

Kinetic Reconstruction of the Nucleation Free-Energy Landscape

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Abstract

We present a new method to **trace back** a lot of **valuable information from molecular dynamics** (MD) simulations of nucleation and activated processes in general. In particular, it is possible to **reconstruct the free energy profile** and the actual rate of attachment of molecules to a cluster of a given size **from the pure kinetics** of the process. We illustrate these ideas by their **application to a real MD simulation of nucleation** in a Lennard-Jones vapor. We then analyze the results of the simulations using this technique and compare them to the predictions of the classical nucleation theory.

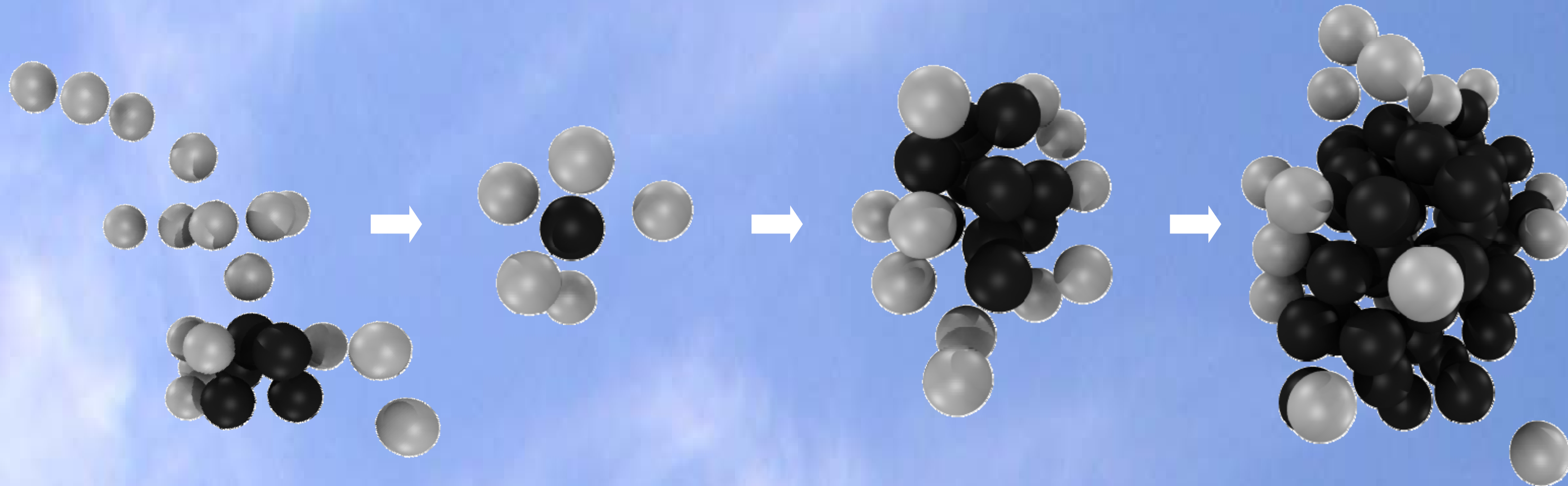


FIG. 1 (right): Typical snapshot of a molecular dynamics simulation of a nucleating droplet. The box contains 343 Ar atoms (red) in a simulation box of $V = (16 \text{ nm})^3$ at 50 K. In this example, the temperature is kept constant by 988 He atoms (blue), which are connected to a velocity rescaling thermostat. The cluster in the snapshot has already nucleated successfully and grown to $n = 50$ atoms.

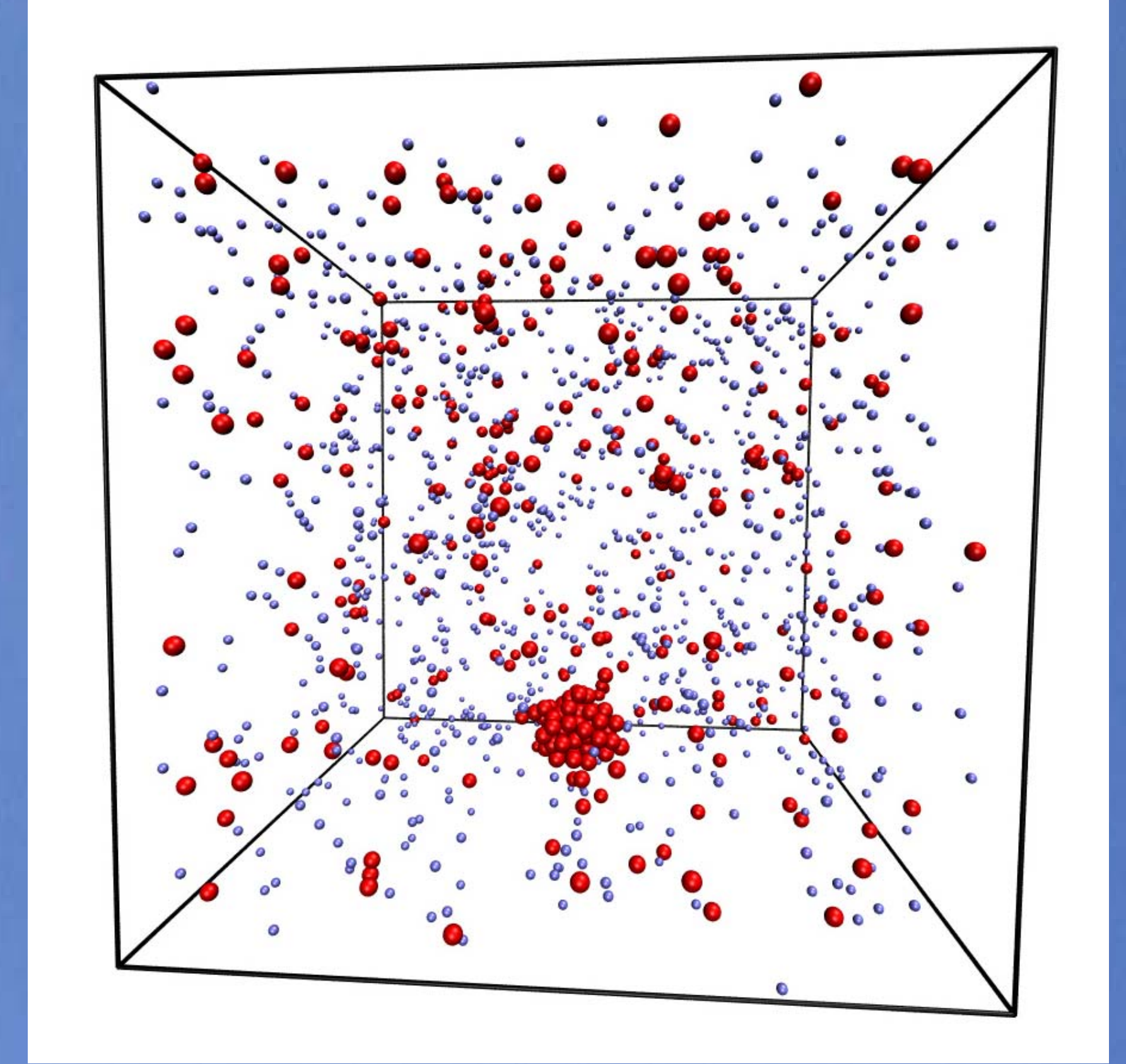


FIG. 2 (left): Snapshots of nucleating and growing argon clusters from the simulations. Clusters are identified using the cluster definition of ten Wolde and Frenkel (black atoms) and, at the same time, by the common Stillinger criterion (black + gray atoms). From left to right: a sub-critical, critical, and post-critical cluster, respectively.

Motivation

Molecular Dynamics simulations offer an **excellent way to investigate** the dynamics of **nucleation**. Recently, it has also become possible to monitor the formation time of clusters in the crystallization of colloids¹⁾ experimentally using confocal microscopy. Yet, the activated nature of nucleation limits the range of applicability of these techniques to situations in which the nucleation barrier is low or moderately high. Although more complicated *equilibrium* simulation techniques allow exploring higher barrier cases, the appeal of direct MD simulations is the possibility of monitoring the **real dynamics without artifacts**.

Recently, we have shown how to **extract the nucleation rate** as well as the **critical cluster size** and the Zeldovich factor accurately, efficiently, and **purely from the kinetics** using the concept of **mean first-passage time** (MFPT).²⁾

Here we present results that facilitate to **trace back even more information**, again purely from its kinetics. In particular, we can **reconstruct the free energy landscape and even the rate of attachment** of molecules directly from MD simulations.

This method can also be applied to Brownian Dynamics simulations, experiments, and, in general, to any sort of activated process.

Theory

The **dynamics of nucleation** and many activated processes³⁾ can be described in terms of a **Fokker-Planck equation**,

$$\frac{\partial P(n,t)}{\partial t} = \frac{\partial}{\partial n} \left(D(n) e^{-\beta \Delta G(n)} \frac{\partial}{\partial n} (P(n,t) e^{\beta \Delta G(n)}) \right) \quad (1)$$

where $P(n,t)$ is the probability of finding a cluster of size n at time t , $D(n)$ is the rate of attachment of molecules, $\Delta G(n)$ the free energy of formation of a cluster of size n , and $\beta = 1/kT$.

When the nucleation barrier is sufficiently high, the system reaches a steady state after a short transient time. The **steady state** is characterized by a constant current (the **nucleation rate J** , independent of n), and a time independent **probability distribution $P^{st}(n)$** . This probability is connected to the free-energy of cluster formation through

$$\beta \Delta G(n) = -\ln P^{st}(n) - J \int \frac{1}{D(n') P^{st}(n')} dn' + C \quad (2)$$

where C is a constant. This formula establishes that, **from the knowledge of $P^{st}(n)$, $D(n)$ and J** , one can **reconstruct the free energy** landscape of cluster formation.

An even more useful result can be proven:

The steady-state rate is also related to the **mean first-passage time (MFPT) $\tau(n)$** . In our case, the MFPT $\tau(n)$ is defined as the average time that the system, starting at size n_0 , takes to reach size n for the first time. It is given by:²⁾

$$\tau(n) = \int_{n_0}^n \frac{\exp(\beta \Delta G(y))}{D(y)} dy \int_a^y \exp(-\beta \Delta G(z)) dz \quad (3)$$

By **combining the steady-state distribution** with the **mean first-passage time**, we obtain:

$$\beta \Delta G(n) = \ln f(n) - \int \frac{1}{f(n')} dn' + C \quad (4)$$

$$f(n) = \frac{1}{P^{st}(n)} \left[\int_0^n P^{st}(n') dn' - J \tau(n) \right] \quad (5)$$

Thus, it is **possible to reconstruct the free energy landscape** from the knowledge of $P^{st}(n)$ and $\tau(n)$. This information can be obtained easily from MD simulations.

References:

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Simulation Results

We have performed a set of MD simulations of $N = 343$ Lennard-Jones argon atoms in $V = (11 \text{ nm})^3$ at $T = 50 \text{ K}$ (details: Ref. 4) to illustrate the power of our method. We obtained the mean first-passage time and the steady-state probability simultaneously for two different cluster definitions: the Stillinger⁶⁾ and the ten Wolde/Frenkel⁷⁾ definition.

Fig. 3 shows the **MFPT and steady state probability distribution** obtained from 285 realizations of our MD simulations. With these two inputs, we **can reconstruct the free energy landscape** through Eq. (4) as plotted in Fig. 4.

For comparison, we have plotted the free energy reconstructed using Eq. (2) with the CNT expression of $D(n)$. It is also possible to obtain an expression for $D(n)$ that can be evaluated directly from the MD simulations but it is numerically more challenging to get for all cluster sizes. We have evaluated $D(n)$ in the vicinities of the critical size, obtaining $D(n^*) = 30 \text{ ns}^{-1}$. This estimate coincides nicely with the value calculated by measuring the diffusivity around the critical size.⁵⁾

FIG. 3. Left: Mean first-passage times as a function of the cluster size obtained from the MD simulations of LJ argon at 70K. Right: Steady-state probability distribution of cluster sizes obtained from the same simulations.

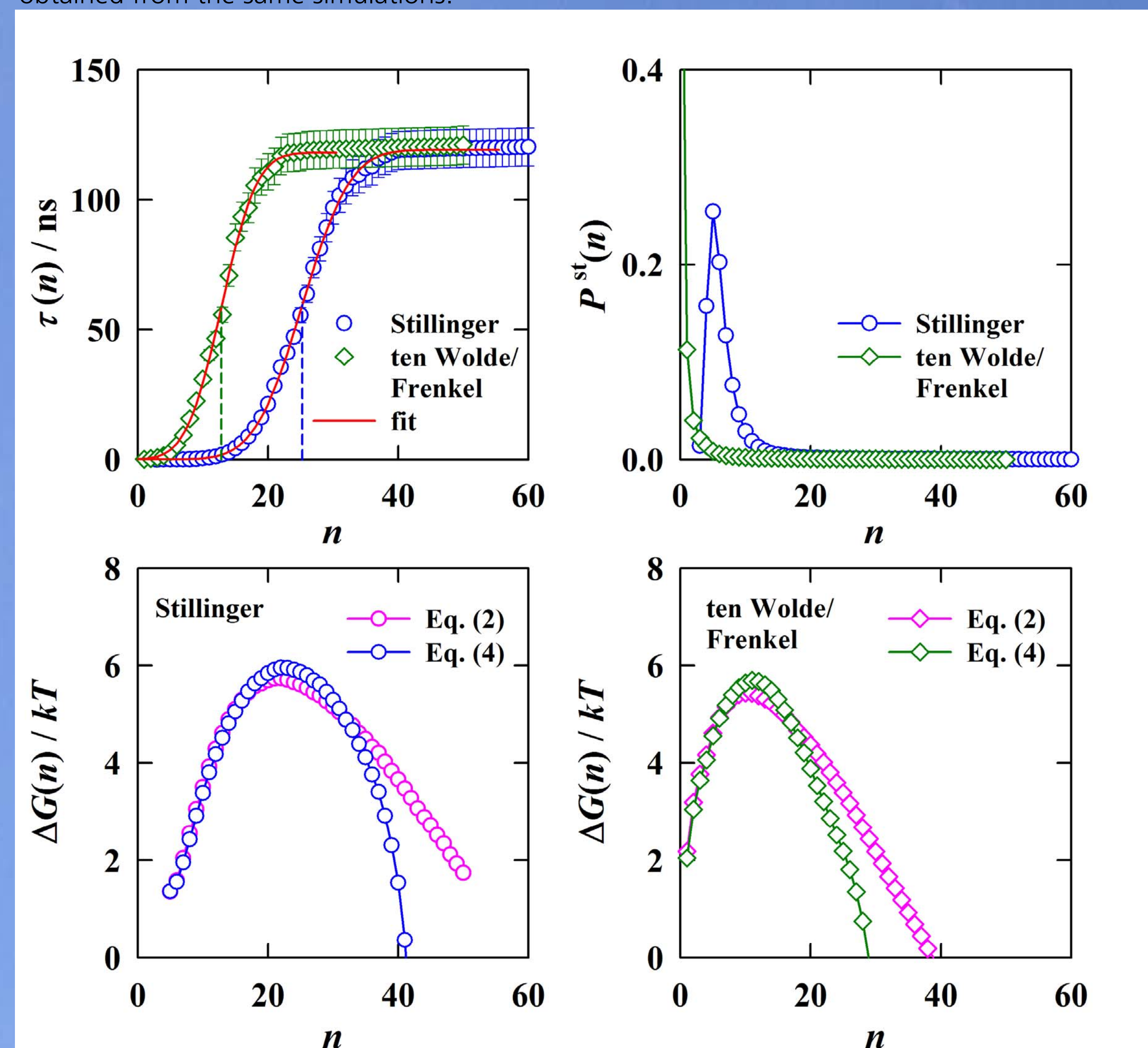


FIG. 4. Left: Kinetic reconstruction of the free energy of cluster formation obtained from the MD simulations for the Stillinger cluster definition using Eq. (4) (blue) and Eq. (2) and the $D(n)$ of CNT (pink). Right: Same for the ten Wolde/Frenkel cluster definition.

Discussion and Conclusion

We see that **the nucleation barrier is just a few kT** high. Such a value is common in direct MD simulation, where the supersaturation is very high to facilitate the observation of a nucleation events and the **barrier can be $< 2 kT$ or even vanish**. In that case we do not strictly observe nucleation but rather something alike to **spinodal decomposition**. Here, the kinetics are controlled only by the rate of attachment of molecules to a cluster. Our new method is a direct way to reveal these situations and realize, which part of the kinetics of cluster formation corresponds to the energetic nucleation barrier and which one to the kinetic prefactor.

In addition, we can **compare the actual barriers** from the true kinetics of nucleation with equilibrium barriers obtained from e.g. advanced **Monte-Carlo, umbrella-sampling** techniques or **theoretical predictions**.

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