Supporting information

Theoretical Insights into Thermodynamics and Kinetics of Graphene Growth on Copper Surfaces

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Derivation of $\partial H/\partial n$

Consider an edge with *N* adsorption sites and *n* randomly attached particles, the kink number is 2*m* which means that *n* particles are arranged into *m* groups separated by void sites. The energy (enthalpy) of this system depends on the number of kinks:

$$H = 2m \times \Delta E$$

where ΔE is the formation energy of a kink.

For a specific particle density $\lambda = n/N$, we calculate $\langle m \rangle$, the average of *m*, in the random mode. The number of possible particle distributions is

$$C_N^n \equiv \binom{N}{n}$$

The number of possible configurations where particles are separated into *m* groups is

$$\left[\binom{N-n-1}{m} + 2 \times \binom{N-n-1}{m-1} + \binom{N-n-1}{m-2}\right] \times \binom{n-1}{m-1} = \binom{N-n+1}{m}\binom{n-1}{m-1}$$

The first/second/third part in the square bracket on the left hand side counts the configurations where two ends are void sites, only one end is a void site, and no end is void site, respectively. The average value of *m* is

$$\langle m \rangle = \frac{\sum_{m=1}^{n}\left[m \times \binom{N-n+1}{m}\binom{n-1}{m-1}\right]}{\binom{N}{n}} = \frac{N-n+1}{\binom{N}{n}} \times \sum_{m=1}^{n}\binom{N-n}{m-1}\binom{n-1}{m-1}$$

$$= \frac{N-n+1}{\binom{N}{n}} \times \binom{N-1}{n-1} = \frac{(N-n+1)\times n}{N} = (1-\lambda) \times n$$

The Vandermonde's identity is used in the derivation.

To confirm the above expression, we also perform Monte Carlo simulations for random adsorption of *n* particle at an edge with 1000 adsorption sites. For each *n*, 100 random samples are generated. As shown in Figure S1, the obtained $\langle m \rangle / n$ agree with

the analytical expression $1-\lambda$.

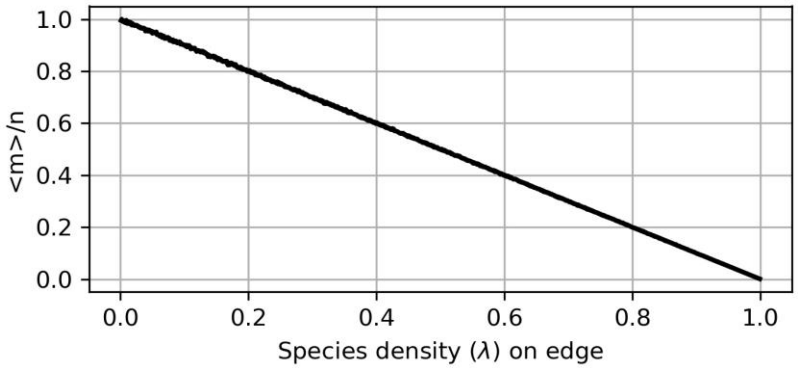

Figure S1. The statistic result of $\langle m\rangle/n$ using random scattering method.

The average energy of the system is

$$H = 2\langle m\rangle \times \Delta E = 2(1-\lambda) \times n \times \Delta E$$

Thus, we have

$$\partial H/\partial n = 2(1-\lambda) \times \Delta E - 2\lambda \times \Delta E = 2(1-2\lambda) \times \Delta E$$

which is a linear function of λ and equals to 0 at $\lambda = 0.5$. If we include the onsite energy of species in the enthalpy calculation, it becomes:

$$\partial H/\partial n = 2(1-2\lambda) \times \Delta E + E^{onsite}$$