) = k_B T \ln\left(1 - e^{-K_p}\right)$$

$$\langle \bar{N}_m \rangle = \frac{e^{-mK_p}}{\sum_{m'=0}^{\infty} e^{-m'K_p}} = e^{-mK_p}\left(1 - e^{-K_p}\right) \quad \text{(Pascal distribution)}$$

Isobaric Expansion

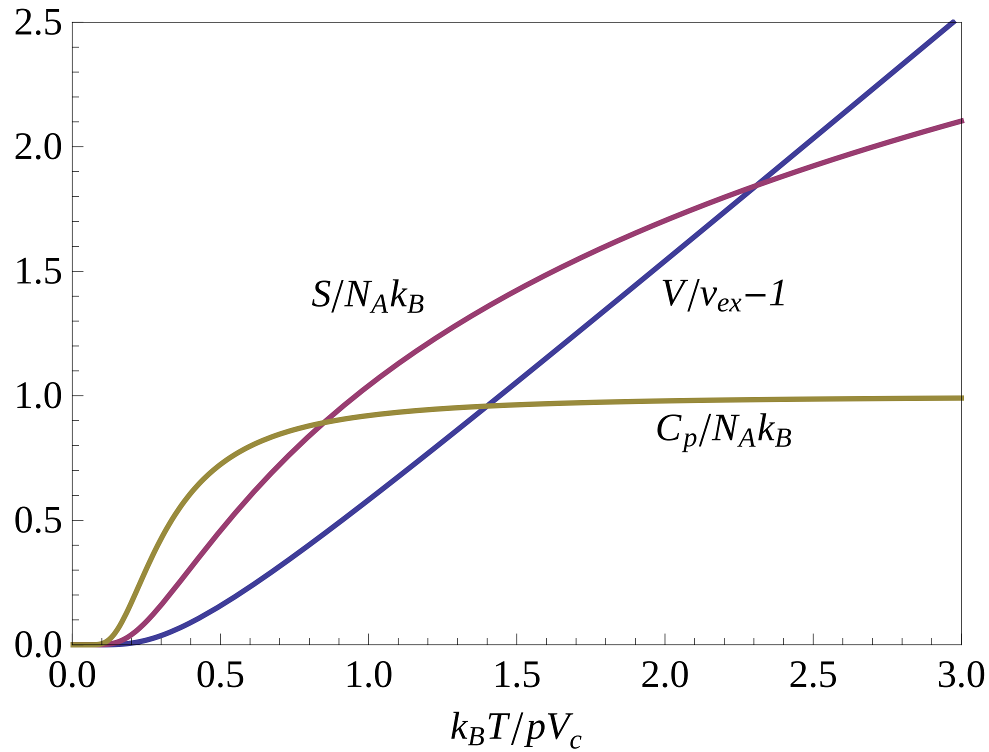
Volume: $\frac{V}{V_{ex}} - 1 = \frac{1}{e^K - 1}, \quad K \doteq \frac{pV_c}{k_B T}$ (bosonic)

Entropy: $\frac{S}{N_A k_B} = \frac{K}{e^K - 1} - \ln\left(1 - e^{-K}\right)$

Heat capacity: $\frac{C_p}{N_A k_B} = \frac{K^2 e^K}{(e^K - 1)^2}$

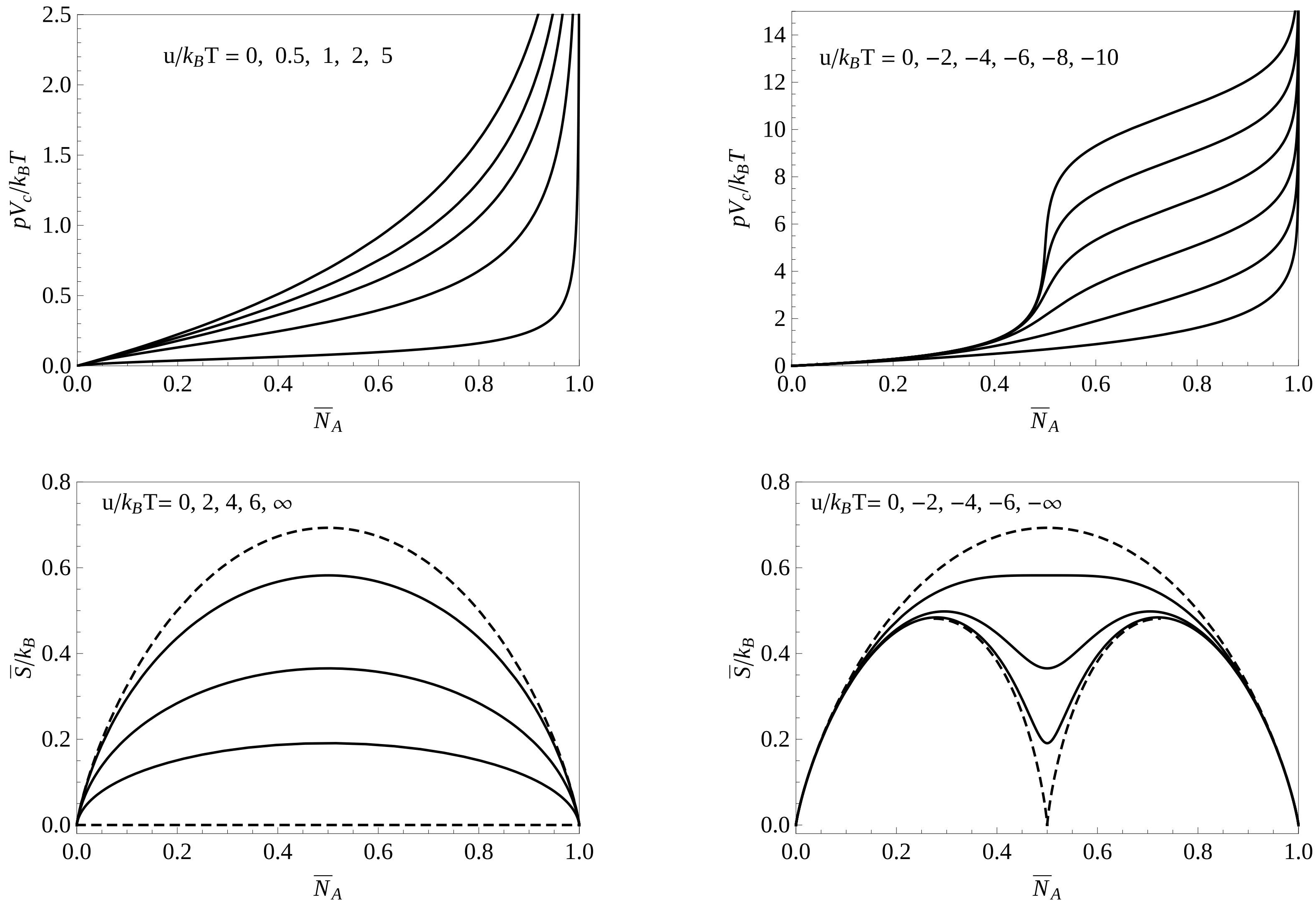
Work performance: $\Delta W = -p\Delta V = -\Delta E$

Heat transfer: $\Delta Q = \int_{T_{ini}}^{T_{fin}} C_p dT = +\Delta E$



Nearest-Neighbor Cell Coupling

$$\Omega(T,V,\mu) = -Nk_BT\left[w + \ln\left(\cosh w + \sqrt{\sinh^2 w + e^{-\beta u}}\right)\right], \quad w = \frac{1}{2}\beta(u+\mu)$$



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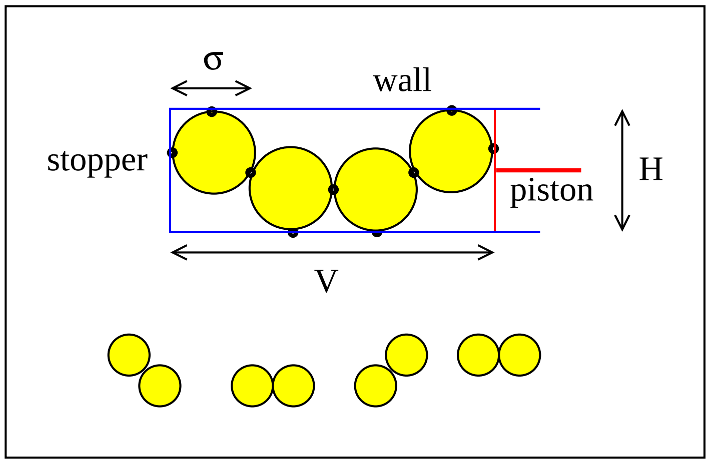
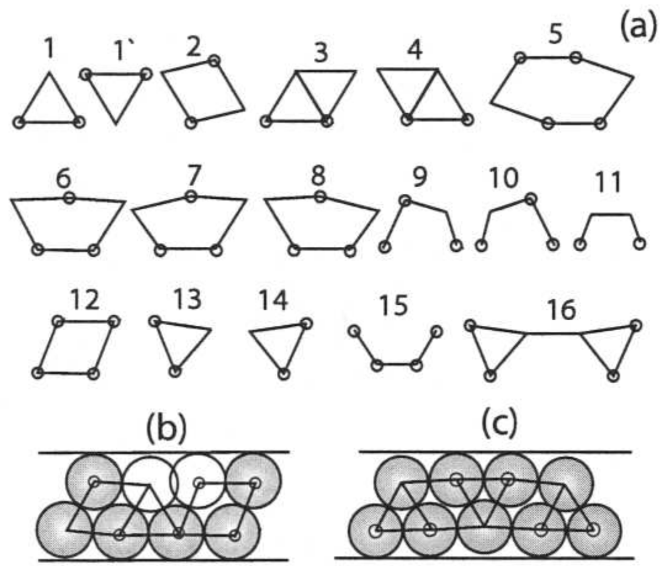
Jammed Hard Disks

Three regimes:

1. $1 < H/\sigma < 1 + \sqrt{3/4}$: all disks in contact with wall
2. $1 + \sqrt{3/4} < H/\sigma < 2$: some disks jammed by three disks
3. $H/\sigma > 2$: non-local jamming condition





regime 1: 4 tiles

Bowles and Saika-Voivod (2006)

regime 2: 32 tiles

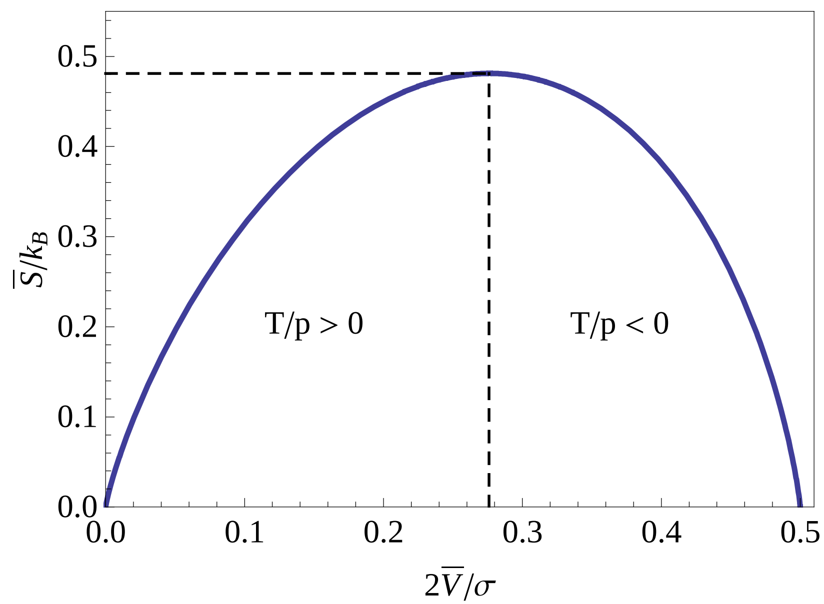
Ashwin and Bowles (2009)

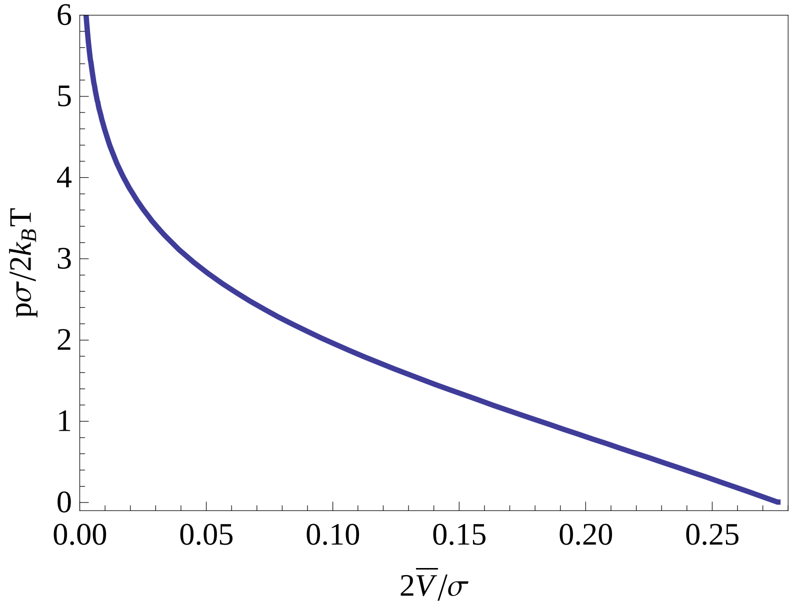
Compactivity

Configurational entropy (regime 1)

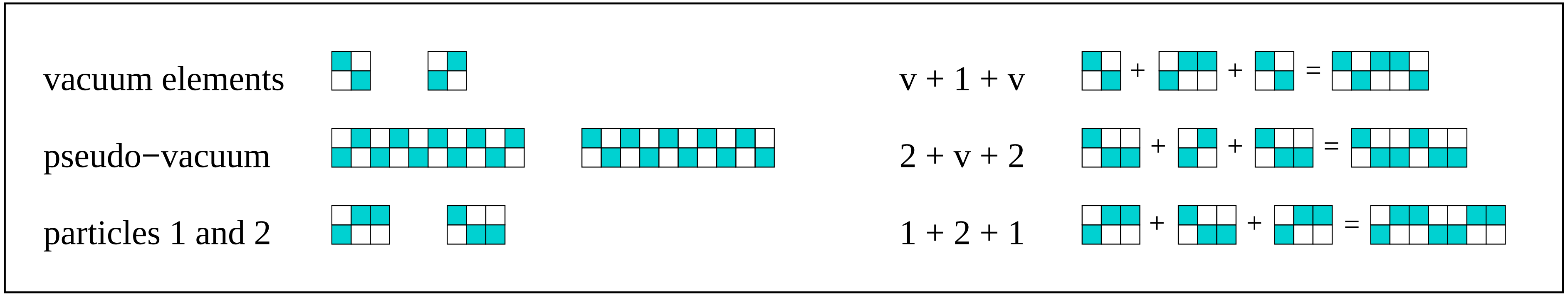
$$\frac{\bar{S}}{k_B} = (1-\tilde{V})\ln(1-\tilde{V}) - \tilde{V}\ln\tilde{V} - (1-2\tilde{V})\ln(1-\tilde{V}), \qquad \tilde{V} \doteq \frac{2\bar{V}}{\sigma}, \quad \bar{V} \doteq \frac{V-V_0}{N_A}$$

Compactivity: $X \doteq \left(\frac{\partial \bar{S}}{\partial \bar{V}}\right)^{-1}_{\bar{U}} = \frac{T}{p}, \qquad \tilde{X} \doteq \frac{2k_BT}{p\sigma}$





Motifs of statistically interacting particles

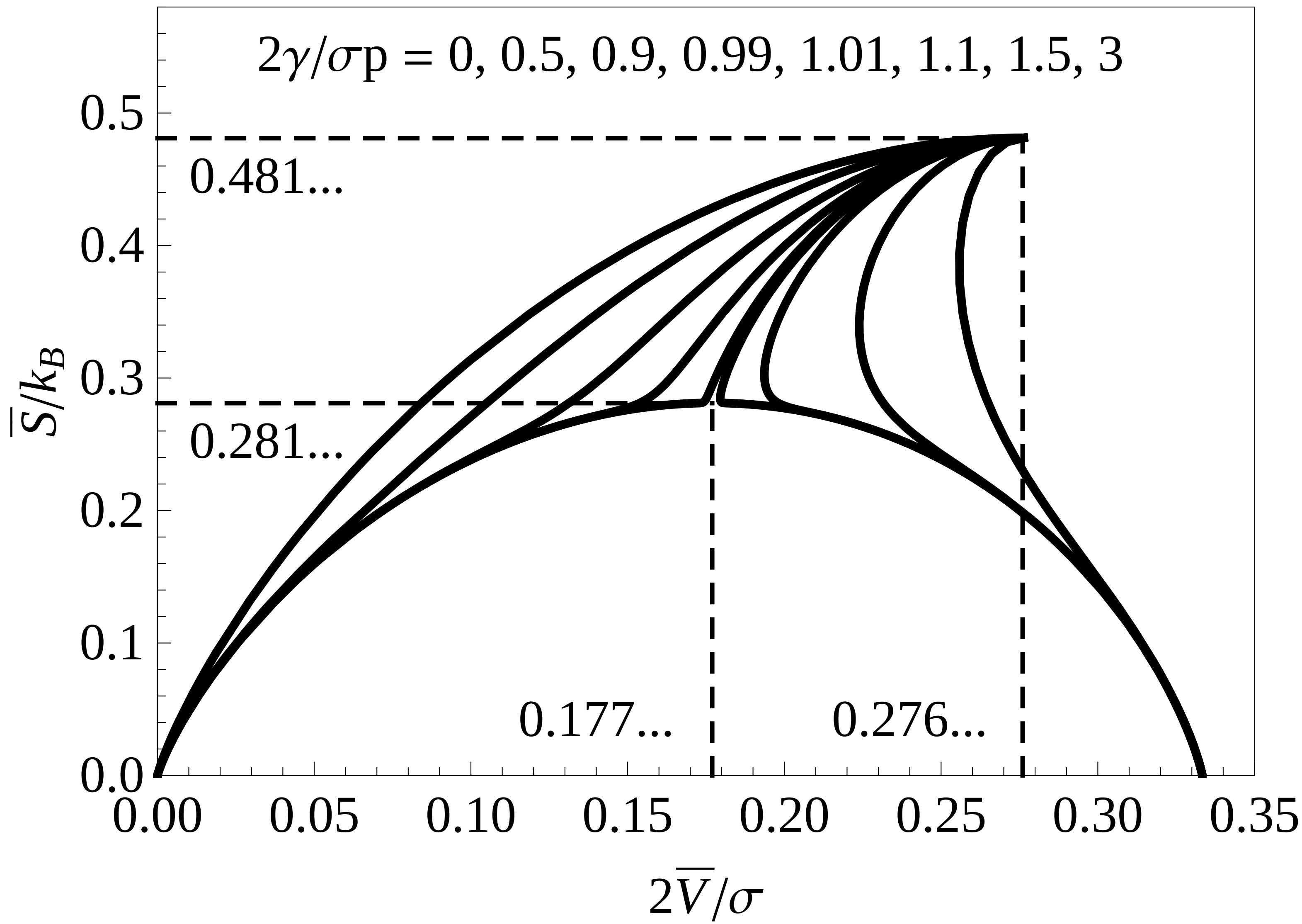


Specifications of statistically interacting particles

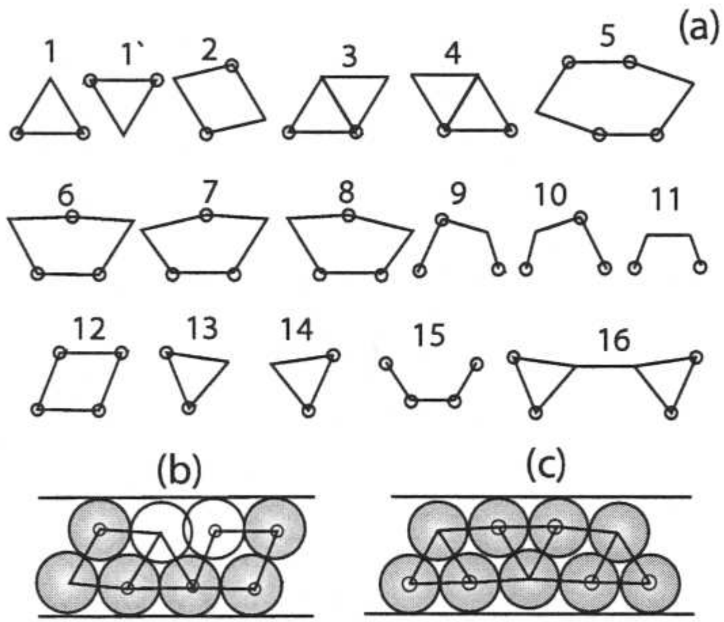
motif	category	m	v_m	ϵ_m	A_m
□■■ ■□□	compact	1	$\frac{1}{2}\sigma$	$\frac{1}{2}\sigma p + \gamma$	$\frac{1}{2}(N_A - 3)$
■□□ □■■	compact	2	$\frac{1}{2}\sigma$	$\frac{1}{2}\sigma p - \gamma$	$\frac{1}{2}(N_A - 3)$

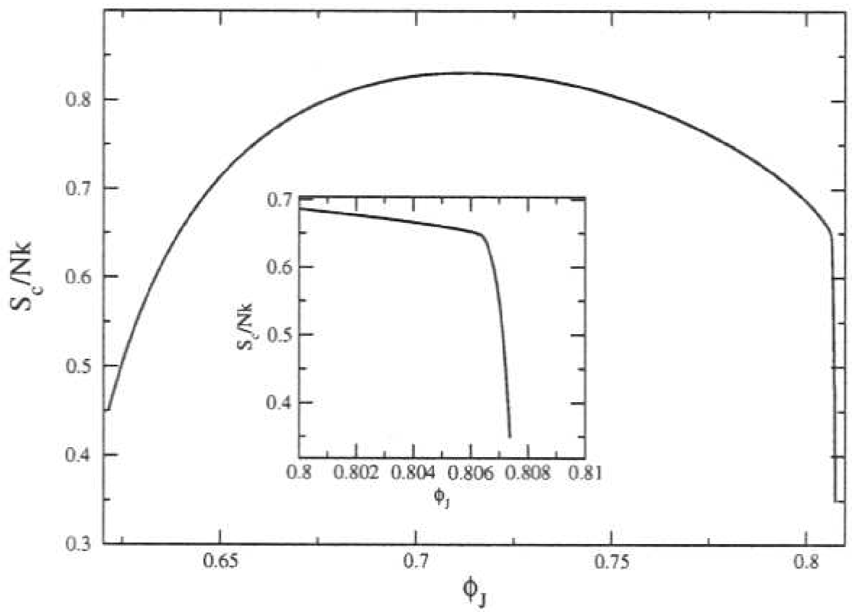
$g_{mm'}$	1	2
1	$\frac{3}{2}$	$\frac{1}{2}$
2	$\frac{1}{2}$	$\frac{3}{2}$

Phase Separation



Tiles of three kinds: high-density – interface – low-density





Ashwin and Bowles (2009)

Structural Crossover (2)

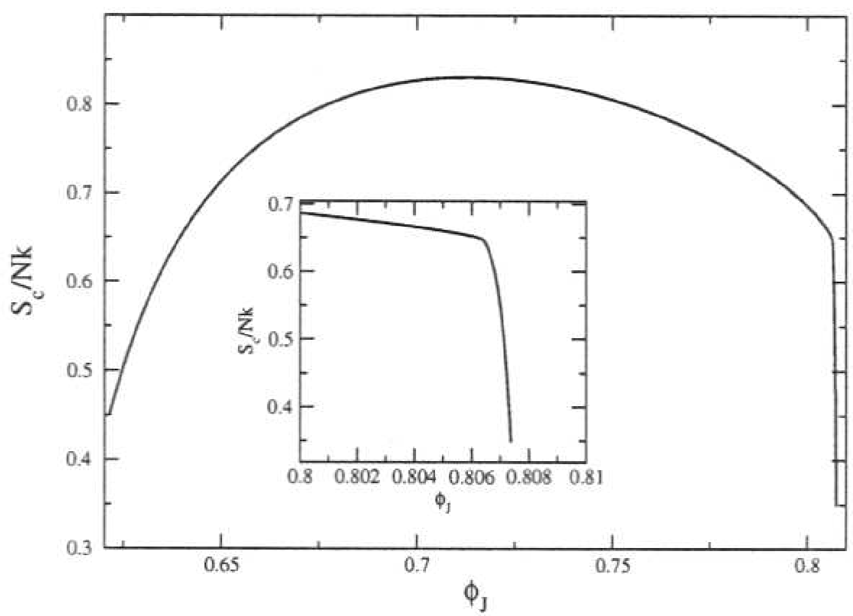
Particles of three kinds: compacts – hosts – hybrids

motif	category	m	v_m	A_m
■□■	compact	1	v_1	$N_A - 1$
■ ○ ■ ○ ■	host	2	v_2	$N_A - 2$
■ △ ■	hybrid	3	v_3	0
■ ▽ ■	hybrid	4	v_4	0

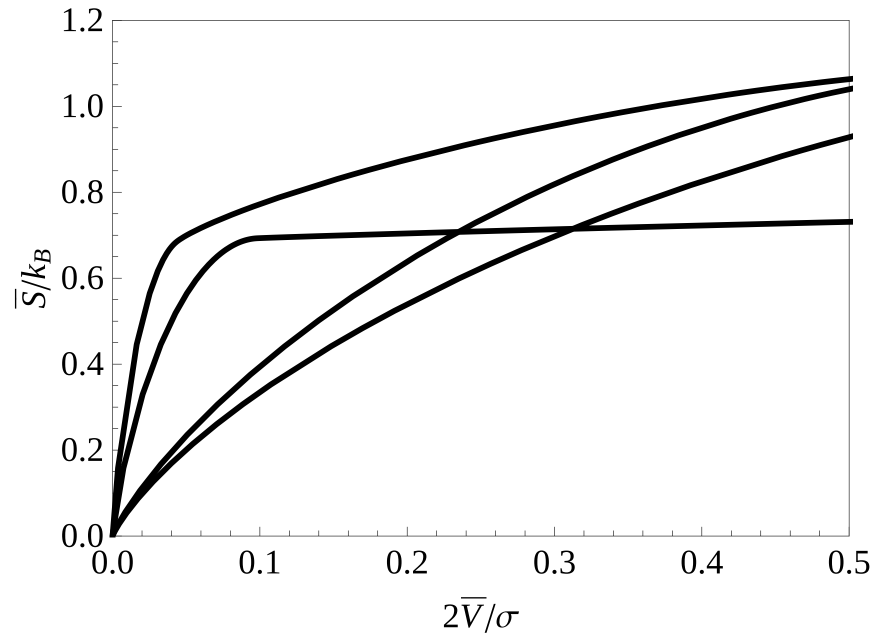
$g_{mm'}$	1	2	3	4
1	1	1	1	1
2	1	2	1	1
3	0	-1	0	-1
4	0	-1	0	0

Structural Crossover (3)

32 tiles



4 particles



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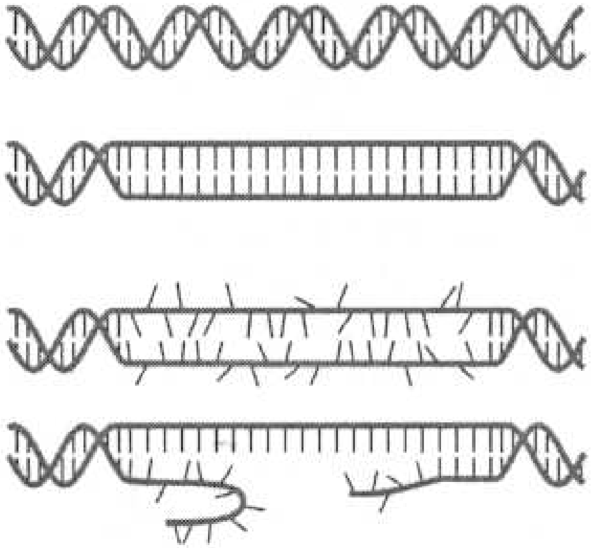
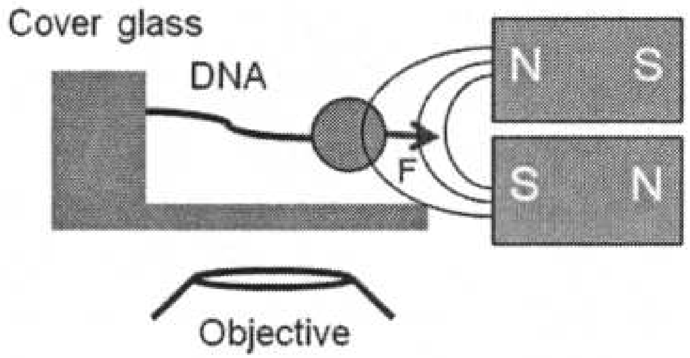
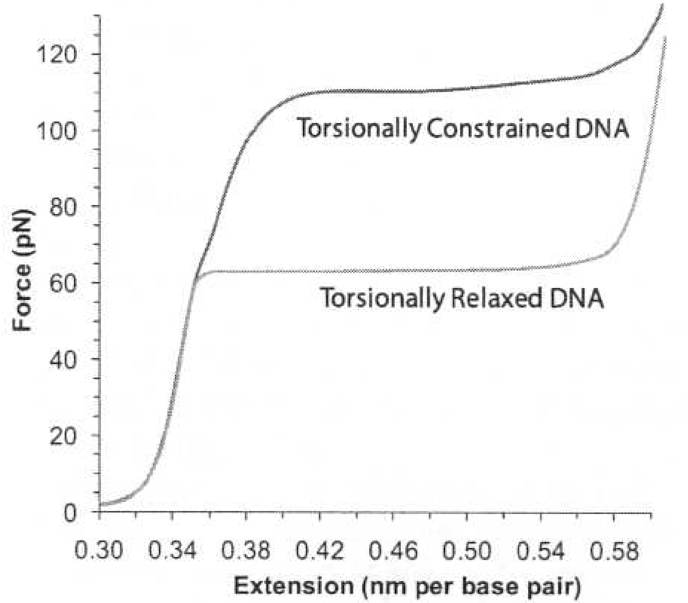
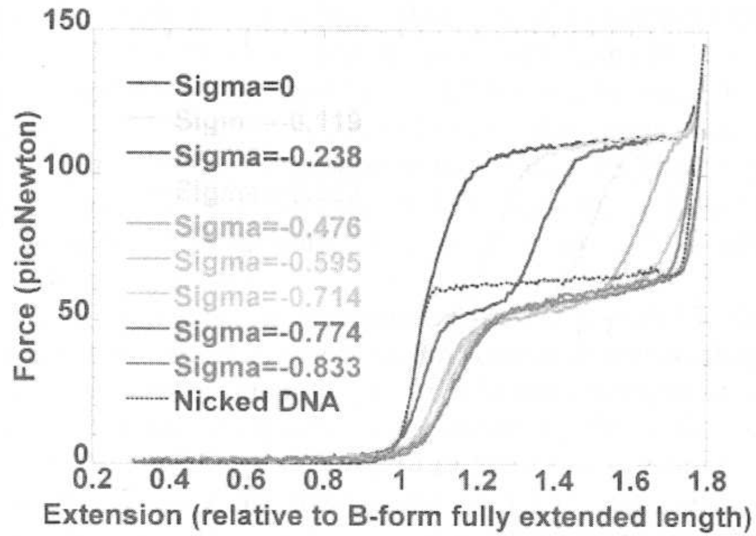
DNA Helix Under Tension and Torque



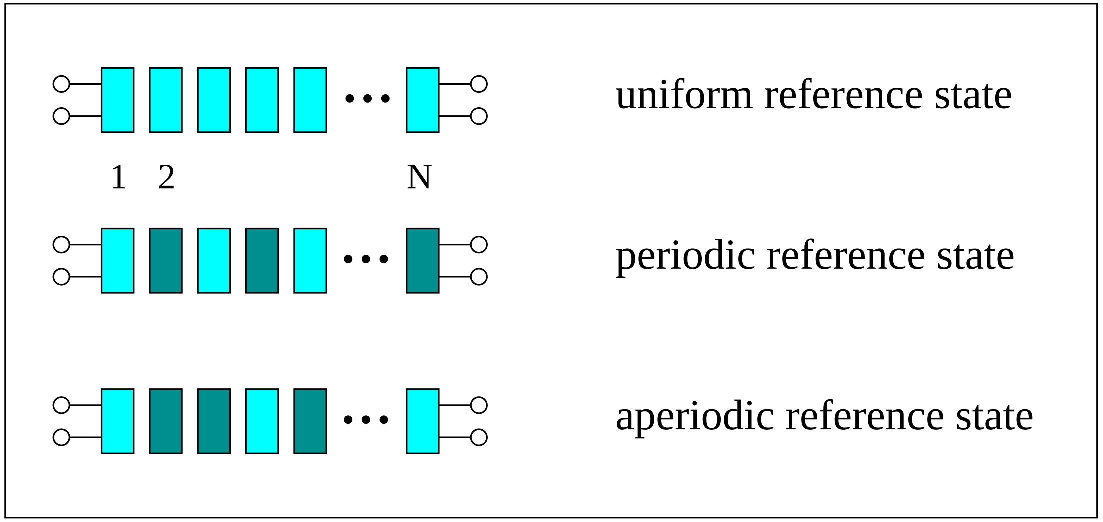


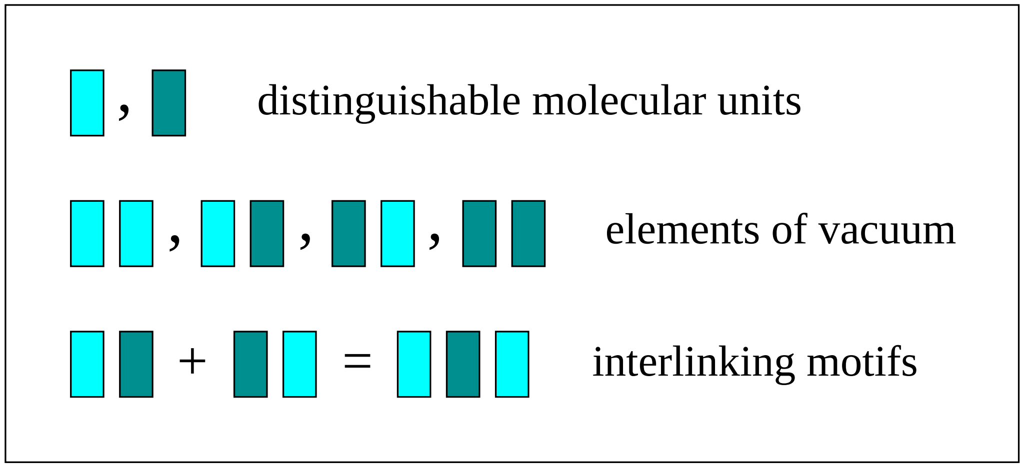




Chains – Vacua – Links – Motifs

Molecular chain of N links $(N \gg 1)$ under minimal tension and torque

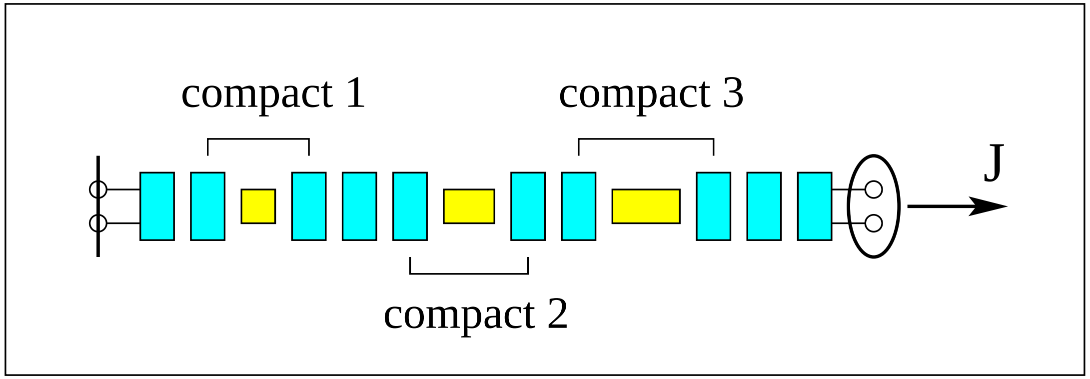


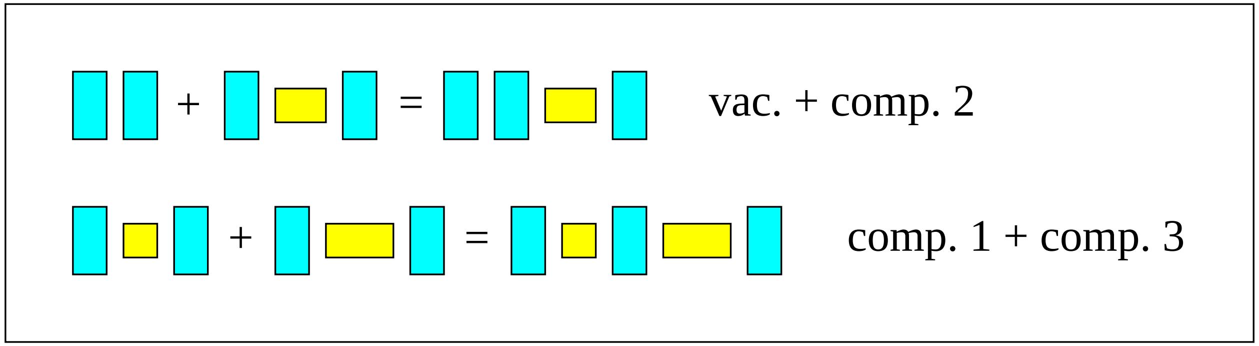


Links Modified by Tension (1)

Applied tension J causes extension: $\Delta L = \sum_m \langle N_m \rangle L_m, \ m = 1, 2, \ldots$

Particle activation energies: $\epsilon_m = B_m - JL_m, \ m = 1, 2, \ldots$





Compacts: Fermi-Dirac Statistics

Uniform vacuum

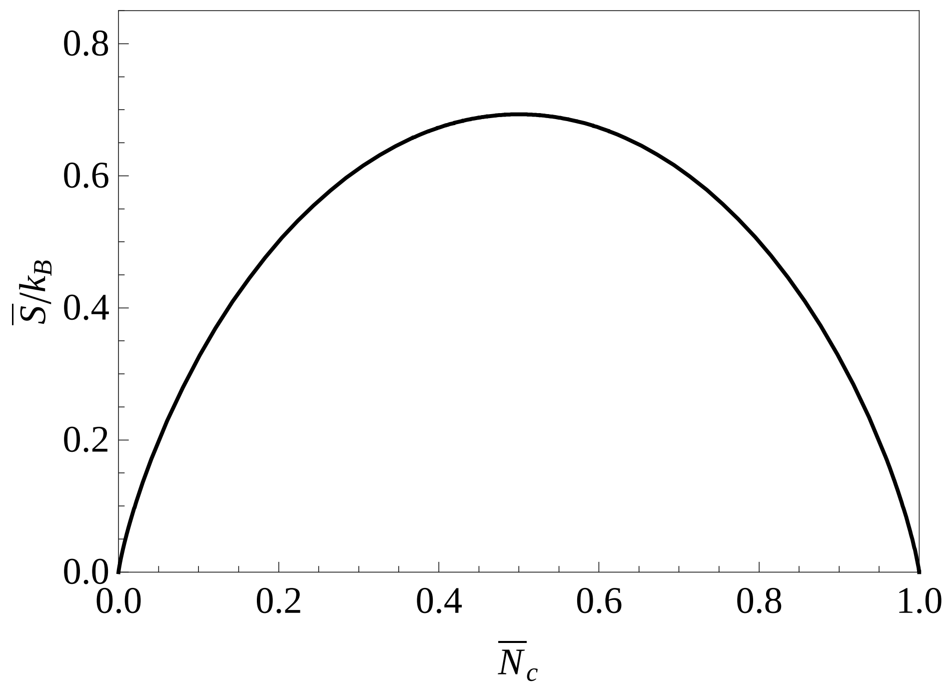
Chain of N links

One species of compacts

motif	category	m	ϵ_m	A_m	g_{mm}
■■	vacuum	–	–	–	–
■□■	compact	c	$B_c - JL_c$	$N-1$	1

Entropy landscape:

$$\bar{S}/k_B = -\bar{N}_c \ln \bar{N}_c - (1-\bar{N}_c)\ln(1-\bar{N}_c)$$



Gibbs free energy:

$$\bar{G}(T,J) = -k_BT\ln\left(1+e^{-K_c}\right)$$

Particle population density:

$$\bar{N}_c = \frac{1}{e^{K_c}+1}, \quad K_c \doteq \frac{B_c - JL_c}{k_BT}$$

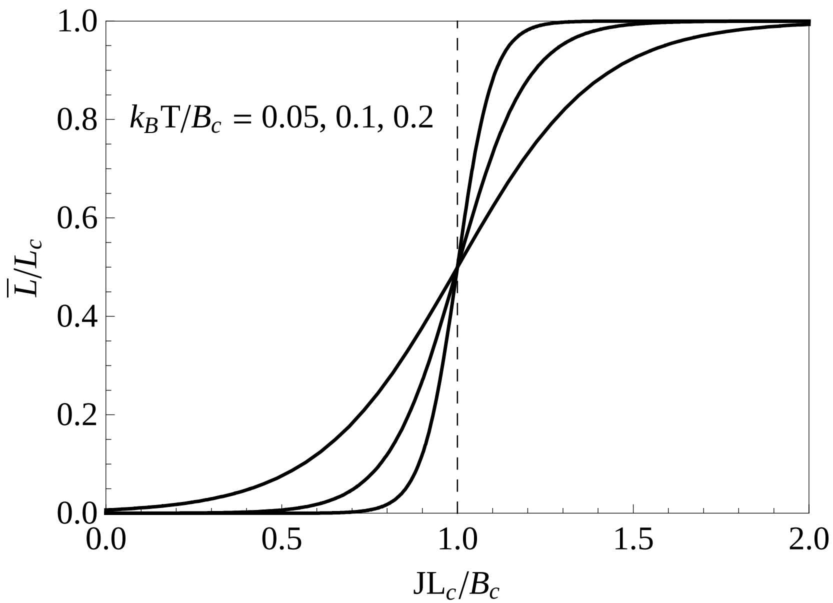
Force-Extension Characteristics

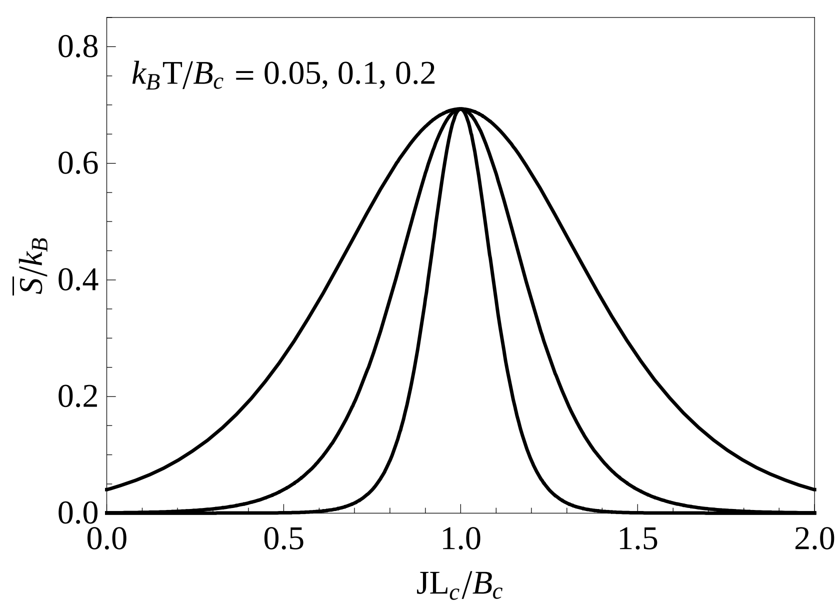
$$\bar{G}(T,J) = -k_B T \ln\left(1 + e^{-K_c}\right) \quad \text{(Gibbs free energy)} \qquad K_c \doteq \frac{B_c - JL_c}{k_B T}$$

$$\bar{L} = -\left(\frac{\partial \bar{G}}{\partial J}\right)_T = \frac{L_c}{e^{K_c}+1} = L_c \bar{N}_c \quad \text{(excess length)}$$

$$\bar{S} = -\left(\frac{\partial \bar{G}}{\partial T}\right)_J = k_B\left[\ln\left(1+e^{-K_c}\right) + \frac{K_c}{e^{K_c}+1}\right] \quad \text{(entropy)}$$

$$\bar{U} = \bar{G} + T\bar{S} + J\bar{L} = \frac{B_c}{e^{K_c}+1} \quad \text{(internal energy)}$$





Additional control variable μ_c (chemical potential)

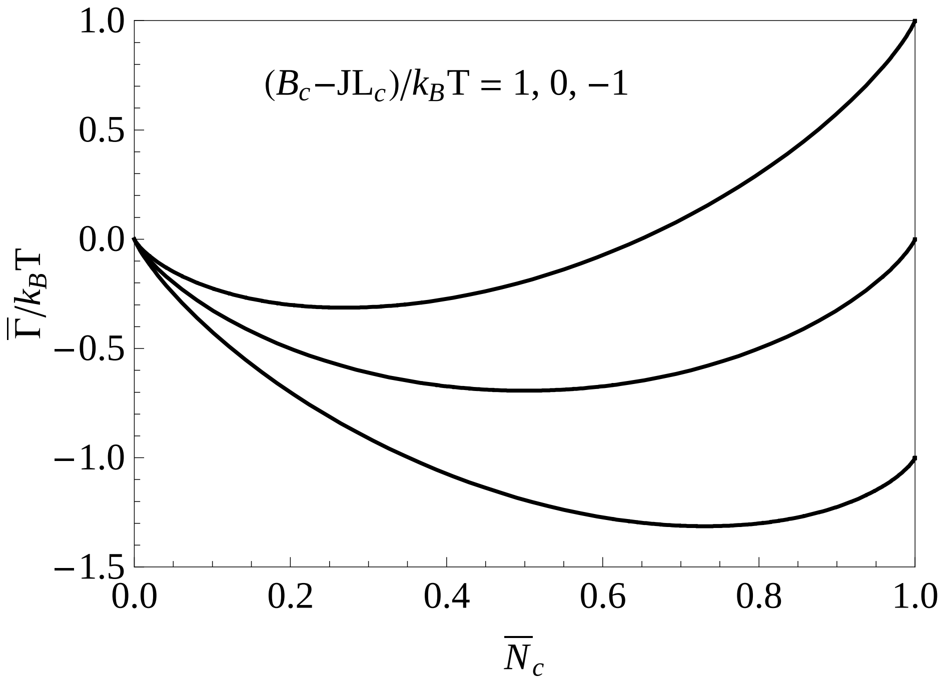
Thermodynamic potential: $\bar{\Xi}(T, J, \mu_c) = -k_B T \ln\left(1 + e^{-K_c - \mu_c/k_B T}\right)$, $\qquad K_c \doteq \dfrac{B_c - J L_c}{k_B T}$

Legendre transform: $\bar{\Gamma}(T, J, \bar{N}_c) = \bar{\Xi}(T, J, \mu_c) + \mu_c \bar{N}_c$

$$\frac{\bar{\Gamma}(T, J, \bar{N}_c)}{k_B T} = \bar{N}_c \ln \bar{N}_c + (1 - \bar{N}_c)\ln(1 - \bar{N}_c) + \left(\frac{B_c - J L_c}{k_B T}\right)\bar{N}_c$$

$$\left(\frac{\partial \bar{\Gamma}}{\partial \bar{N}_c}\right)_{T,J} = 0$$

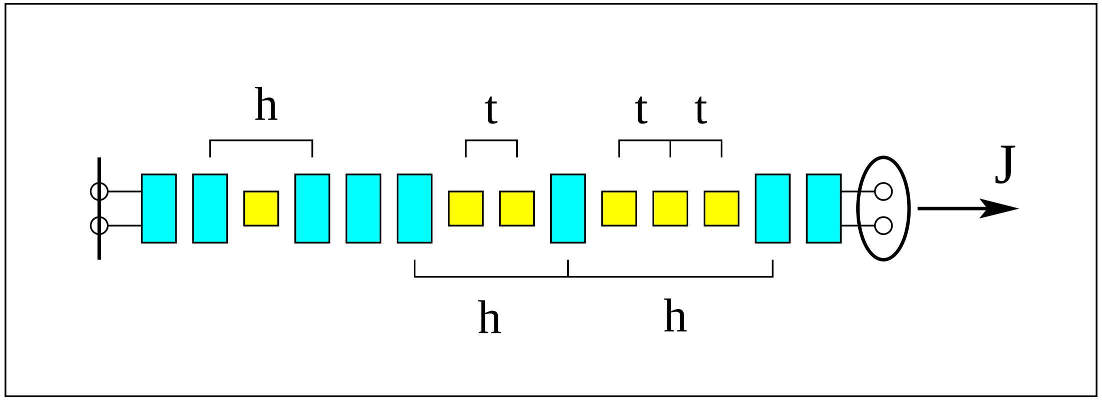
$$\Rightarrow \bar{N}_c = \frac{1}{e^{K_c} + 1}$$

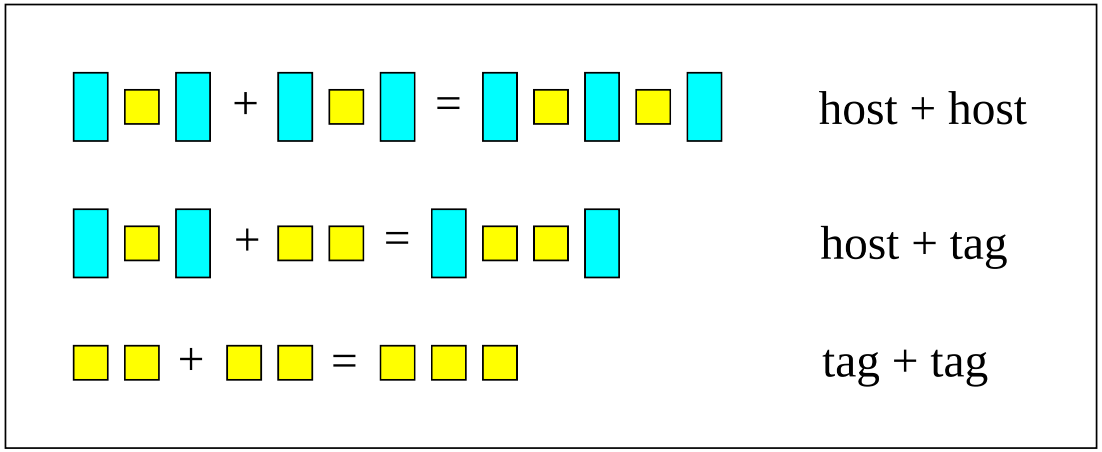


Links Modified by Tension (2)

Applied tension J causes extension, $\Delta L = \langle N_h \rangle L_h + \langle N_t \rangle L_t$, or rupture.

Particle activation energies: $\epsilon_m = B_m - JL_m$, $m = h, t$





Hosts and Tags: Bose-Einstein Statistics

motif	category	m	ϵ_m	A_m
■□■	host	h	$B_h - JL_h$	$N - 1$
□□	tag	t	$B_t - JL_t$	0

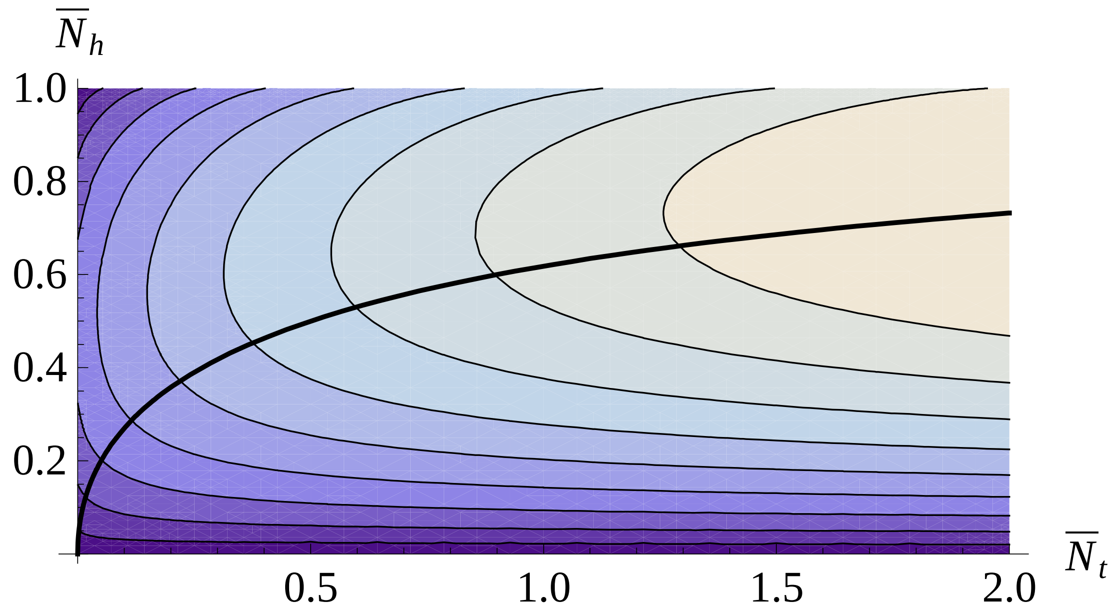
$g_{mm'}$	h	t
h	1	0
t	-1	0

Entropy landscape and BE limit:

$$\bar{S}/k_B = (\bar{N}_h + \bar{N}_t)\ln(\bar{N}_h + \bar{N}_t) - (1 - \bar{N}_h)\ln(1 - \bar{N}_h) - 2\bar{N}_h \ln \bar{N}_h - \bar{N}_t \ln \bar{N}_h$$

$$\bar{N}_b = \bar{N}_h + \bar{N}_t, \quad \bar{N}_t = \frac{\bar{N}_h^2}{(1 - \bar{N}_h)}$$

$$\bar{S}/k_B = (1 + \bar{N}_b)\ln(1 + \bar{N}_b) - \bar{N}_b \ln \bar{N}_b$$



Extension, Thermal Expansion, Rupture

Gibbs free energy:

$$\bar{G}(T,J) = k_BT\left[\ln\left(1-e^{-K_t}\right) - \ln\left(1-e^{-K_t}+e^{-K_h}\right)\right], \qquad K_m \doteq \frac{B_m - JL_m}{k_BT}, \quad m = h,t$$

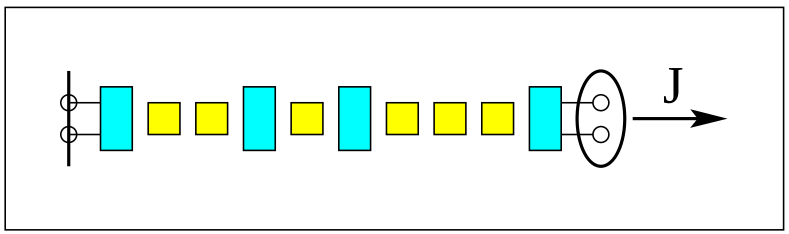
Population densities of hosts and tags:

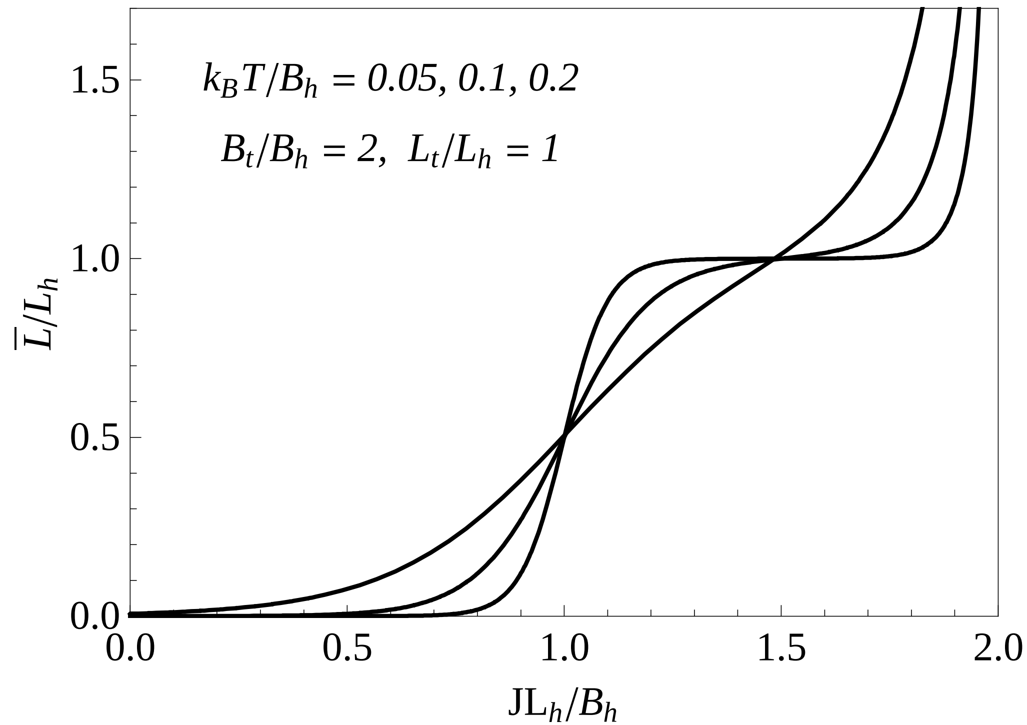
$$\bar{N}_h = \frac{1}{1+e^{K_h}\left(1-e^{-K_t}\right)}, \qquad \bar{N}_t = \frac{1}{\left(e^{K_t}-1\right)\left[1+e^{K_h}\left(1-e^{-K_t}\right)\right]}$$

Excess length: $\bar{L} = \bar{N}_hL_h + \bar{N}_tL_t$

Thermal expansion:

$$\frac{1}{e^{K_t}-1} \xrightarrow{k_BT/B_t \gg 1} \frac{k_BT/B_t}{1-JL_t/B_t}$$





Hosts and Caps

motif	category	m	ϵ_m	A_m
■□■	host	h	$B_h - JL_h$	$N-1$
□▷	cap	p	$B_p - JL_p$	0

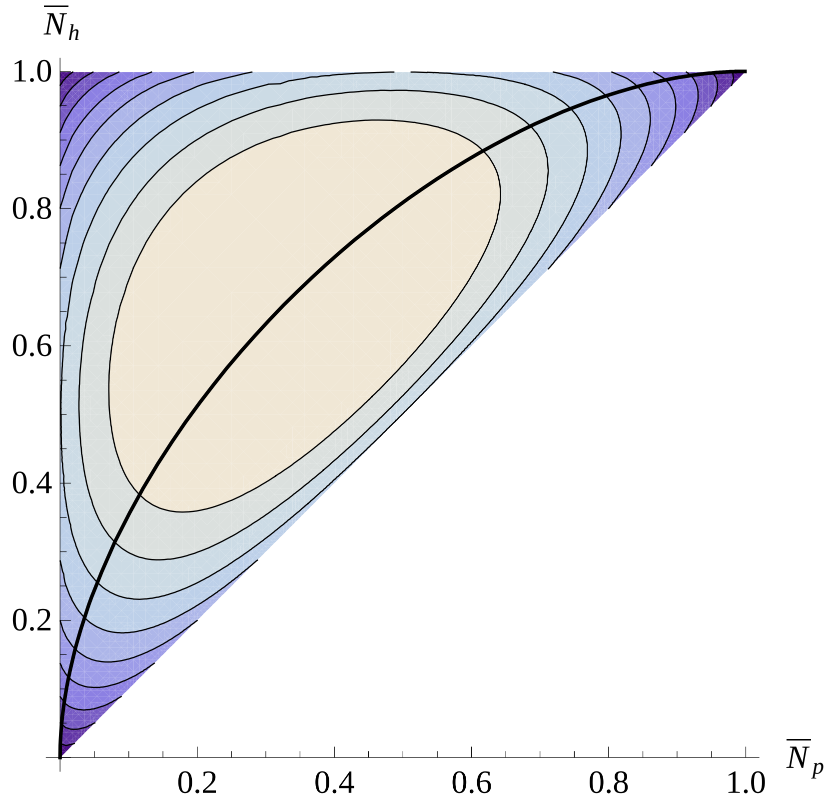
$g_{mm'}$	h	p
h	1	0
p	-1	1

Entropy landscape and:

$$\bar{S}/k_B = -(1-\bar{N}_h)\ln(1-\bar{N}_h) \\ -(\bar{N}_h-\bar{N}_p)\ln(\bar{N}_h-\bar{N}_p) - \bar{N}_p \ln \bar{N}_p$$

Maximum-entropy mix:

$$\bar{N}_h = \frac{1}{2}\left(\bar{N}_p + \sqrt{\bar{N}_p(4-3\bar{N}_p)}\right)$$



Two-Stage Extension

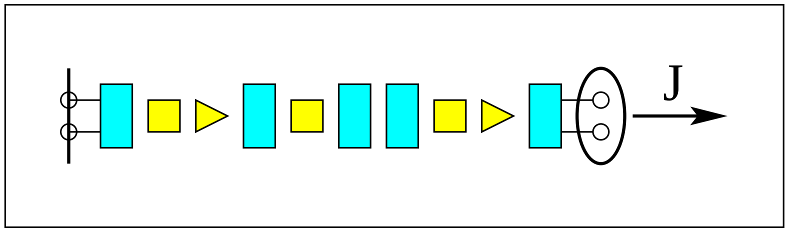
Gibbs free energy:

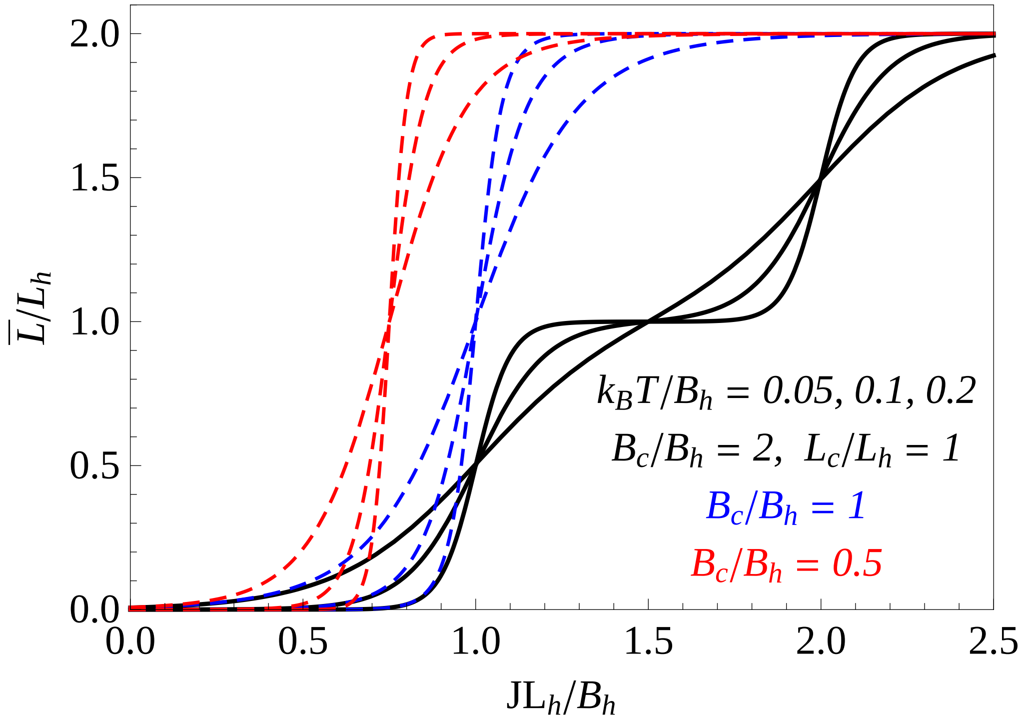
$$\bar{G}(T,J) = -k_BT\ln\left(1+e^{-K_h}+e^{-K_h-K_p}\right), \qquad K_m \doteq \frac{B_m - JL_m}{k_BT}, \quad m=h,p$$

Population densities of hosts and tags:

$$\bar{N}_h = \frac{1+e^{-K_p}}{1+e^{K_h}+e^{-K_p}}, \qquad \bar{N}_p = \frac{e^{-K_p}}{1+e^{K_h}+e^{-K_p}}$$

Excess length: $\bar{L} = \bar{N}_h L_h + \bar{N}_p L_p$



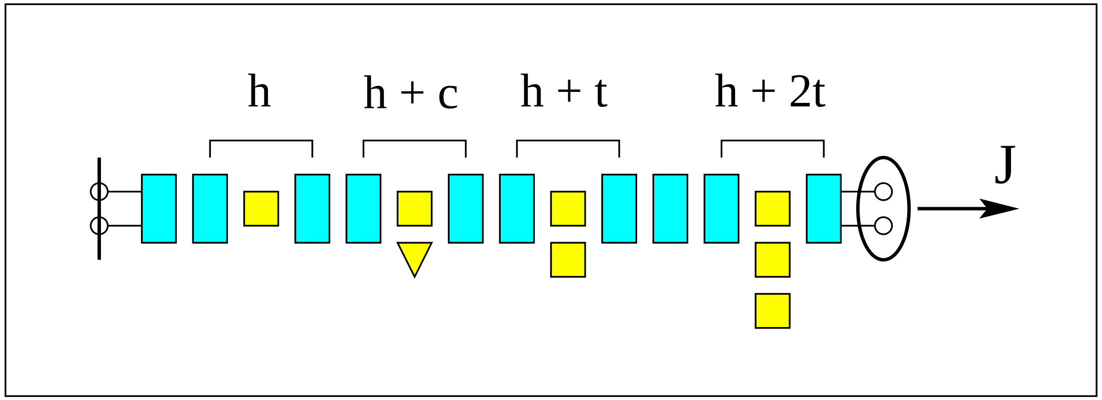


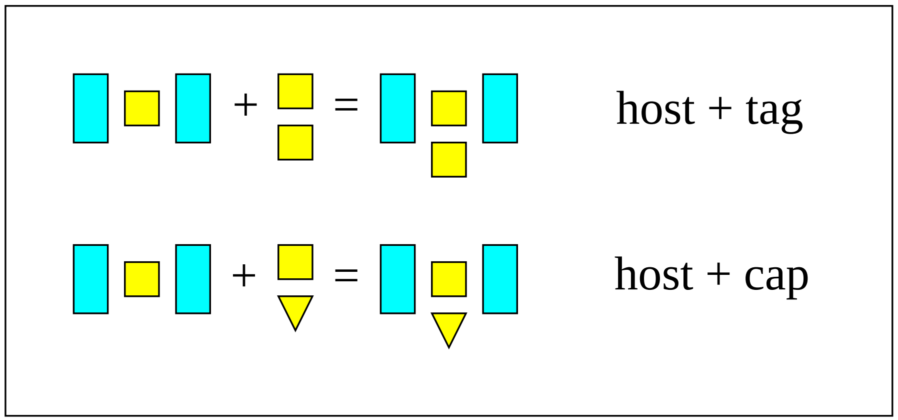
Links Modified by Tension (3)

Applied tension J causes extension, $\Delta L = \langle N_h \rangle L_h$.

Fluid particles modify elasticity (entropic effect).

Particle activation energies: $\epsilon_h = B_h - JL_h, \ \epsilon_t = -\mu_t, \ \epsilon_c = -\mu_c$.





Entropically Modified Elasticity (Caps)

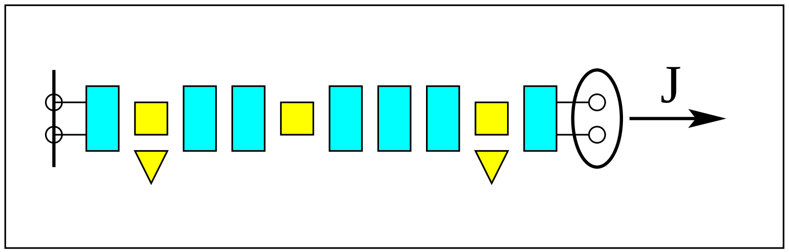
Gibbs free energy:

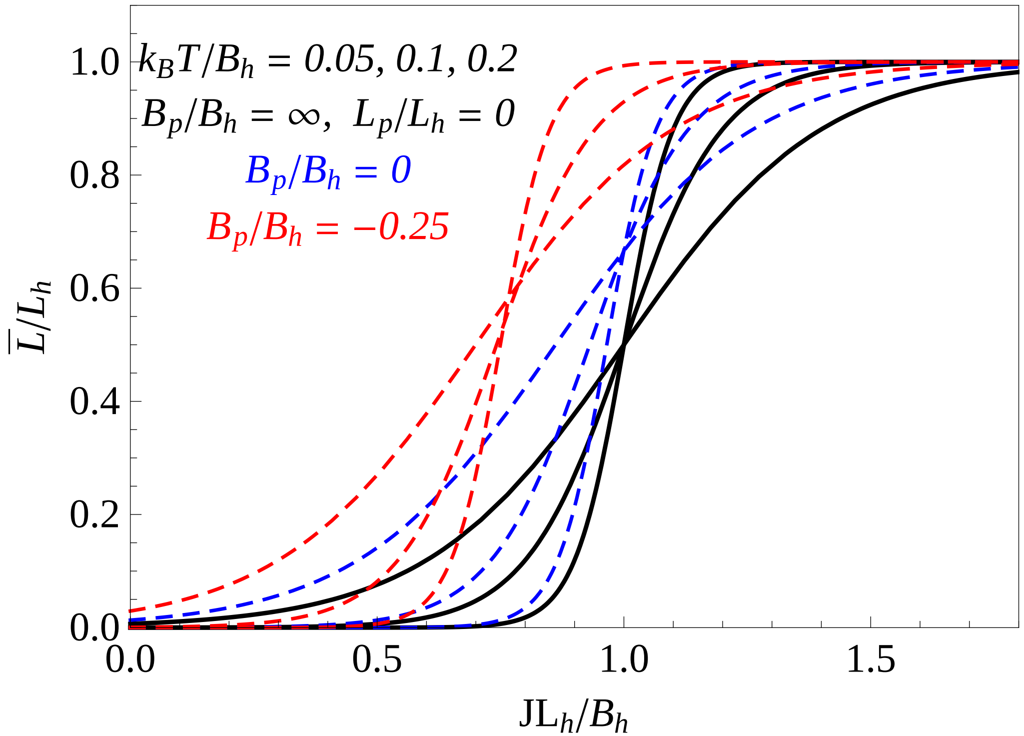
$$\bar{G}(T,J) = -k_BT\ln\left(1+e^{-K_h}+e^{-K_h-K_p}\right), \qquad K_h \doteq \frac{B_h - JL_h}{k_BT}, \quad K_p = \frac{B_p}{k_BT} = -\frac{\mu_p}{k_BT}$$

Population densities of hosts and tags:

$$\bar{N}_h = \frac{1+e^{-K_p}}{1+e^{K_h}+e^{-K_p}}, \qquad \bar{N}_p = \frac{e^{-K_p}}{1+e^{K_h}+e^{-K_p}}$$

Excess length: $\bar{L} = \bar{N}_h L_h$





Entropically Modified Elasticity (Tags)

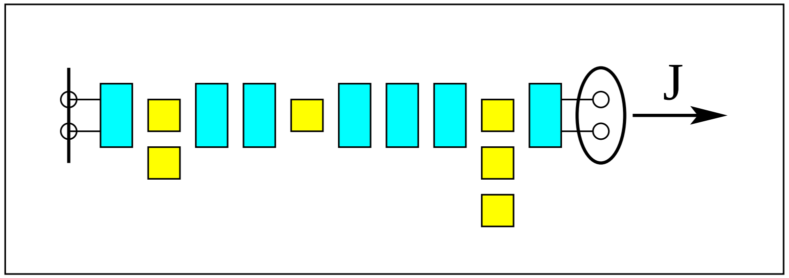
Gibbs free energy:

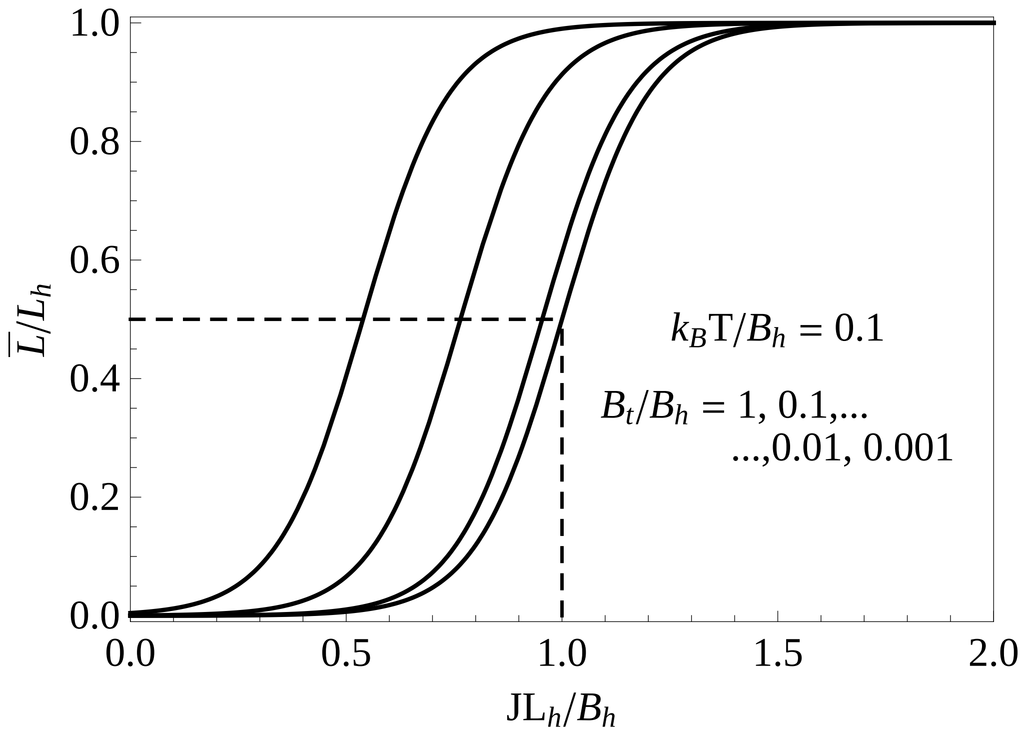
$$\bar{G}(T,J) = k_BT \ln \frac{1-e^{-K_t}}{1-e^{-K_t}+e^{-K_h}}, \qquad K_h \doteq \frac{B_h - JL_h}{k_BT}, \quad K_t = \frac{B_t}{k_BT} = -\frac{\mu_t}{k_BT}$$

Population densities of hosts and tags:

$$\bar{N}_h = \frac{1}{1+e^{K_h}\left(1-e^{-K_t}\right)}, \qquad \bar{N}_t = \frac{1}{\left(e^{K_t}-1\right)\left[1+e^{K_h}\left(1-e^{-K_t}\right)\right]}$$

Excess length: $\bar{L} = \bar{N}_h L_h$



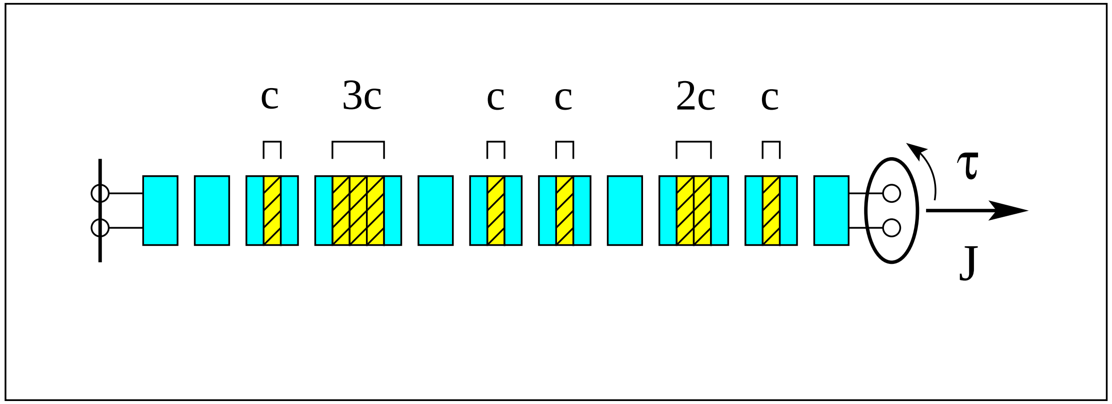


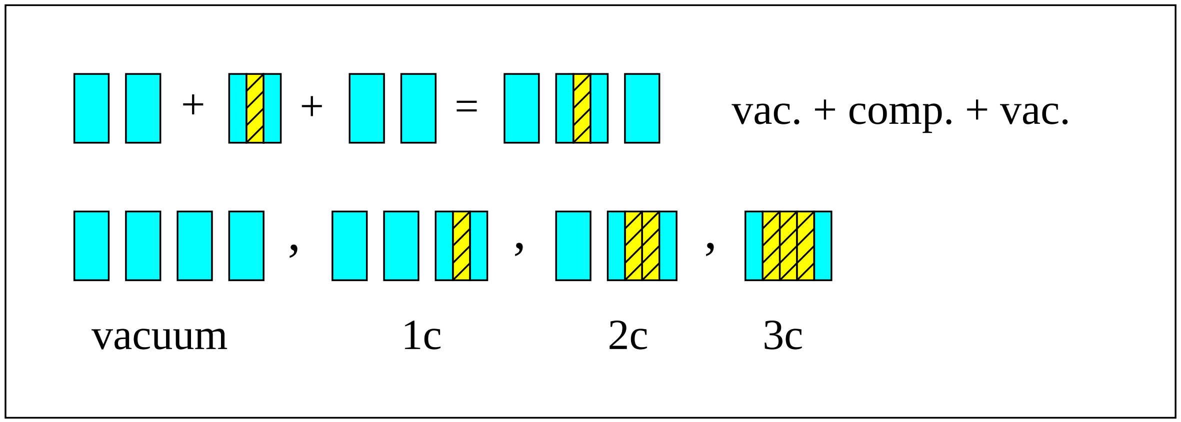
Links Modified by Tension and Torque (1)

Causes: torque τ and tension J.

Effects: twist $\Delta\phi = \langle N_c \rangle \phi_c$ and contraction $\Delta L = -\langle N_c \rangle L_c$.

Activation energy of compacts: $\epsilon_c = B_c + JL_c - \tau\phi_c$.



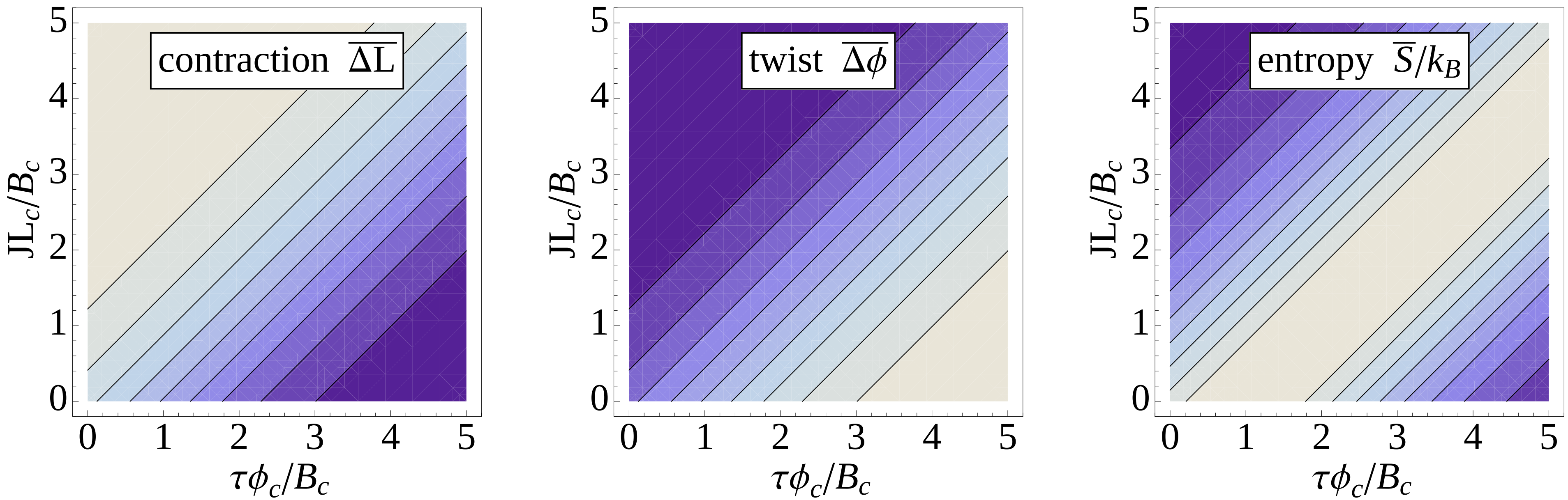


Ladder Under Tension and Torque

$$\bar{G}(T,J,\tau) = -k_B T \ln\left(1+e^{-K_c}\right), \quad K_c \doteq \frac{B_c + JL_c - \tau\phi_c}{k_B T}$$

$$\overline{\Delta L} = -\left(\frac{\partial \bar{G}}{\partial J}\right)_{T,\tau} = -\frac{L_c}{e^{K_c}+1}, \qquad \overline{\Delta\phi} = -\left(\frac{\partial \bar{G}}{\partial \tau}\right)_{T,J} = \frac{\phi_c}{e^{K_c}+1}$$

$$\bar{S} = -\left(\frac{\partial \bar{G}}{\partial T}\right)_{J,\tau} = k_B\left[\ln\left(1+e^{-K_c}\right) + \frac{K_c}{e^{K_c}+1}\right]$$



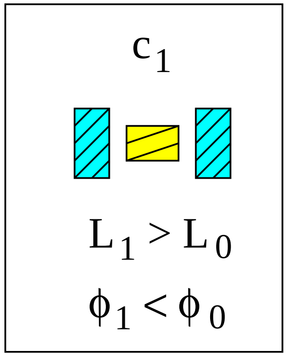
Links Modified by Tension and Torque (2)

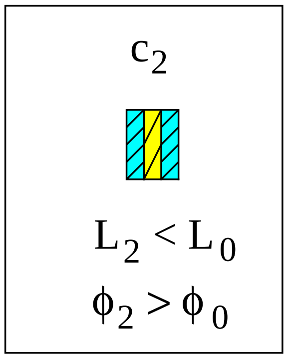
Pseudo-vacuum: $\phi_{pv} = N\phi_0, \quad L_{pv} = NL_0$

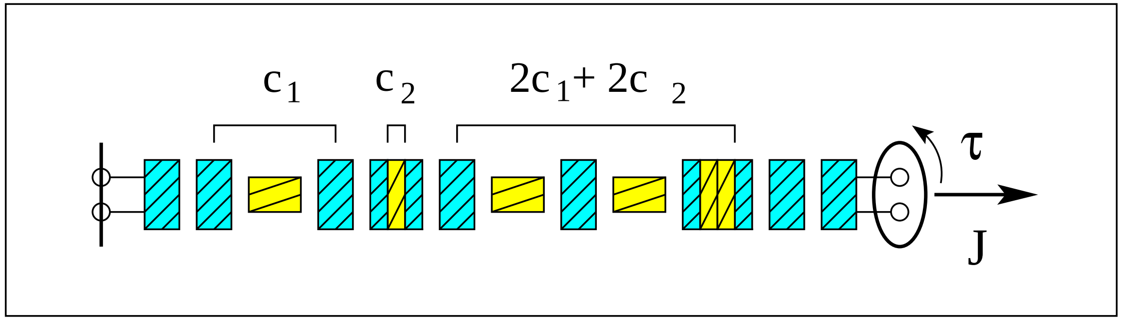
Twist: $\Delta\phi = \langle N_1\rangle\phi_1 + \langle N_2\rangle\phi_2$

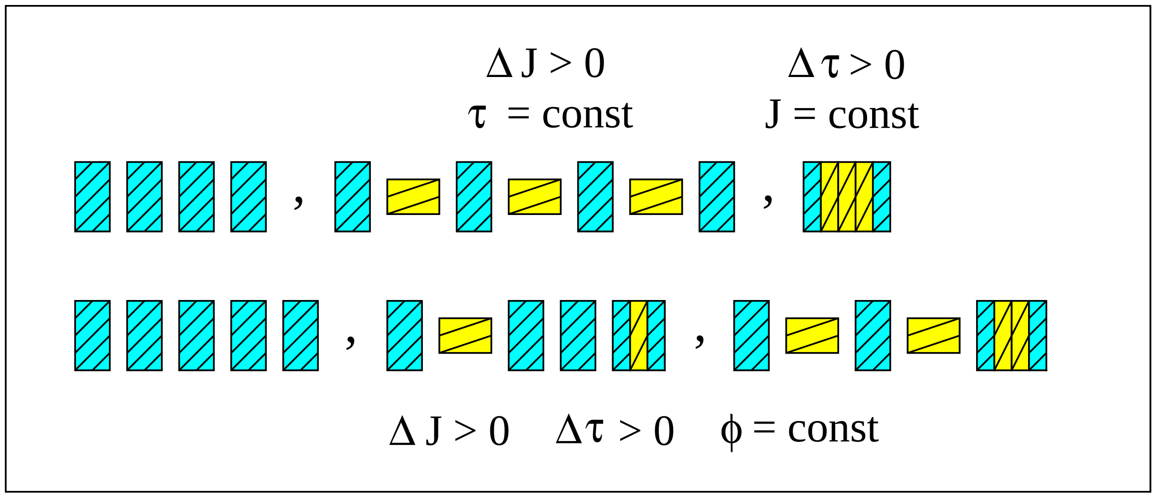
Contraction: $\Delta L = \langle N_1\rangle L_1 + \langle N_2\rangle L_2$

Activation energy of compacts: $\epsilon_m = B_m - J(L_m - L_0) - \tau(\phi_m - \phi_0), \quad m = 1, 2$









Two Species of Compacts

motif	category	m	ϵ_m	A_m
■⊗■	compact	1	$B_1 - J\Delta L_1 + \tau\Delta\phi_1$	$N-1$
■⊙■	compact	2	$B_2 + J\Delta L_2 - \tau\Delta\phi_2$	$N-1$

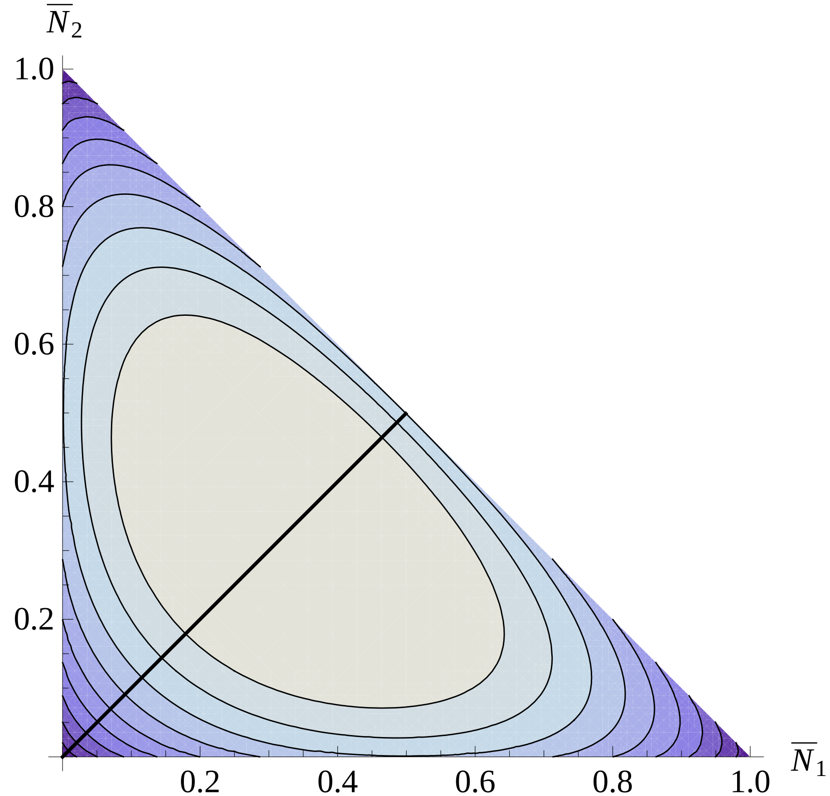
$g_{mm'}$	1	2
1	1	1
2	0	1

Entropy landscape:

$$\bar{S}/k_B = -\bar{N}_1 \ln \bar{N}_1 - \bar{N}_2 \ln \bar{N}_2$$
$$-(1-\bar{N}_1-\bar{N}_2)\ln(1-\bar{N}_1-\bar{N}_2)$$

Maximum-entropy mix:

$$\bar{N}_1 = \bar{N}_2$$



$$\bar{G}(T,J,\tau) = -k_BT\ln\left(1+e^{-K_1}+e^{-K_2}\right), \quad K_m = \frac{B_m - J(L_m - L_0) - \tau(\phi_m - \phi_0)}{k_BT} \quad m=1,2$$

$$\langle\bar{N}_1\rangle = \frac{e^{-K_1}}{1+e^{-K_1}+e^{-K_2}}, \quad \langle\bar{N}_2\rangle = \frac{e^{-K_2}}{1+e^{-K_1}+e^{-K_2}}$$

Stretching at constant angle: $\langle\bar{N}_1\rangle\Delta\phi_1 + \langle\bar{N}_2\rangle\Delta\phi_2 = 0 \quad \Rightarrow \quad \dfrac{\langle\bar{N}_1\rangle}{\langle\bar{N}_2\rangle} = \dfrac{\Delta\phi_2}{\Delta\phi_1} = R = \text{const.}$

$$\langle\bar{N}_1\rangle = R\langle\bar{N}_1\rangle = \frac{1}{e^{K_1} + \frac{R+1}{R}}$$

$$K_1 = \frac{R}{1+R}\left[\frac{B_1 - J\Delta L_1}{k_BT}\right] + \frac{1}{1+R}\left[\frac{B_2 + J\Delta L_2}{k_BT}\right] - \frac{\ln R}{1+R}$$

$$\Delta L_1 \doteq L_1 - L_0, \quad \Delta\phi_1 \doteq \phi_0 - \phi_1$$

$$\Delta L_2 \doteq L_0 - L_2, \quad \Delta\phi_2 \doteq \phi_2 - \phi_0$$