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Role of many-body correlations in dynamics of liquids

Puneet Sharma, K. Tankeshwar, and K. N. Pathak
Centre of Advanced Study in Physics, Panjab University, Chandigarh 160 014, India

S. Ranganathan
Department of Physics, Royal Military College, Kingston, Ontario, Canada K7K 7B4

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A time correlation function is written exactly in terms of infinite series with each term containing contributions separately due to two, three, and higher body static correlations. For a time correlation function of force acting on a tagged particle, it is found that contributions due to two and three body static correlation functions are sufficient to understand dynamics of dense gases whereas at the triple point and in the glassy phase it is necessary to include contributions due to a four body correlation function.

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I. INTRODUCTION

Dynamics of simple liquids exhibit most of the important features of complex systems which makes them excellent candidates to test theories for understanding the basic phenomena responsible for many of their properties. There exists an enormous amount of research work in which dynamics of the simple fluids like Ar/Kr have been investigated covering a wide range of densities and temperatures. One of the aims of such studies has been to extend the available theories for dilute gases in predicting properties of dense gases and liquids. During the last few decades, efforts have been made to extend these theories to supercooled liquids and glasses. One of the theoretical methods to study self- or collective phenomena in these systems is the evaluation of an appropriate time correlation function (TCF). A TCF has been commonly calculated using memory function formalism [1,2] either in the phase-space or in the space-time framework. There exists a mode-coupling theory for calculating memory function which has been successful in understanding the dynamics of both liquid state [3] and glassy phase [4]. On the other hand, exact properties, i.e., sum rules of the time correlation function, can be calculated to understand the microdynamics of dense gases. Such studies [5], which have been using memory function with a single relaxation time, revealed that only first few sum rules are sufficient to obtain a reasonable value of the transport coefficients in simple systems. These studies have also emphasized the role played by triplet and quadruplet correlation functions. However, to understand the dynamics of the system at different length and time scales, two relaxation time models have met with more success [6]. Recently, a memory function with three relaxation times has been used [7] to explain the line shape of the dynamical structure factor of liquid metals. Though these two or three relaxation times have been assigned some physical meaning, it is not yet possible to extract these contributions from the first principle.

An alternative approach for calculating a TCF is through developing models for it without making use of the memory function. One successful approach is due to Zwanzig [8] who proposed to separate the stable packed configuration of the system from the vibrational one. Such an approach exploited by other workers [9] too have predicted good results as far as the transport coefficients are concerned. Microscopically, a TCF can be calculated directly using the cluster expansion technique [10] but so far it has been possible to calculate [11–13] the binary contribution only. Recently, we have combined [14] the binary contribution determined in a microscopic way with the multiparticle contribution for the force autocorrelation function. This method has provided a good description of the velocity autocorrelation function and self-diffusion coefficient. In spite of the success of various models and theories, it is still not known how to combine the contributions due to two particles, three particles, four particles, and so on. It is also important to investigate whether these different contributions are responsible for the requirement of two, three or, a multirelaxation function to explain the dynamics of liquids. Therefore, in the present work, we express a time correlation function as a time series in terms of the contribution from all possible cluster of particles. Various terms of the series represent, separately, contributions due to two particles, three particles, four particles, and so on. We have used a microscopic expression for the two particle contribution obtained using the cluster expansion of a Liouville operator. Three and four particle contributions have been estimated by using superposition approximation. It is shown that at intermediate densities, at least two relaxations are needed corresponding to two and three particle correlations. On the other hand, at the thermodynamic state close to the triple point, at least three relaxation times are needed; a third one is attributed to the four particle correlations.

The layout of the paper is as follows. In Sec. II we present theory. Results obatined are discussed in Sec. III. The paper is summed up in Sec. IV.

II. THEORY

A time correlation function $C(t)$ of any dynamical variable $A(t)$ defined as

$$C(t) = \langle A^{*}(t)A(0)\rangle, \tag{1}$$

can be expressed as a Taylor series expansion,

$$C(t)=\sum_{n=0}(-1)^n M_{2n}\frac{t^{2n}}{2n!}. \tag{2}$$

In the above equation, M_{2n} is the second order sum rule and is defined as

$$M_{2n}=\left\langle \frac{d^n}{dt^n}A(t)\frac{d^n}{dt^n}A(t)\right\rangle_{t=0}. \tag{3}$$

The time dependence of any dynamical variable $B(t)$ is determined through the Liouville equation

$$\frac{\partial B(t)}{\partial t}=i\mathcal{L}B(t), \tag{4}$$

where $\mathcal{L}$ is the Liouville operator defined by

$$\mathcal{L}=\mathcal{L}_0+\sum_{j<k}\mathcal{L}_1(jk)=-i\sum_j\frac{\mathbf{p}_j}{m}\cdot\frac{\partial}{\partial\mathbf{r}_j}-i\sum_{j<k}\mathbf{F}_{jk}\cdot\left[\frac{\partial}{\partial\mathbf{p}_j}-\frac{\partial}{\partial\mathbf{p}_k}\right], \tag{5}$$

with $\mathbf{F}_{jk}=-\partial u(r_{jk})/\partial r_j$, the force, and $r_{jk}=|\mathbf{r}_j-\mathbf{r}_k|$. $u(r_{ij})$ is the pair potential.

For $A(t)=dB(t)/dt$, the Fourier-Laplace transform of $C(t)$ can be written as

$$\tilde{C}(\omega)=\left\langle \mathcal{L}B(0)\left|\frac{1}{\mathcal{L}-\omega}\right|\mathcal{L}B(0)\right\rangle. \tag{6}$$

The binary contribution to $C(t)$ can be obtained using the well established cluster expansion technique [10]. The cluster expansion formula is

$$\frac{1}{\mathcal{L}-\omega}\approx\mathcal{L}\frac{1}{\mathcal{L}_0-\omega}+\sum_{j<k}\left[\frac{1}{\mathcal{L}_0+\mathcal{L}_1(jk)-\omega}-\frac{1}{\mathcal{L}_0-\omega}\right]+\ \dots\ . \tag{7}$$

The first term involves the free propagation and the second term contains a sum over a pair of particles. Microscopic expressions for the binary contribution to time correlation functions of force on a tagged particle, transverse stress, and longitudinal stress have already [11–13] been obtained. The binary contribution $C^{(2)}(t)$ contains complete information about the two particle contribution to all the sum rules and can be expanded as

$$C^{(2)}(t)=\sum_{n=0}(-1)^n M_{2n}^{(2)}\frac{t^{2n}}{2n!}, \tag{8}$$

where $M_{2n}^{(m)}$ represents the m body contribution to second sum rule. Using the knowledge [5] that each sum rule of second order contains the contribution of the static correlation functions up to $(2+n)$th order, we obtain from Eqs. (2) and (8)

$$C(t)=C^{(2)}(t)+\sum_{n=1}(-1)^n\frac{t^{2n}}{2n!}M_{2n+2}^{(3)}+\sum_{n=2}(-1)^n M_{2n+2}^{(4)}\frac{t^{2n}}{2n!}+\sum_{n=3}(-1)^n\frac{t^{2n}}{2n!}M_{2n+2}^{(5)}+\ \dots\ . \tag{9}$$

The first term represents the time dependent two body contribution, the second term only the three body contribution, the third term only the four body contribution, and so on. Replacing each individual summation in Eq. (9) by a time dependent function, we obtain

$$C(t)=C^{(2)}(t)-M_2^{(3)}\frac{t^2}{2!}C^{(3)}(t)+M_4^{(4)}\frac{t^4}{4!}C^{(4)}(t)-\ \dots\ , \tag{10}$$

where $C^{(n)}(t)$ represents the n body time dependent contribution. The above equation expands a TCF in terms of time dependent contributions due to all possible clusters of particles.

The formalism presented here is applicable to time correlation functions like that for the force on a tagged particle, transverse, and longitudinal current correlation functions. However, in the present work, we consider $A(t)$ as force on a tagged particle, i.e., $m(d/dt)v_{1x}(t)$; v_{1x} is the velocity of the tagged particle at time t. Using Mori's projection operator procedure, the relation between the velocity autocorrelation function $\tilde{\psi}(\omega)$ and the first order memory function $\tilde{\mathcal{K}}(\omega)$ in Fourier-Laplace space can be written as

$$\tilde{\psi}(\omega)=-\frac{\psi(0)}{\omega+\tilde{\mathcal{K}}(\omega)}. \tag{11}$$

The memory function is related [14] to the force autocorrelation function $\tilde{C}(\omega)$ as

$$\tilde{\mathcal{K}}(\omega)=\frac{\omega\tilde{C}(\omega)}{\omega-\tilde{C}(\omega)}. \tag{12}$$

Writing

$$\tilde{C}(\omega)=C'(\omega)+iC''(\omega), \tag{13}$$

where $C'(\omega)$ and $C''(\omega)$ are the real and imaginary parts of $\tilde{C}(\omega)$, we obtain expressions for the real and imaginary parts of $\tilde{\mathcal{K}}(\omega)$, respectively, given by

$$\mathcal{K}'(\omega)=\frac{\omega^2C'(\omega)-\omega[C'^2(\omega)+C''^2(\omega)]}{[\omega-C'(\omega)]^2+C''^2(\omega)}, \tag{14}$$

and

$$\mathcal{K}''(\omega)=\frac{\omega^2C''(\omega)}{[\omega-C'(\omega)]^2+C''^2(\omega)}. \tag{15}$$

The Green-Kubo expression for the self-diffusion coefficient is given as

$$D=\frac{k_BT}{m\mathcal{K}''(0)}, \tag{16}$$

where k_B, T, and m are the Boltzmann constant, temperature, and atomic mass of the particle, respectively. In order to calculate $\mathcal{K}''(0)$ from Eq. (15) , we make use of the following relations

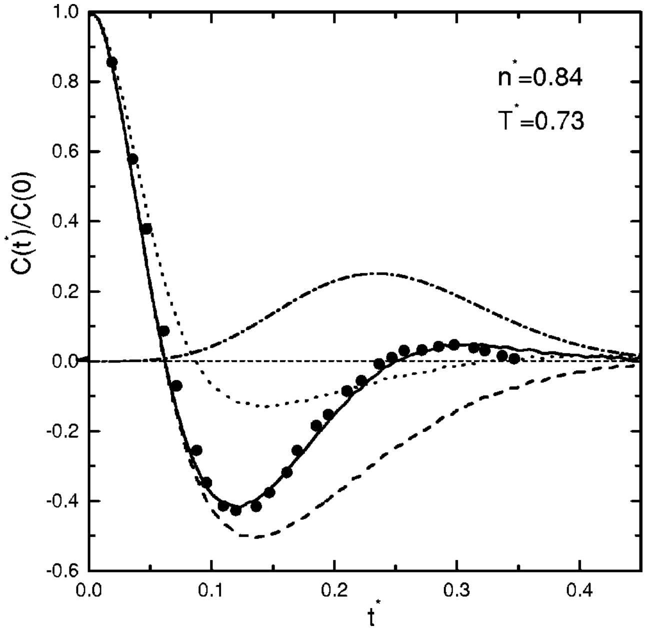

FIG. 1. Variation of the force autocorrelation function $C(t^*)/C(0)$ with reduced time $t^*[=t(\epsilon/m\sigma^2)^{1/2}]$; at $T^*=0.73$ and $n^*=0.84$. The dotted line represents $C^{(2)}(t^*)/C(0)$, the dashed line represents the sum of two and three body contributions. The full line represents the sum of two, three, and four body contributions. The solid circles are MD results [17]. The dashed-dotted line is the contribution due to, quadruplet correlation.

$$\lim_{\omega\to 0} C'(\omega) = -\lim_{\omega\to 0}\int_0^\infty C(t)\sin(\omega t)dt = 0, \tag{17}$$

and

$$C''(\omega) = \int_0^\infty C(t)\cos(wt)dt = \int_0^\infty C(t)[\cos(wt)-1]dt. \tag{18}$$

For writing the above equation, we have used the following exact relation [1]:

$$\int_0^\infty C(t)dt = 0. \tag{19}$$

Using Eqs. (17) and (18) in Eq. (15) , we obtain

$$\lim_{\omega\to 0}\mathcal{K}''(\omega) = \lim_{\omega\to 0}\frac{\omega^2}{C''(\omega)} = \frac{1}{\int_0^\infty C(t)\lim_{\omega\to 0}\left(\frac{\cos(\omega t)-1}{\omega^2}\right)dt} = \frac{-2}{\int_0^\infty dt C(t)t^2}. \tag{20}$$

Equations (20) and (16) provide us a relation for the diffusion coefficient given [14] as

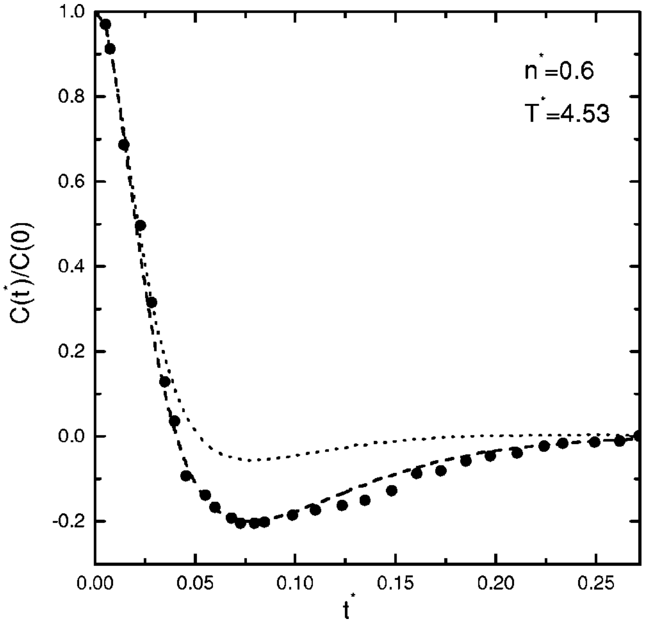

FIG. 2. Variation of the force autocorrelation function $C(t^*)/C(0)$ with reduced time $t^*[=t(\epsilon/m\sigma^2)^{1/2}]$; at $T^*=4.53$ and $n^*=0.6$. The dotted line represents $C^{(2)}(t^*)/C(0)$, the dashed line represents the sum of two and three body contributions. The solid circles are MD results [17].

$$D = -\frac{k_BT}{2m}\int_0^\infty C(t)t^2dt. \tag{21}$$

This relation has been verified to provide the same results [14] as that obtained using the Green-Kubo formula for self-diffusion. An alternative derivation of Eq. (21) is presented in the Appendix. To calculate self-diffusion from this expression we need to know the time evolution of the force autocorrelation function $C(t)$. The contribution due to the pair correlation is given [11] by

$$C^{(2)}(t) = \frac{n}{m2\sqrt{2}}\int\int d\mathbf{r}d\mathbf{p}\mathrm{G}\left[\frac{p}{\sqrt{2}}\right]\frac{\partial g(r)}{\partial x}F_x(r(t)), \tag{22}$$

where $g(r)$ and $G(p)=(1/2\pi p_0^2)^{3/2}e^{-(p^2/2p_0^2)}$ with $p_0=(mk_BT)^{1/2}$ are, respectively, the static pair correlation function and the Maxwellian momentum distribution. The position vector $\mathbf{r}(t)$ and the momentum vector $\mathbf{p}(t)$ of a particle moving in a central potential field $u(r)$ obey the Newton's equation of motion given by

$$\frac{1}{2}\frac{dp_x}{dt} = \frac{m}{2}\frac{d^2x}{dt^2} = F_x(r) = -\frac{\partial u(r)}{\partial x}, \tag{23}$$

where x, p_x, and r are the initial values of these quantities at time $t=0$.

III. RESULTS AND DISCUSSION

The six dimensional integral in Eq. (22) has been evaluated using the Monte Carlo method [15] and the Verlet algorithm [16] for the evaluation of $r(t)$ for the Lennard-Jones fluid. The microscopic contribution due to the two body correlation is shown in Figs. 1 and 2 as dotted lines at $T^{*}(=k_BT/\epsilon)=0.73$, $n^{*}(=n\sigma^3)=0.84$, and at $T^{*}=4.53$ and $n^{*}=0.6$, respectively (where σ and ϵ are two parameters of Lennard-Jones potential). It can be seen from the figures that the pair contribution is in agreement with molecular dynamics (MD) simulation data [17] (solid circles) only up to $t^{*}\approx 0.03$. Therefore it becomes essential to include contributions due to the higher order static correlation function. The three body contribution $C^{(3)}(t)$ is estimated so as to include exactly the triplet contribution to the sum rules of the force autocorrelation function up to fourth order. We assume $C^{(3)}(t)=\operatorname{sech}(at)$ with $a=(M_4^{(3)}/6M_2^{(3)})^{1/2}$. We prefer $\operatorname{sech}(at)$ over the simple exponential function due to its symmetric property which is one of the requirements of the expansion (10). For the calculation of $M_4^{(3)}$ and $M_2^{(3)}$, we have used the Kirkwood superposition approximation for the static triplet correlation function. The values of $M_2^{(3)}$ [in units of $(\epsilon/m\sigma^2)^2$] and a [in units of $(\epsilon/m\sigma^2)^{1/2}$] are 49 137.94 and 16.22 at $T^{*}=0.73$ and $n^{*}=0.84$ and 75 697.6 and 27.04 at $T^{*}=4.53$ and $n^{*}=0.6$. The value of a at $T^{*}=4.53$ and $n^{*}=0.6$ is obtained by adjusting the value of $M_4^{(3)}$ by about 20% which is within the error limit due to the superposition approximation [5]. The results obtained by combining two and three body contributions are shown as dashed curves in Figs. 1 and 2. It can be seen from the Fig. 2 that at $T^{*}=4.53$ and $n^{*}=0.6$, the dashed curve is in very good agreement with molecular dynamics results [17]. This implies that contributions due to four and higher body correlation functions to $C(t)$ will have a negligible effect due to their cancellation nature. However, at the triple point, it is noted that the triplet contribution is effective in correcting the behavior of $C(t)$ only up to $t^{*}\approx 0.09$ as can be judged from comparison with MD data. Therefore at the triple point it appears that it is necessary to add $C^{(4)}(t)$, i.e., the contribution due to four particles. In the present work, we estimate it through a faster decaying function than $\operatorname{sech}(at)$, i.e., $\exp(-bt^2)$. The value of b can be determined from the quadruplet contribution to the sum rules and is given as $\sqrt{M_6^{(4)}/30M_4^{(4)}}$. The expression for $M_4^{(4)}$ is available and can be determined using a decoupling approximation [18]. Since nothing is known about $M_6^{(4)}$, we have fitted this and $M_4^{(4)}$ so as to obtain the MD value of D. It was found that the fitted value of $M_4^{(4)}$ is about 15% less than the value predicted by using the decoupling approximation for the quadruplet correlation function in the fourth sum rule of $C(t)$.

The results obtained by including contributions up to four particles is shown as a full line in Fig. 1, and are in good agreement with MD simulation results (solid circles) up to $t^{*}=0.3$. It can be seen from the Fig. 1 that $C(t)$ becomes positive at the triple point at around $t^{*}[=t(\epsilon/m\sigma^2)^{1/2}]=0.24$. This positive lobe is responsible for the rapid fall of D while approaching the triple point. It is further noted that this positive contribution is arising due to the four body static correlation function and is shown separately as a dashed-dotted line in Fig. 1. Therefore, in a supercooled or glassy state of matter, the four particle contribution is expected to play an important role as it is responsible for the arrest of a tagged particle in the cage formed by a cluster of particles. It is also noted that the four body correlation's contribution starts building only at larger times, implying that these play a vital role in cases where long time effects are quite important. For example, at the triple point, values of t^{*} at which pair, triplet, and quadruplet contributions to $C(t)$ are half of their maxima are 0.035, 0.053, and 0.144, whereas at $n^{*}=0.6$ and $T^{*}=4.53$, corresponding values of t^{*} for pair and triplet contributions are 0.021 and 0.032. At the triple point and at thermodynamic states close to it, the correlation among more than four particles may have a negligible contribution due to the canceling effect.

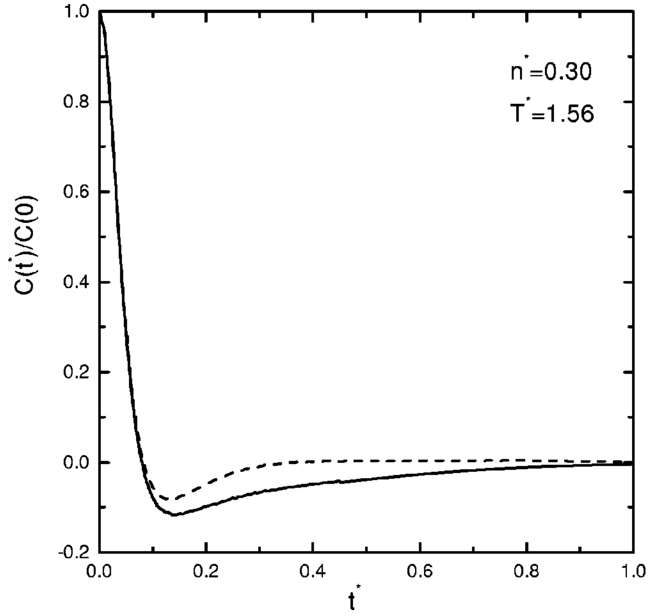

FIG. 3. Variation of the force autocorrelation function $C(t^{*})/C(0)$ with reduced time $t^{*}[=t(\epsilon/m\sigma^2)^{1/2}]$; at $T^{*}=1.56$ and $n^{*}=0.3$. The dashed line represents $C^{(2)}(t^{*})/C(0)$ and the full line represents the sum of two and many-body contributions.

In order to understand the wide role played by three and four body contributions, we have also studied the behavior of $C(t)$ at the critical point of Lennard-Jones fluids. The results obtained for $C^{(2)}(t)$ and that by adding the multiparticle contribution [14] are shown in Fig. 3 as a dashed line and full line, respectively. Since MD results of $C(t)$ at the critical point is not available, the full line is made to satisfy the two exact conditions $\int_0^\infty C(t)dt=0$ and $\int_0^\infty tC(t)dt=-1$ by adjusting the values of parameters in the multiparticle contribution. It is then found that this predicts the self-diffusion coefficient in good agreement with the MD simulation. It can be seen from Fig. 3 that the two curves are closer to each other than found at the thermodynamic states studied earlier, implying that on further diluting a gas, only the two particle correlation's contribution would be sufficient.

IV. SUMMARY AND CONCLUSION

Summing up, in the present work, it is shown that a TCF can be written as a time series of contributions due to all possible clusters of particles. Each term is associated with at least one relaxation time corresponding to contributions due to static correlations of two particles, three particles, four particles, and so on. It is shown that for a TCF of force acting on a tagged particle, it is essential to include the contribution due to the quadruplet correlation function at the triple point. However, at low densities and/or high temperature, only two and three particle contributions are sufficient. Our work systematically demonstrates that as one goes towards the triple point from the critical point, the role played by multiparticle correlation becomes imperative and hence requires more numbers of relaxation times.

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APPENDIX

We present here an alternate method for deriving Eq. (21). The Green-Kubo expression for the self-diffusion coefficient [1,2] is given as

$$D=\frac{k_{\mathrm{B}}T}{m}\int_0^\infty \psi(t)dt, \tag{A1}$$

where $\psi(t)$ is the normalized velocity autocorrelation function. Integrating Eq. (A1) by parts, we get

$$D=\frac{k_{\mathrm{B}}T}{m}\psi(t)t\Big|_0^\infty-\frac{k_{\mathrm{B}}T}{m}\int_0^\infty\frac{d\psi(t)}{dt}tdt=-\frac{k_{\mathrm{B}}T}{m}\int_0^\infty\frac{d\psi(t)}{dt}tdt. \tag{A2}$$

Again integrating Eq. (A2) by parts, we get

$$\begin{aligned}D&=-\frac{k_{\mathrm{B}}T}{m}\frac{d\psi(t)}{dt}\left.\frac{t^2}{2}\right|_0^\infty+\frac{k_{\mathrm{B}}T}{m}\int_0^\infty\frac{d^2\psi(t)}{dt^2}\frac{t^2}{2}dt\\&=\frac{k_{\mathrm{B}}T}{2m}\int_0^\infty\frac{d^2\psi(t)}{dt^2}t^2dt.\end{aligned} \tag{A3}$$

$-d^2\psi(t)/dt^2=C(t)$ is a force autocorrelation function; we obtain

$$D=-\frac{k_{\mathrm{B}}T}{2m}\int_0^\infty t^2C(t)dt. \tag{A4}$$

In obtaining Eqs. (A2) and (A4), it is required that $\psi(t)$ vanishes faster than t^{-1} for $t\rightarrow\infty$.

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