Canonical Free-energy Barrier of Particle and Polymer Cluster Formation

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Philipp Schierz, Wolfhard Janke

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24 November 2016

Motivation

droplet formation

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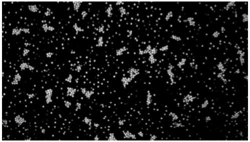
?



cluster formation in protein solutions[#]

droplet formation

[#] from A. Stradner et al., Nature **432**, 492 (2004).

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droplet formation

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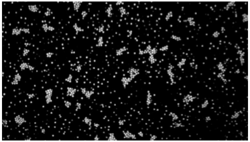

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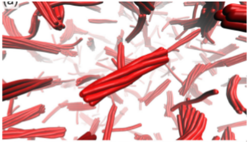
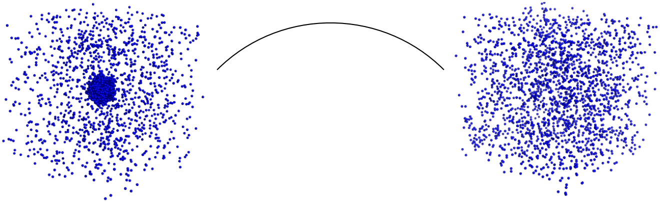


semiflexible filament network[+]
(e.g. actin)

[#] from A. Stradner et al., Nature **432**, 492 (2004).

[+] from R. J. Pandolfi et al., Phys. Rev. E **89**, 062602 (2014); see also H. J. Kouwer et al., Nature **493**, 651 (2013).

Free-energy barrier of droplet formation



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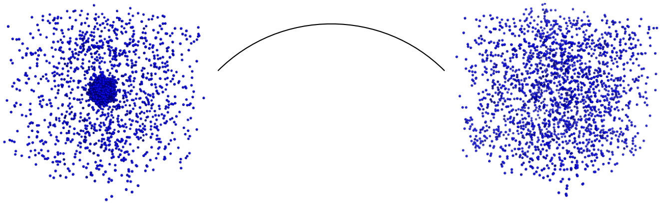

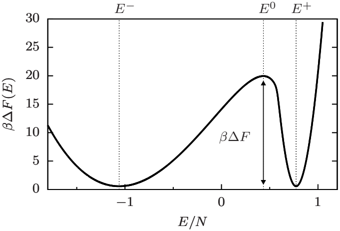

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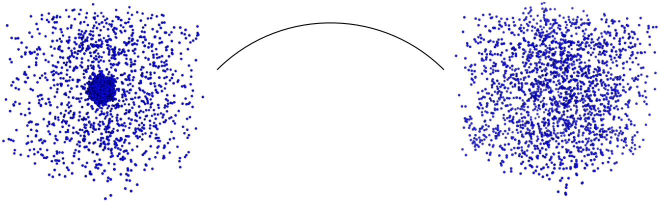

Free-energy barrier proportional to the interface:

$$\beta \Delta F = \sigma \partial V_D \propto \sigma V_D^{2/3}$$

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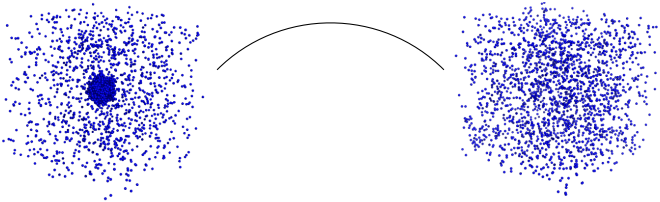

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However,

$$V_D \propto N^{3/4} \rightarrow \beta \Delta F \propto \tau_{\mathrm{eff}} N^{1/2}$$

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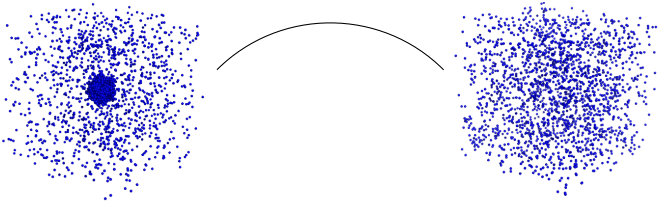

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Additional logarithmic corrections from shape fluctuations yield

$$\boxed{\beta \Delta F = \tau_{\mathrm{eff}} N^{1/2} + a \ln N + c}$$

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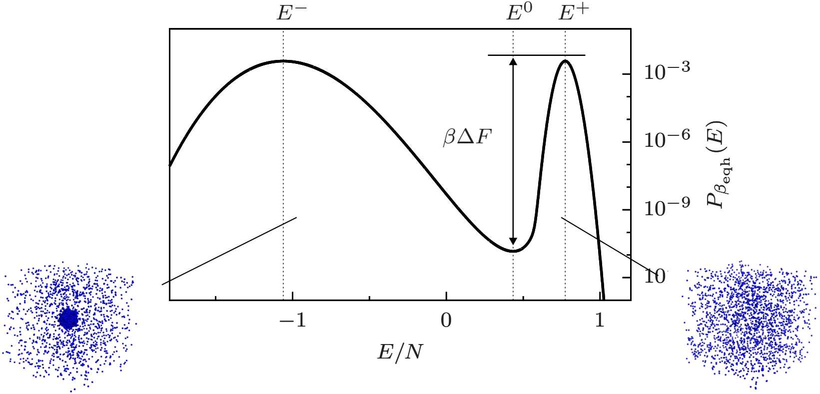
Estimating the free-energy barrier

The free-energy barrier is related to the logarithmic suppression in the canonical energy probability distribution at β_{eqh}

$$P_\beta(E) = \frac{1}{Z}\Omega(E)e^{-\beta E}$$

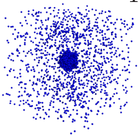
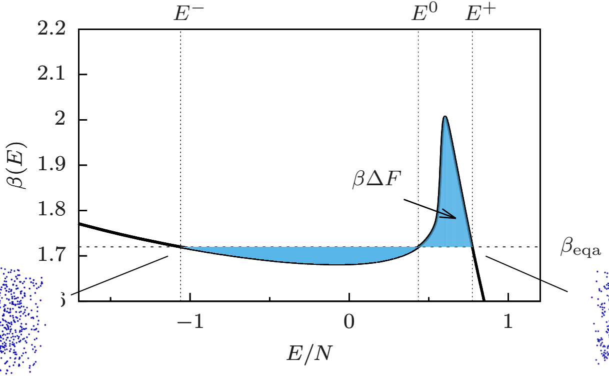


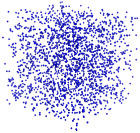
W. Janke, Nucl. Phys. B (Proc. Suppl.) **63** A-C, 631 (1998).

Estimating the free-energy barrier

The free-energy barrier is related to the enclosed area of the inverse microcanonical temperature and $\beta_{\rm eqa} = \beta_{\rm eqh}$

$$\beta(E) = \frac{\partial}{\partial E} \ln \Omega(E)$$



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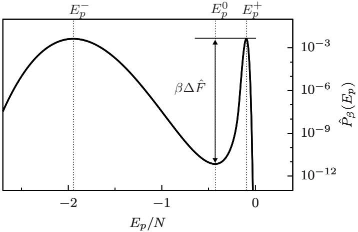
Density of states? Multicanonical simulations!

- efficient MC method for first-order phase transitions
- enhance sampling of suppressed states by $e^{-\beta E_p} \to W(E_p)$
- iteratively adapt $W^{(n)}(E_p)$ based on probability distribution



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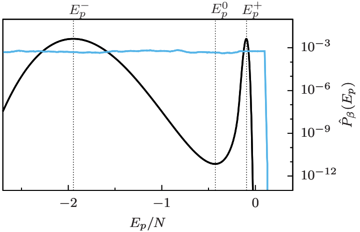

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- efficient MC method for first-order phase transitions
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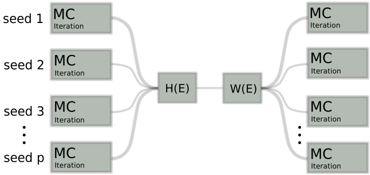
- iteratively adapt $W^{(n)}(E_p)$ based on probability distribution
- since each step in equilibrium: distribute to parallel processes



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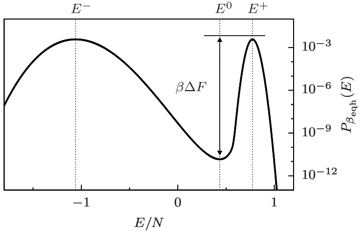
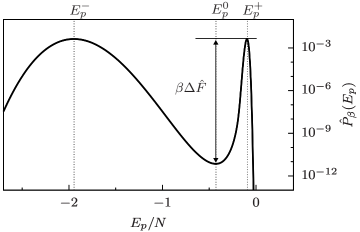
Role of kinetic energy

total energy $E = E_p + E_k$



potential energy E_p



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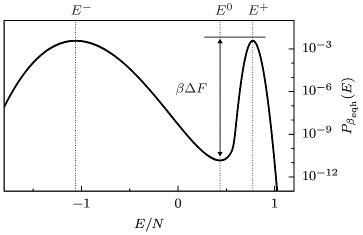

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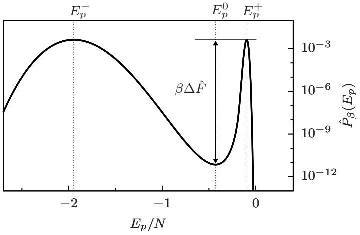

$$P_\beta(E) = \frac{1}{Z_\beta}\Omega(E)e^{-\beta E}$$

$$\Omega(E) = \int \mathcal{D}x\mathcal{D}p\ \delta(E - E_p(x) - E_k(p))$$

$$\hat{P}_\beta(E_p) = \frac{1}{\hat{Z}_\beta}\hat{\Omega}(E_p)e^{-\beta E_p}$$

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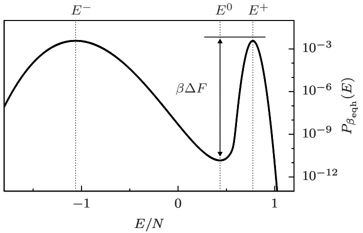

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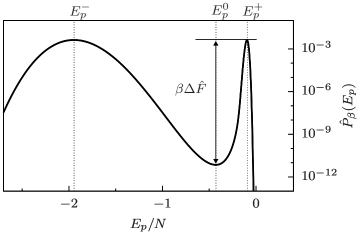

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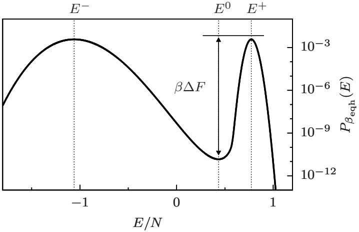
For N momenta $Z_\beta = (2\pi m/\beta)^{3N/2}\hat{Z}_\beta$ and we find

$$P_\beta(E) = \int dE_p \ \hat{P}(E_p) \ P_{\rm MB}(E - E_p) = (\hat{P}_\beta * P_{\rm MB})(E)$$

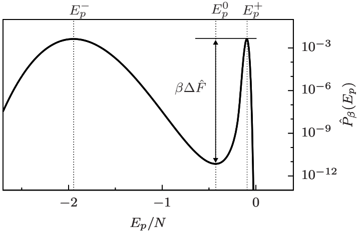
with the Maxwell-Boltzmann distribution $P_{\rm MB}(E_k)$

Role of kinetic energy

total energy $E = E_p + E_k$



potential energy E_p



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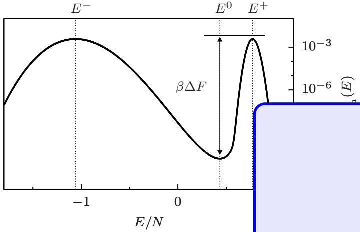
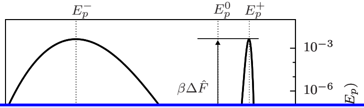
Role of kinetic energy

total energy $E = E_p + E_k$ potential energy E_p



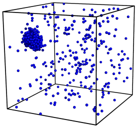


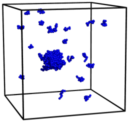
$$P_\beta(E) = \int dE_p \; \hat{P}($$

We thus expect

$$\beta\Delta\hat{F} > \beta\Delta F$$

Particle & Polymer Model





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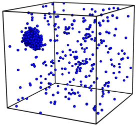
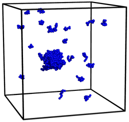


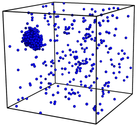


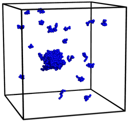
- Lennard-Jones potential: $V_{\mathrm{LJ}}(r_{ij}) = \left(\left(\frac{1}{r_{ij}}\right)^{12} - 2\left(\frac{1}{r_{ij}}\right)^{6} \right)$

  Cutoff at $r_c = 2.5$

  Domain Decomposition

Particle & Polymer Model





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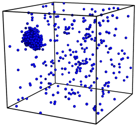

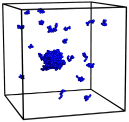

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- **fixed density $\rho = 10^{-2}$**

So what do we expect?

finite-size scaling: $\beta\Delta F = \tau_{\text{eff}} N^{1/2} + a \ln N + c$

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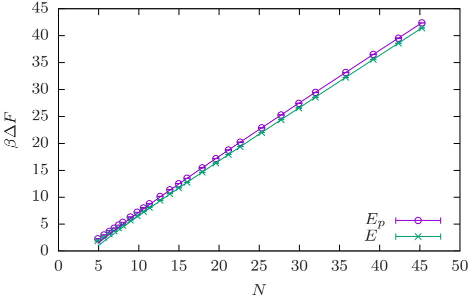
finite-size scaling: $\beta \Delta F = \tau_{\mathrm{eff}} N^{1/2} + a \ln N + c$

$\beta \Delta \hat{F}$(potential energy) $> \beta \Delta F$(total energy)
but $\hat{\tau}_{\mathrm{eff}} = \tau_{\mathrm{eff}}$

Finite-size scaling particles

Free-energy of droplet formation in a supersaturated/undercooled particle gas up to $N = 2048$ particles at fixed density $\rho = 10^{-2}$

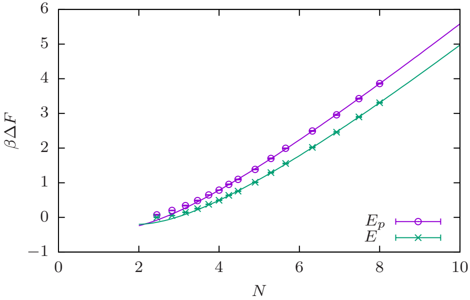


- Leading behavior is clearly $N^{1/2}$
- incl. logarithmic corrections $N > 320$; $Q \approx 0.3$; $\tau_{\text{eff}} = 0.939(4)$ and $\hat{\tau}_{\text{eff}} = 0.935(4)$

J. Zierenberg, P. Schierz, and W. Janke, arXiv:1607.08355 (2016)

Finite-size scaling polymers

Similar picture for flexible bead-spring polymer aggregation:
up to $N = 64$ polymers (13 monomers) at fixed density $\rho_m = 10^{-2}$



- here logarithmic corrections seem to be more relevant
- incl. logarithmic corrections $N > 16$; $Q \approx 0.2$;
  $\tau_{\text{eff}} = 1.06(3)$ and $\hat{\tau}_{\text{eff}} = 1.03(3)$

J. Zierenberg, P. Schierz, and W. Janke, arXiv:1607.08355 (2016)

Conclusions

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Funding:
Deutsche Forschungsgemeinschaft, European Union and the Free State of Saxony

Supported by:
BuildMoNa, DFH-UFA, JSC

Relation between energy-probability distributions

$$
\begin{aligned}
P_\beta(E) &= \frac{1}{Z_\beta}\Omega(E)e^{-\beta E} \\
&= \frac{1}{\hat{Z}_\beta}\int \mathcal{D}x\mathcal{D}p \; \frac{\delta(E - E_p(x) - E_k(p))}{(2\pi m\beta)^{3N/2}} e^{-\beta E_p} e^{-\beta E_k} \\
&= \frac{1}{\hat{Z}_\beta}\int \mathcal{D}x \; e^{-\beta E_p} \int \mathcal{D}p \; f_{\mathrm{MB}}(p) \; \delta(E - E_p(x) - E_k(p)) \\
&= \frac{1}{\hat{Z}_\beta}\int \mathcal{D}x \; e^{-\beta E_p} \int dE_k \; P_{\mathrm{MB}}(E_k) \; \delta(E - E_p(x) - E_k(p)) \\
&= \int dE_p \; \hat{P}(E_p) \; P_{\mathrm{MB}}(E - E_p) \\
&= (\hat{P} * P_{\mathrm{MB}})(E)
\end{aligned}
$$