molecule to the rate at which the junction electrodes deliver tunnelling electrons to the molecule[42].

Single hybrid molecular devices

Quasi-ideal rectification characteristics in nanometre-scale objects have been experimentally observed, by sliding an STM tip along a SWCNT[43] and in electrically contacted MWCNTs[44]. More recently, a single, planar SWCNT comprising tube sections with different tube helicities, one conducting and the other semiconducting and with a kink at the intervening junction, was shown to exhibit rectification behaviour on the molecular scale[45]. Molecular oligomers should also behave as d–s–a HME rectifiers, with dimensions well below 10 nm (ref. 1), and experimental proof for the validity of the d–s–a design principle has been obtained[10,11]. But despite these promising advances, many challenges remain: current technologies do not yet permit the realization of planar single-molecule d–s–a rectifiers fabricated with nanometre-scale dimensions, and whether those SWCNT devices can be scaled down by reducing the inter-electrode distance well below 10 nm remains an open question[46]. Similarly, rectification effects observed in nanopores[17] using molecule **8** (Fig. 1a) and in organic heterostructures[47] still involve several thousand molecules, making it difficult to assess to what extent scaling to a single-molecule level will be possible.

Hysteresis behaviour is a useful property for information storage applications. Manganese acetate (molecule **11** in Fig. 1d), with a total spin magnetic moment of 20 μ_B is the first molecule shown to exhibit a hysteresis cycle under cryogenic conditions[48]. Because magnetic hysteresis is usually seen as a collective property of bulk material, magnetic phenomena associated with single atoms[49] or molecules[50] have attracted much interest in the context of device scaling and quantum micro-reversibility[51]. An alternative approach to storage is to build devices that display negative differential resistance (NDR)[52], that is, a negative slope in their I–V curves like the one exhibited by a tunnel diode. Introduced in a two-terminal device, molecules exhibiting NDR play the equivalent role of a nonlinear material in photonic Fabry–Perot resonators showing a hysteresis cycle[53]. NDR with a high peak-to-valley ratio was observed[54] for molecule **12** (Fig. 1d).

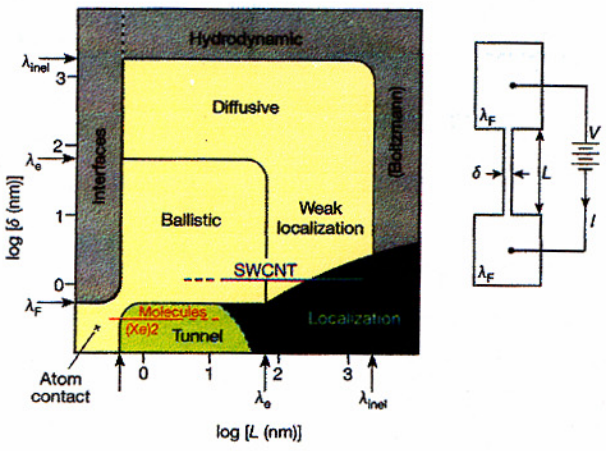

Figure 3 Regimes of electronic transport as a function of the wire width δ and length L. λ_F is the de Broglie carrier wavelength in the contact electrodes (away from the constriction), λ_e the elastic mean free path in the wire and λ_{inel} the inelastic mean free path in the wire. Characteristic orders of magnitude for λ_F, λ_e and λ_{inel} are taken for noble metals at low temperature. Hydrodynamic (Boltzmann), diffusive (weak localization) and ballistic regimes have been well studied in the past for metals and semiconductors. Ballistic and weak localization regimes are now being studied on SWNTs[25], atomic metallic wires[23] and the tunnel regime on single molecules[14,18,19,76] and short atomic wires[96].

Suggestions[55–58] for single-molecule molecular switches have been put forward for some time, but relatively few have been synthesized[6,59]. In an electronic circuit, switching is based on an intrinsic molecular property involving a bistable change of internal structure (such as a conformation change[57] or a unimolecular reaction[6,59]), which induces a modification of T. For example, the photochromic switching of molecule **3** (Fig. 1b) is possible because a photo-induced molecular orbital "up-shift" in the "on" state[6] favours efficient electron transfer through **3**, making this phenomenon an intramolecular analogue of the solid state "valve" effect. Rotaxanes **13** (Fig. 1b) have also been proposed as mechanical molecular switches[60]: the macromolecular ring can move along the molecule's central 'axle' and occupy one of two or more metastable positions or 'stations' along the axle, where one position provides a high-T and the other a low-T state. The gating used for these two switches has a macroscopic origin (light for the photochromic effect, pH and light control for the rotaxane), but the development of near-field integrated optics[61] may provide a more controlled means to optically gate molecular switches on the mesoscopic scale.

Proposals of HME transistors are numerous[62], yet their realization[55] remains challenging because logic circuit applications require a three-electrode configuration with high gain. SWCNTs have been used as the channel of a field-effect transistor[63], but the device is still mesoscopic in dimension because it operates by controlling the Schottky barrier height at the single-wall nanotube (SWNT)–electrode contacts (Fig. 2b). Plans to move the control of transparency T from the contact between the active molecule and the electrodes to the active molecule itself involve the electromechanical amplification effect of C_{60} (Fig. 2a), which might be planarized[64] using nano-electromechanics (NEMS)[65]. Oxidation–reduction processes provide another way of controlling the transparency of a molecular tunnel pathway. For instance, conjugated molecules such as polyacetylene, polythiophene or polypyrrole conduct with $T > 1$ when a few electrons are removed or added to introduce electronic states in the HOMO–LUMO gap of the molecule generally in resonance with the electrode Fermi level, at low bias voltage. Using a perpendicular electric field, those electrons can be driven from one molecular chain to another (molecule **14** in Fig. 1e), acting as a transistor source–drain channel[66]. Synthetic work has produced a number of spiro-bridge compounds (such as **14**)[67] that confirm the presence of an electronic double-well potential at the bridge site[68]. As in many designs employing electromechanical, electrical-field or even electronic interference effects[69], the third electrode, which gates the HME transistor, is mesoscopic and not readily scalable to nanoscale dimensions. Coulomb-blockade devices[16] and molecular junctions consisting of two different molecular components[35,47] have similar scalability problems.

Architecture of hybrid molecular electronic circuits

Given the proposed mode of operation of HME devices and reliability issues, circuit design is emerging as a crucial aspect in the development of future molecular electronic systems, with input/output interconnects, clock frequency and the increase of logic complexity constituting particularly challenging problems. Although NEMS technology may represent a potential solution to reduce the area occupied by the interconnection pads on a wafer, the bandwidth of these interconnects is limited to a few megahertz. The potential switching rate of the molecular component in an HME device, in contrast, is of the order of several terahertz[15,63], but it may require optical interconnects, such as subwavelength photonic waveguides[61], to use these frequencies.

Continuation of the 'top-down' approach indicates that a conservative architecture with metallic wires interconnecting many devices to form a complex network is feasible using well-defined and spatially localized logic gates, registers and memory cells (Fig. 4). In this case, high-gain three-terminal HME devices are essential for