Configurational Temperature

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1 Derivation From Virial Theorem

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \{f, H(\tau)\} \tag{1}$$

where, f is arbitrary dynamic variable, and $H(\tau)$ is the Hamiltonian of the system and $\tau = \{q_1, ...q_{3N}, p_1, ...p_{3N}\}$ stands for the space vector, representing 6N coordinates of the system, including positions and velocities of particles.

Also, $\{..\}$ represents the Poisson's Bracket, and $< .. >$ represents the average.

Let, f does not explicitly depends on t. Then, we get our Virial Theorem as:

$$< f, H(\tau) >= 0 \tag{2}$$

$$\sum_i^{3N} \langle \frac{\partial H}{\partial q_i} \frac{\partial f}{\partial p_i} \rangle = \sum_i^{3N} \langle \frac{\partial H}{\partial p_i} \frac{\partial f}{\partial q_i} \rangle \tag{3}$$

Now, let us exploit the availability of function f, and let restrict it to one degree in momentum

$$f(\tau) = p_l Q(\{q_j\}) \tag{4}$$

The two equation will proceed as:

$$\sum_i^{3N} \langle \frac{\partial H}{\partial q_i} \frac{\partial f}{\partial p_i} \rangle = \langle Q \frac{\partial H}{\partial q_l} \rangle = \langle Q \frac{\partial V(\{q_i\})}{\partial q_l} \rangle \tag{5}$$

and, since the momenta and position are uncorrelated,

$$\sum_i^{3N} \langle \frac{\partial H}{\partial p_i} \frac{\partial f}{\partial q_i} \rangle = \sum_i^{3N} \langle \frac{\partial H}{\partial p_i} p_l \rangle \langle \frac{\partial Q}{\partial q_i} \rangle = \langle \frac{\partial H}{\partial p_i} p_i \rangle \langle \frac{\partial Q}{\partial q_i} \rangle \tag{6}$$

Now, we know from standard kinetic definition that,

$$\langle p_i \frac{\partial H}{\partial p_i} \rangle = k_B T \tag{7}$$

where, T is the kinetic temperature.

Thus, we relate Eq.(3), Eq.(5), Eq.(6) and finally implementing the value from Eq.(7) to get:

$$k_B T = \left\langle Q \frac{\partial V(\{q_i\})}{\partial q_l} \right\rangle \left\langle \frac{\partial Q}{\partial q_i} \right\rangle^{-1} \tag{8}$$

Now, again modifying f, so as that $Q = {F_s}^i = \frac{\partial V(q_s)}{\partial q_i}$, we get our final derivation as:

$$k_B T_{config} = \frac{\langle \nabla V . \nabla V \rangle}{\langle \nabla^2 V \rangle} \tag{9}$$

Using Virial Theorem, i.e; Eq.(3) and Kinetic Temperature Definition, Eq.(7); one can derive other General Temperature Definitions:

$$k_B T = \frac{\langle \nabla H(\tau) . B(\tau \rangle}{\langle \nabla B(\tau) \rangle} \tag{10}$$

where, B can be any continuous and differentiable vector in phase space τ. For example, Kinetic Temperature (Equipartition Theorem) can be calculated by taking $B(\tau) = \{0, ...0, p_1, ...p_{3N}\}$. Also, in our case, configurational temperature can be derive from above formula using $B(\tau) = -\nabla V(\{q_i\})$