

## Molecular Dynamics Modeling and Simulations of Carbon Nanotube-based Gears (Permodelan Dinamik Molekul dan Simulasi Gear Berasaskan Nanotub Karbon)

YEAK SU HOE\*, CHE LOKMAN JAAFAR & NG TENG YONG

### ABSTRACT

*A molecular dynamics (MD) modeling method was applied to investigate the properties of carbon nanotube-based gears (CNT gears). The Brenner's reactive hydrocarbon potential was used in order to calculate the short range interatomic forces. The Lennard-Jones 6-12 (LJ) was used to calculate the long range van der Waals potential for intermolecular interactions between gears. One gear was powered by forcing the atoms near the end of the first CNT to rotate, and a second gear was allowed to rotate by keeping the atoms near the end of second CNT constrained to a cylinder. We used the hybrid minimization to simulate the CNT-gears by coupling the unconstrained conjugate gradient minimization with the one-dimensional minimization, Brent's method. The hybrid minimization was successfully implemented by introducing two regions in CNT gear. The switch function will affect the smoothness of the gear rotation. The switch function also affects the minimization process where simulation time will be reduced.*

*Keywords: Carbon nanotube-based gears; hybrid minimization; modeling; molecular simulation*

### ABSTRAK

*Permodelan dinamik molekul telah dijalankan ke atas gear nanotub karbon (CNT). Potensi Brenner jenis hidrokarbon telah digunakan dalam pengiraan julat pendek daya antara atom. Lennard-Jones 6-12 digunakan dalam julat jauh potensi van der Waals untuk interaksi antara molekul dengan roda gigi. Gear tiub pertama diberi kuasa berdekatan dengan pinggir tiub supaya berputar dan gear kedua dibenarkan berputar pada paksi yang ditetapkan. Kami gunakan teknik minimum hibrid untuk simulasi gear CNT dengan bergading dengan minimum tanpa kekangan jenis kecerunan konjugat dan kaedah Brent. Minimum hibrid telah berjaya digunakan dengan bantuan dua bahagian dalam gear CNT. Fungsi suis didapati memberi kesan dalam kelicinan putaran gear. Fungsi suis juga berjaya memendekkan masa simulasi dalam proses minimum.*

*Kata kunci: Gear nanotub karbon; meminimuman hibrid; permodelan; simulasi molekul*

### INTRODUCTION

Due to the excellent mechanical and electrical properties, carbon nanotubes (CNTs) have undergone intense study by researcher since the discovery by Iijima (1991). Some exceptional properties including miniature size, low density, high stiffness and high strength. The research being carried out on CNTs in recent years were very broad, ranging from investigations into their mechanical properties to their application in gear rotation, as well as fundamental studies into their physical and chemical characteristics. Due to their angstrom-scale dimensions and the associated experimental difficulties at these scales, the approach of employing numerical methods to study CNTs forms a significant component in the overall research inquiry into this promising material. Jakobson et al. (1996) simulated CNTs under axial compression and their results showed that at large deformations, an abrupt release of energy is accompanied by a reversible switch into a different morphological pattern. Globus et al. (1998) presented some experimental and theoretical work relating fullerene gears which in future possible to design and build atomically precise programmable machines composed of functionalized fullerenes.

In the present work, a carbon nanotube-based gears (CNT gears) model was developed to simulate the rotation of CNT gears in vacuum environment. As pointed out by Han (1997), CNT gears can be designed by bonding rigid planar benzyne molecules onto a CNT. Srivastava (1997) showed that CNT gears can be rotated by applying a single laser-powered molecular motor. The rotation rate can be controlled by varying laser power density and arrangement of free charges in the body of the gears. By applying hybrid minimization technique, the CNT gear rotation can be simulated with designed orientation. The short range and long range potential function will be used in order to represent each atom energy and forces.

### THEORY AND FORMULATION

#### EMPIRICAL MOLECULAR DYNAMICS

In the present work, for the molecular dynamics (MD) model, the calculation of the short-range interaction force is based on the second-generation reactive empirical bond-order (REBO) potential of Brenner et al. (2002). In addition, the long range van der Waals potential (Mao et

al. 1999) and Sinnott et al. (1998)) is applied. The potential sum is thus:

$$E = \sum_i \sum_{j>i} (E_{ij}^{REBO} + E_{ij}^{vdw}), \quad (1)$$

$$E_{ij}^{REBO} = [V_R(r_{ij}) + b_{ij}V_A(r_{ij})], \quad (2)$$

where  $V_R$  and  $V_A$  are pair-additive interactions that represent all interatomic repulsion and attraction from valence electrons, and  $b_{ij}$  is the reactive empirical bond order between atoms.  $E^{REBO}$  and  $E^{vdw}$  represent REBO potential and van der Waals potential, respectively.

For the CNT gears, the Lennard-Jones 12-6 (LJ) potential with a switch function, (Yeak et al. (2005)), is used for the van der Waals potential as:

$$E^{vdw,s} = \begin{cases} 0, & r < D_{\max} \\ E_{ij}^{vdw} \cdot S(r), & D_{\max} \leq r \leq D_{\max} + d \\ E_{ij}^{vdw}, & r > D_{\max} + d \end{cases}, \quad (3)$$

where  $D_{\max}$  is the distance at which the van der Waals potential becomes zero, and  $d$  is the neighbor distance that causes the switch function to vary from zero to one. As pointed out by Mao et al. (1999), it is advisable to incorporate the van der Waals potential only when the

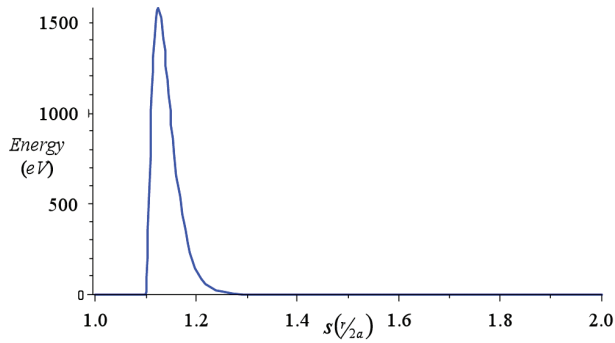
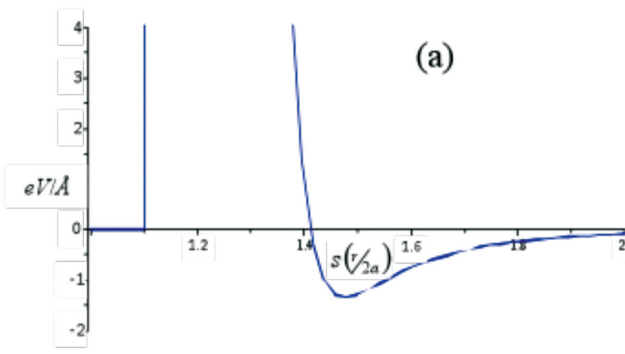


FIGURE 1. Potential  $\phi(r)$  with switch function near the overlapping distance



short-range potential becomes zero. This is to prevent an artificial reaction barrier from forming due to the steep repulsive wall of the Lennard-Jones 12-6 potential in the short range.

The switch function is applied in order to produce a smooth van der Waals potential around the truncation distance where potential becomes zero. This is important in the process of relaxation of energy using gradient type minimization techniques.

We also applied variation of Lennard-Jones 12-6 potential with parameters derived from fitting graphite and  $C_{60}$  experimental data (Girifalco 1992; Liu 2003) as below:

$$\phi(r) = -\alpha \left[ \frac{1}{s(s-1)^3} + \frac{1}{s(s+1)^3} - \frac{2}{s^4} \right] + \beta \left[ \frac{1}{s(s-1)^9} + \frac{1}{s(s+1)^9} - \frac{2}{s^{10}} \right], \quad (4)$$

where  $s = r/2a$ ,  $r$  is the distance between two  $C_{60}$  centers,  $a$  (0.355 nm) is the radius of the  $C_{60}$  molecule.  $\alpha = 74.94 \times 10^{-17}$  erg and  $\beta = 135.95 \times 10^{-18}$  erg. This potential was used to calculate the intermolecular interaction between different gear atoms.

Figure 1 shows the potential  $\phi(r)$  near the two  $C_{60}$  molecules overlap distance,  $s = 1$ . We used cubic polynomial as the switch function with neighbor distance,  $d = 0.1$ .

According to Figure 2(a) and 2(b), it is obvious that the force from  $C_{60}$  potential grew very fast when their distance approaching to overlapping distance between two molecules  $C_{60}$ . Subsequently, the switch function becomes critical in order to produce smooth force which will be used in minimization process.

#### ROTATION DYNAMICS OF GEARS

Molecular dynamics simulations were performed on the relaxed energy structures. The essence of MD is to solve the governing equations of particle dynamics based on Newton's second law. These equations of motion were integrated using a fourth-order predictor-corrector

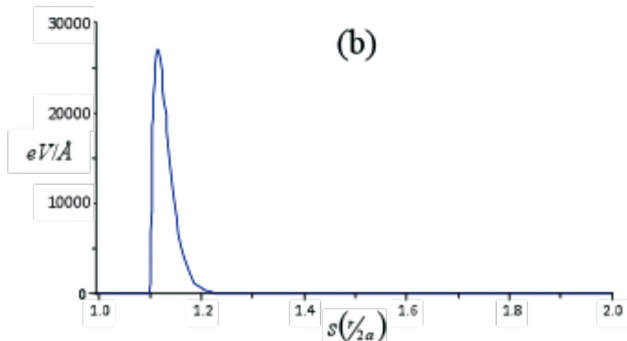


FIGURE 2. Potential force  $\phi'(r)$  with switch function near the overlapping distance

algorithm with a time step of 1 fs. The gear's temperature was controlled by Berendsen's thermostat every time step with time constant,  $\tau$  of 0.4 ps. Each gear's input angular velocity is calculated by averaging each atom angular velocity on respective gear. This MD program was executed mostly on Intel processor with Windows Vista/7 as platform.

In order to simulate the rotation of CNT gear, the CNT as well as gears must be aligned closely and correctly. In our research, we use hybrid minimization technique instead of spring model as proposed by Han et al. (1997) in order to constrain the movement of atoms near the end of each tube that located two rows of rings at each end.

#### HYBRID MINIMIZATION OF CARBON NANOTUBE-BASED GEARS

Han et al. (1997) proposed a spring model in order to position correctly each tube for gear rotation. They connect each atom to a massless mount and model the interaction between them with massless mount atoms. The interaction potential was represented by a harmonic function that resembles a bond stretching potential with a force constant of 19.0 eV. However, in our approach, we did not apply spring model that request a harmonic function representing bond stretching potential.

We constrained the motion of atoms near the end of each tube by minimizing the CNT gears with introducing two regions. The first region,  $R_1$  is the two rows of rings at each end. The second region,  $R_2$  represents all the other atoms that exclude in region  $R_1$ . The first region,  $R_1$  is a fixed ring geometry that will rotate with angle  $\theta$ . The second region,  $R_2$  is relaxed using conjugate gradient method. The whole relaxation of the structure can be represented as:

$$E = \sum_{i=1}^N E_i = f(r_1, r_2, \dots, r_i, \theta) \Big|_{i \in R_2}, \quad (5)$$

where  $N$  is total of atoms,  $i \in R_2$  indicate the atoms that belong to region  $R_2$ . We couple the conjugate gradient method with linear search minimization technique using Brent's method. We use linear search minimization in order to calculate the optimum value of angle  $\theta$  that will

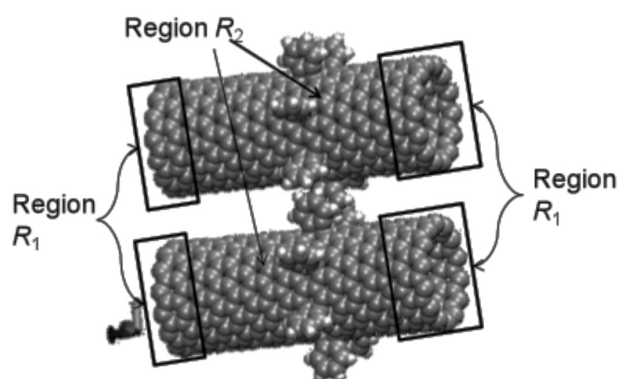


FIGURE 3. Hybrid minimization in two regions:  $R_1$  and  $R_2$ .

produce minimum energy after the minimization of atom's energy in  $R_2$ .

In the minimization of total potential energy, the geometry of atoms in region  $R_1$  is fixed and will rotate with angle  $\theta$ . By introducing the region  $R_1$ , we can correctly position each tube for gear rotation.

#### SIMULATION RESULTS AND DISCUSSION

The simulation involve the molecular dynamics that based on Newton's second law as well as structure relaxation process. The equations of motion were integrated using a fourth-order predictor corrector algorithm with time step of 1 fs. We used Berendsen's thermostat for CNT(14,0). The simulated CNTs having diameter with 11 Å where each tube has seven benzyne teeth. Each benzyne teeth represented by six-membered rings and are also known as 2+2 adduct in organic chemistry. The atoms located at the ends of the CNT are rotated according to varying angular speed with input rpps (rotation per pico second).

In this MD simulation, the geometry and velocity of the atoms are calculated according to Gear's fifth-order predictor-corrector algorithm. The entire region  $R_2$  of CNT gears was relaxed by the conjugate gradient algorithm in order to minimize the energy of CNT gear without affecting the atoms at the four ends. In addition, to validate the presently developed MD formulations, we carry out several comparisons with published data which employed various existing methodologies. Here, comparisons are made for the Young's modulus and strain energy.

In the microcanonical ensemble molecular dynamics simulations of CNTs, strain is derived as  $\varepsilon = (L - L_0)/L_0$ , with  $L_0$  and  $L$ , being the undeformed and deformed lengths of the CNT, respectively. The stress was calculated as  $\sigma = F/S$ , where  $F$  is axial force and the cross-sectional area is given by  $S = \pi dh$ , with  $d$  being the CNT diameter and  $h$  the thickness, which is usually takend to be 0.34 nm.

In the first validation, we compared the strain energy of single-walled carbon nanotubes, SWCNT (8,0) undergoing axial compression. Here, 352 atoms were considered with length-to-diameter ratio  $L/D=7.2$ . Figure 4 shows the comparison of the present MD results made those obtained via the quantum GTBMD method, as well as MD results computed with Tersoff-Brenner potential reported by Srivastava et al. (1999). The reported results show that collapse occurs at the respective strains of 0.12 and 0.8-0.9 for GTBMD and MD (using Tersoff-Brenner potential), whereas the present MD with REBO potential yields a collapse strain of 0.1. The present results are thus agree with publish data and are more refined than those obtained using MD with Tersoff-Brenner potential.

Validation of the present MD algorithm is also carried out for SWCNTs under axial tension. For the second comparison, we examine the stress-strain relations of SWCNT (12,12) with  $L/D=9.1$ . Figure 5 shows the comparison with the MD (using modified Morse potential) results of Belytschko et al. (2002). The present results yield a slightly higher collapse strain at a lower stress value.

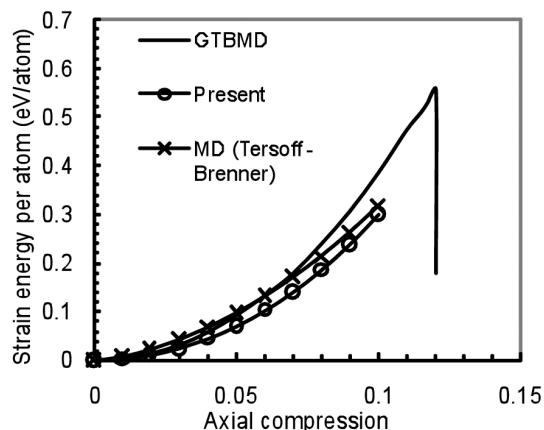


FIGURE 4. Comparison of strain energy curve of SWCNT (8,0) under axial compression

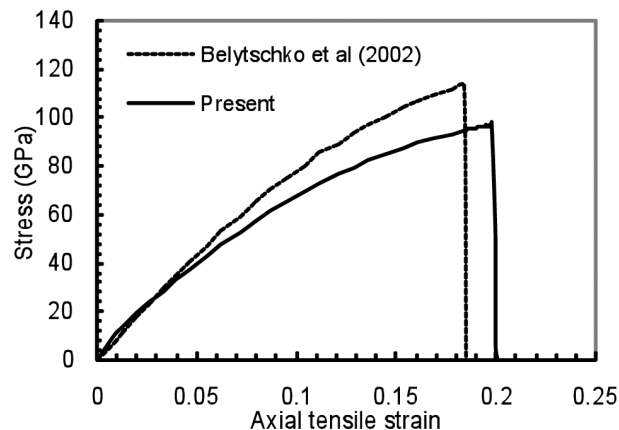


FIGURE 5. Comparison of stress-strain curve of a SWCNT (12,12) under axial tension

TABLE 1. Comparison of bond energy and distance between DFT and REBO potential

	Density functional theory		REBO potential (Brenner 2002)		REBO (present )	
	Bond energy (eV)	Bond distance (Å)	Bond energy (eV)	Bond distance (Å)	Bond energy (eV)	Bond distance (Å)
C-H bonds	4.422	1.09	4.526	1.09	4.526	1.09

TABLE 2. Switch function in Lennard-Jones and  $C_{60}$  potentials

	LJ with switch $C_{60}$ without switch	LJ without switch $C_{60}$ with switch	LJ with switch $C_{60}$ with switch
Behaviour of total potential stable	Less stable	Stable	Stable
Behaviour of gears rotation	Movement not smooth Gear slips occur	Both gears rotate smoothly No gear slip	Both gears rotate smoothly No gear slip
Total simulation time used for 10 ps. (normalized)	5.56	1.00	0.99

The third comparison carried out was for the bond energy for CH molecule. The amount of energy needed to separate one mole of two bonded species is called the bond energy. The average bond energy for CH molecule is generally given as 4.27 eV (Brady & Senese 2004). These results are tabulated in Table 1. The density functional theory (DFT) result is based on pseudopotential for carbon (with cutoff energy 16 Rydberg) and hydrogen (with cutoff energy 32 Rydberg). It can be observed that both present REBO and REBO introduced by Brenner (2002) are same.

The system of interest is shown in Figure 3. For the first 10 ps of this simulation, we applied the atoms in region  $R_1$  of driven CNT gear with input rpps (revolutions per ps) from 0 to 0.2 and then stayed at 0.2 rpps up to 17 ps. The results of this simulation can be summarized in

Table 2. The normalized time is used by running the same simulation in different Windows platform and different PC. According to Table 2, obviously the simulation time is reduced if we apply switch function for potential functions. This is due to minimization technique that will converge faster with smooth energy gradient or force even though additional calculation is required for switch function.

Figures 6 to 8 show the total potential energy of CNT gear over ps. Obviously for  $C_{60}$  potential without smooth cutoff, the potential energy behave unstable. However, Figure 6 shows that the minimum potential value tend to energy for potential with smooth cutoff.

Figure 9 shows the gear slip in CNT gear. The black colour atoms represent hydrogen were are not dismantled but tilted with large angle when slip occurs.

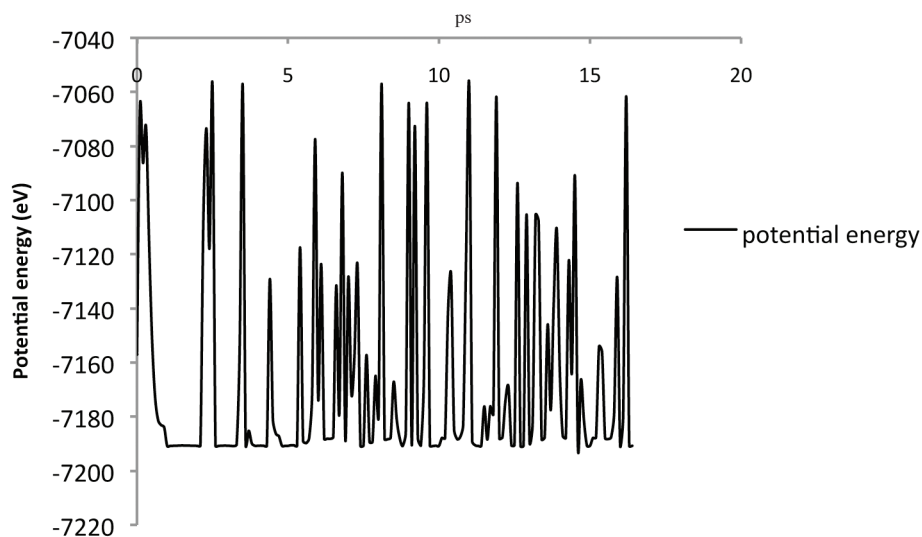


FIGURE 6. Potential energy with LJ (with switch function) and  $C_{60}$  (without switch function)

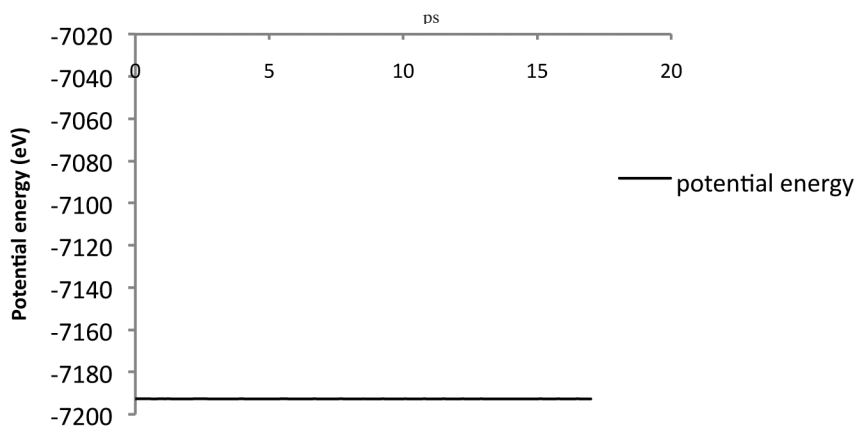


FIGURE 7. Potential energy with LJ (with switch function) and  $C_{60}$  (with switch function)

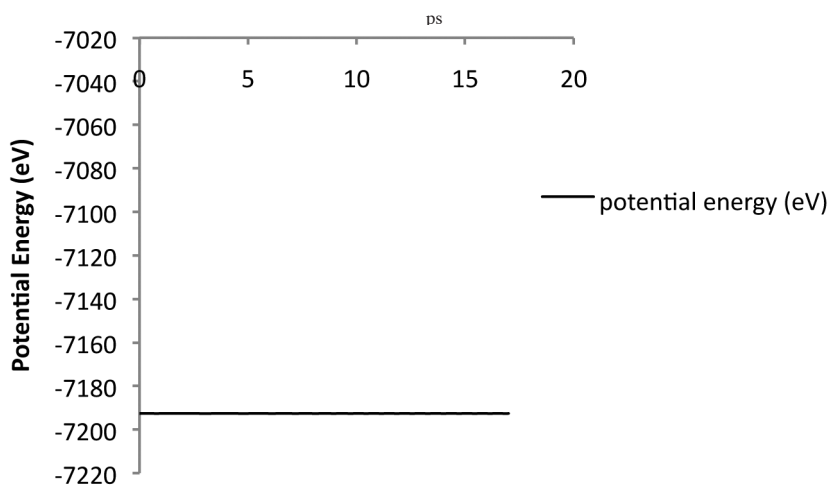


FIGURE 8. Potential energy with LJ (without switch function) and  $C_{60}$  (with switch function)

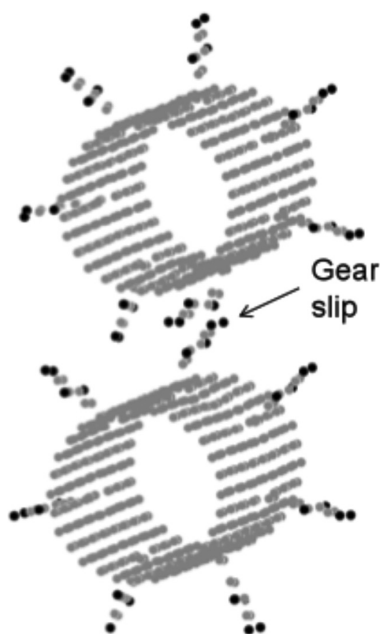


FIGURE 9. Gear slip occur using potential  $C_{60}$  without switch function

#### CONCLUSION

In this paper, we performed a microcanonical ensemble MD with Berendsen thermostat and successfully developed a CNT gear model using hybrid minimization for energy relaxation. The hybrid minimization successfully constrains the alignment of two CNT for gear rotation. From the simulated results, we note that the total energy fluctuated when the cutoff of potential function was without switch function. Logically the complexity of simulation will increase with switch function. However, simulation results showed the opposite tendency due to shorter simulation time. This was due to faster convergence rate of hybrid minimization in smooth gradient calculation.

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