Electronic Supplementary Material (ESI) for Soft Matter.

Electronic Supplementary Information:

Evaporation of liquid droplets of nano- and micro-meter size as a function of molecular mass and intermolecular interactions: experiment and molecular dynamics simulations

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Simulation parameters and results

	σ_{11}	T_b	ρ_2^0	m_1	A	χ^2/σ_{11}^2	T_{liq}	$\rho_{liq}\sigma_{11}^2$	$R(0)$	λ
1	1.0	1.05	0.0150	1.0	3.01	0.0014	0.720	0.846	36.9	17.4
2	1.0	1.05	0.0150	3.0	4.49	0.0051	0.734	0.844	36.7	17.4
3	1.0	1.05	0.0150	8.0	9.08	0.0072	0.725	0.847	37.1	17.4
4	1.0	1.15	0.0150	1.0	2.84	0.0030	0.741	0.840	37.4	17.7
5	1.0	1.15	0.0150	2.0	3.52	0.0023	0.752	0.838	36.7	17.7
6	1.0	1.15	0.0150	3.0	4.34	0.0031	0.752	0.838	37.3	17.7
7	1.0	1.15	0.0150	5.0	6.16	0.0106	0.749	0.839	37.3	17.7
8	1.0	1.15	0.0150	8.0	8.84	0.0054	0.742	0.842	37.5	17.7
9	1.0	1.25	0.0150	1.0	2.72	0.0040	0.760	0.834	36.2	18.0
10	1.0	1.35	0.0150	1.0	2.60	0.0052	0.777	0.829	35.5	18.3
11	1.0	1.45	0.0150	1.0	2.51	0.0090	0.793	0.823	34.7	18.5
12	1.0	1.55	0.0150	1.0	2.38	0.0088	0.808	0.818	35.1	18.7
13	2.0	0.85	0.0065	3.0	3.88	0.071	0.755	0.838	73.6	38.5
14	2.0	0.85	0.0065	8.0	7.35	0.090	0.747	0.841	73.8	38.5
15	2.0	1.05	0.0065	3.0	3.60	0.039	0.838	0.810	74.6	40.4
16	2.0	1.05	0.0065	8.0	6.62	0.046	0.827	0.814	75.1	40.4
17	2.0	1.05	0.0065	20.0	13.5	0.026	0.808	0.822	76.4	40.4
18	2.0	1.25	0.0065	3.0	3.41	0.104	0.901	0.786	75.5	41.7
19	2.0	1.25	0.0065	8.0	6.05	0.082	0.891	0.791	73.7	41.7
20	2.0	1.25	0.0065	20.0	12.5	0.047	0.856	0.801	74.8	41.7

Table S1. Simulation parameters and results. A – the parameter from the fit to Eq.(5); $R(t)$ obtained directly from the simulations (and corresponding χ^2). The data used for analysis included sizes R(t) down to $R = 10\sigma_{11}$. $R(0)$ is the droplet radius at time t=0 i.e. when the system attained quasi-stationary stage of evaporation. T_{liq}, ρ_{liq} are the liquid droplet temperature and density averaged from $t = 0$ to t_μ: $R(t_\mu) = 25\sigma_{11}$. λ is the mean free path (eq(4)) for gas 2 at ρ_2^0, T_b.

The gas liquid equilibrium properties and the critical temperature

T_{eq}	p_{eq}	ρ_{liq}^{eq}	ρ_{gas}^{eq}
0.375	0.0007	0.836	0.0020
0.400	0.0014	0.820	0.0036
0.423	0.0025	0.802	0.0063
0.452	0.0043	0.781	0.0105
0.477	0.0069	0.759	0.0165

0.501	0.010	0.736	0.0244
0.526	0.015	0.709	0.0358
0.552	0.021	0.676	0.0521
0.564	0.025	0.658	0.0627
0.575	0.029	0.638	0.0750

Table S2. The gas liquid equilibrium temperature, pressure and densities for the potential given by Eq.(1) for $\varepsilon_{ii} = \sigma_{ii} = 1.0$. The simulation were performed using two phase constant energy and volume MD NVE simulations [1] for the total number of particles $N = 1.6\times10^5$.

The critical temperature for the potential (1) was estimated as $T_c \approx 0.65\varepsilon_{ii}$ by comparing the density temperature dependences from Table S2 to that for LJ potential for $r_c = 2.5$ [S1].

The self-diffusion constant in the vapor

The self-diffusion constant, D, for the gas of particles 2 was determined from the Einstein formula (S1) [1] by performing MD NVE simulations for $N = 10^6$.

$$D = \lim_{t\to\infty}\left(\frac{1}{6\mathrm{N}t}\sum_{i=1}^{\mathrm{N}}(\mathbf{r_i}(t)-\mathbf{r_i}(0))^2\right) \tag{S1}$$

where $\mathbf{r}_i(t)$ denotes the position of the i-th particle at time t.

ρ	T	D
0.0065	0.800	32.03
0.0065	1.025	38.25
0.0065	1.357	46.31
0.0065	1.717	54.26
0.0150	0.801	13.84
0.0150	1.025	16.52
0.0150	1.355	20.02
0.0150	1.715	23.45

Table S3. The self-diffusion constant, D, for a pure gas 2 at different densities ρ and temperatures T.

The heat conductivity in the vapor

The heat conductivity, κ_v, for the gas of particles 2 was measured using a direct method proposed by Muller-Plathe (MP) [12] with the modifications as in supplementary information to Refs. 7, 8. The simulations were performed for total number of particles $N = 2457600$. Both the total energy and the momentum of the system were conserved. The values of κ_v evaluated from the formula of MP (S2) are given in Table S4.

$$\kappa_v = \frac{\Delta E_{\mathrm{k}}}{2 < \partial T/\partial z > L_{\mathrm{x}} L_{\mathrm{y}} \Delta \mathrm{t}} \tag{S2}$$

The relative errors in κ_v are much larger than that in *D*. For dilute gases, κ_v and *D* can be approximated by very similar formulas [S2]. In order to reduce the errors from (S2), the values of κ_v used in Eq (5) were correlated with the self-diffusion constant *D* using:

$$\kappa_v = \alpha \rho D \tag{S3}$$

The α constant were estimated from Tables S3 and S4 as 2.78 for $\rho = 0.015$ and 2.65 for $\rho = 0.0065$.

ρ	T	κ_v
0.0065	0.859	0.582
0.0065	1.026	0.650
0.0065	1.240	0.758
0.0150	1.033	0.700
0.0150	1.133	0.739
0.0150	1.325	0.809
0.0150	1.545	0.905

Table S4. Thermal conductivity coefficient κ_v for a pure gas 2 at different densities ρ and temperatures *T*. All expressed in standard L-J units.

The enthalpy of evaporation for glycols used in experiments

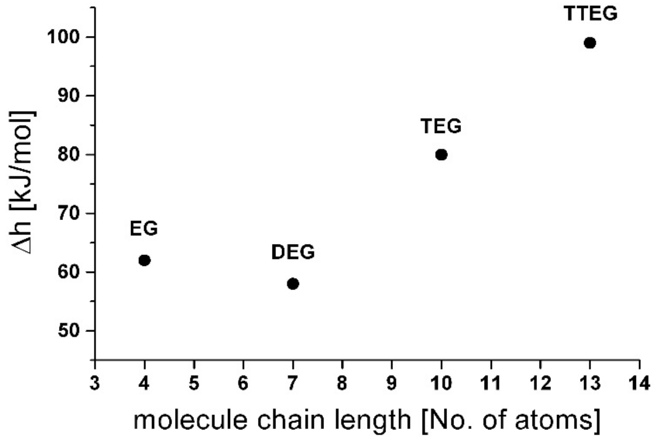

Fig.7 The enthalpy of evaporation used to estimate the interaction energy of molecules forming a liquid droplet at 273 K. The compounds are as follows: ethylene glycol (EG); diethylene glycol (DEG); triethylene glycol (TEG) and tetraethylene glycol (TTEG). (S3)

References

S1 – J. Vrabec, G. K. Kedia, G. Fuchs and H. Hasse, Mol. Phys. **104**, 1509 (2006)
S2 – S. Chapman and T.G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press 1990)
S3 -- J.B.Pedley, R.D. Naylor and R.B.Kirby, *Thermochemical Data of Organic Compounds*, Chapman and Hall, New York, 1986, 1-792.