Using VACF to Calculate Diffusion Coefficient

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1 Introduction to Diffusion Coefficient

The diffusion coefficient D is a measure of how particles spread out over time. It is defined as:

$$D = \lim_{t\to\infty} \frac{1}{6t} \left\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \right\rangle$$

where:

- $\mathbf{r}(t)$ is the position vector of a particle at time t.
- $\langle \cdot \rangle$ denotes an ensemble average.
- $|\mathbf{r}(t) - \mathbf{r}(0)|^2$ is the mean squared displacement (MSD).

2 Definition of Velocity Autocorrelation Function (VACF)

The velocity autocorrelation function $C_v(t)$ is defined as:

$$C_v(t) = \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle$$

where:

- $\mathbf{v}(t)$ is the velocity vector of a particle at time t.
- $\langle \cdot \rangle$ denotes an ensemble average.

3 Relationship between Diffusion Coefficient and VACF

The diffusion coefficient D can be expressed using the VACF as:

$$D = \frac{1}{3} \int_0^\infty C_v(t)\, dt$$

3.1 Derivation Steps

1. **Position and Velocity Relationship**:

$$\mathbf{r}(t) = \mathbf{r}(0) + \int_0^t \mathbf{v}(t')\, dt'$$

2. **Mean Squared Displacement**:

$$\left\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \right\rangle = \left\langle \left| \int_0^t \mathbf{v}(t')\, dt' \right|^2 \right\rangle$$

$$= \left\langle \int_0^t \int_0^t \mathbf{v}(t') \cdot \mathbf{v}(t'')\, dt'\, dt'' \right\rangle$$

3. **Exchange of Ensemble Average and Time Integral**:

$$= \int_0^t \int_0^t \langle \mathbf{v}(t') \cdot \mathbf{v}(t'') \rangle \, dt' \, dt''$$
$$= \int_0^t \int_0^t C_v(t'' - t') \, dt' \, dt''$$

4. **Simplification Using Variable Substitution**:

$$\left\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \right\rangle = 2 \int_0^t (t - \tau) C_v(\tau) \, d\tau$$

5. **Long Time Limit**:

$$\left\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \right\rangle \approx 2t \int_0^\infty C_v(\tau) \, d\tau$$

6. **Final Expression for Diffusion Coefficient**:

$$D = \frac{1}{3} \int_0^\infty C_v(\tau) \, d\tau$$

4 Physical Interpretation

- **VACF** $C_v(t)$: Represents the correlation between the velocity of a particle at time 0 and at time t. Indicates how persistent the motion of the particle is over time.
- **Diffusion Coefficient** D: Measures how quickly particles spread out over time. A higher diffusion coefficient means faster spreading.
- **Relationship**: VACF describes the time evolution of particle motion, and integrating VACF over time gives the diffusion coefficient, quantifying the spread of particles.

5 Detailed Explanation of Key Steps

5.1 Exchange of Ensemble Average and Time Integral

1. **Ensemble Average**:

$$\langle \mathbf{v}(t') \cdot \mathbf{v}(t'') \rangle = C_v(t'' - t')$$

2. **Time Integral**:

$$\int_0^t \int_0^t C_v(t'' - t') \, dt' \, dt''$$

3. **Variable Substitution**:
   - Let $t'' - t' = \tau$
   - t' ranges from 0 to t
   - τ ranges from 0 to $t - t'$

4. **Simplified Integration**:

$$\int_0^t \int_0^{t-t'} C_v(\tau) \, d\tau \, dt'$$
$$= \int_0^t \int_0^{t-\tau} C_v(\tau) \, dt' \, d\tau$$
$$= \int_0^t (t - \tau) C_v(\tau) \, d\tau$$

6 Conclusion

The relationship between VACF and the diffusion coefficient provides a powerful method to calculate D from molecular dynamics simulations. Understanding the derivation and the physical meaning behind these equations is crucial for interpreting the results in computational materials science.